Quantitative characterization of precipitate free zones in Al–Zn–Mg(–Ag) alloys by microchemical analysis and nanoindentation measurement

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Abstract

To correlate quantitatively the mechanical properties of precipitate free zones (PFZ) with the corresponding microstructural and compositional characteristics, TEM observation, EDX analysis and nanoindentation measurement have been performed in the vicinity of grain boundaries in Al–4.9 mass%Zn–1.8 mass%Mg (–0.28 mass%Ag) alloys. The remarkable decreases in hardness and solute concentrations were observed towards grain boundaries even in the regions just outside PFZ. With increasing aging time, it is firstly revealed that the hardness inside PFZ monotonously decreases although the hardness inside grains increases in the earlier stage of aging. Three distinct regions of “PFZ”, “Transition-area” and “Grain-region” were therefore proposed to explain the origins of such age-hardening behavior observed in this work. In the Ag-added alloy, on the other hand, the hardness could be maintained up to closer regions to grain boundaries at the same level as that inside grains.

Keywords: Al–Zn–Mg(–Ag) alloys; Age-hardening; EDX analysis; Precipitate free zone; Nanoindentation

1. Introduction

Al–Zn–Mg based alloys, having the highest mechanical strength among the age-hardenable aluminum alloys, have been widely utilized as an aircraft structural material. The precipitation process of this alloy system has been extensively investigated by numerous researchers, and the following precipitation sequence is generally accepted [1].

\[ \text{super saturated solid solution } \alpha \rightarrow \text{GP zone } \rightarrow \eta' \rightarrow \eta(\text{MgZn}_2) \rightarrow T((\text{Al, Zn})_{48}\text{Mg}_{32}) \] (1)

The intermediate \( \eta' \) phase mainly contributes to the age-hardening of the alloy due to the finer dispersion inside grains during the aging process after quenching from a solution treatment temperature. However, TEM observation has shown that precipitate free zones (PFZ) are also formed around grain boundaries, regardless of transgranular precipitation being taken place. The PFZ is often formed in many aluminum alloys, suggesting that the nucleation of precipitates is affected to some extent in the vicinity of grain boundaries. Several researchers have tried to explain the formation mechanism of PFZ mainly by two theories. One is the vacancy depletion theory, which takes into account the depleted vacancy concentration smaller than a certain critical vacancy concentration required for the nucleation [2,3]. The other is the solute depletion theory taking into account the depleted solute concentrations near grain boundaries, resulting in the decrease in supersaturation for precipitation [4]. In addition, the PFZ has been believed to affect greatly the mechanical properties of alloys because microcracks are generated inside PFZ due to the preferential deformation of PFZ [5]. However, it was also reported that slip bands and stress concentration are preferentially relaxed in PFZ, resulting in the increased strength and elongation [6]. Therefore, the definitive conclusions on the formation mechanism of PFZ and the effects on the mechanical properties have not been established yet. One of the reasons is the difficulty of quantitative characterization of such fine-scale features (< ~1 \( \mu \)m) using the mechanical properties of PFZ has been also extremely difficult using conventional experimental techniques. Therefore, a newly developed
The nanoindentation technique becomes quite effective in investigating local deformation and hardness within alloys in the nanometer scale. The nanoindentation method is expected to make clear the characteristics of PFZ and to identify the formation mechanism of PFZ. Note that such information is quite useful to control the microstructures in alloys.

In this work, the nanoindentation method was successfully utilized to Al–4.9 mass%Zn–1.8 mass%Mg (0.3 mass%Ag) alloys to estimate the mechanical properties of the vicinity of grain boundaries with PFZ. Microstructure observation and energy dispersive X-ray (EDX) analysis were also performed inside grains and near grain boundaries to compare with the results obtained by the nanoindentation method.

### 2. Experimental procedure

The chemical compositions of the two alloys are listed in Table 1. The ingots were homogenized at 743 K for 172.8 ks, then hot- and cold-rolled to 1.3 mm thick sheets. Specimens were solution-treated at 743 K for 3.6 ks in a salt bath (NaNO₃:KNO₃ = 1:1), and were water-quenched into iced-water and kept for 60 s. Aging treatments were carried out in a silicon oil bath at 433 K. The nanoindentation measurement was performed around grain boundaries using ENT-1100a. The specimens were electrically polished in the ethanol 90% + percloric acid 10% solution. The applied load was 20 mgf and the load and release times were 10 and 1 s, respectively. MicroVickers hardness was also measured with a load of 500 g for 15 s. Microstructure observation and EDX analysis were performed using a JEM-3010 TEM with an EDX system and a JSM-890 FE-SEM.

### 3. Results

#### 3.1. Hardness change and TEM microstructures

The isothermal aging curves of hardness for the ternary and Ag-added alloys aged at 433 K are shown in Fig. 1. In the Ag-added alloy, the increase in hardness is more pronounced and the peak hardness is higher than that of the ternary alloy. The marked effects of Ag addition on the age-hardening behavior of Al–Zn–Mg alloys are discussed later in 3.4. The microstructural change around grain boundaries is shown in Fig. 2 for the ternary alloy aged at 433 K. The precipitates inside grains were identified to be η’ and/or η from the corresponding diffraction patterns. PFZ is observed along grain boundaries with a width less than 500 nm. Although the width of PFZ was previously reported to increase with aging time [7,8], such a change is not clearly observed in Fig. 2 (This discrepancy may be due to the difference of contact angles between neighboring grains). Furthermore, it is also shown in Fig. 2 that a large number of fine precipitates are distributed homogeneously inside grains, whereas larger precipitates are formed with a lower number density in the vicinity of PFZ especially in the specimens under peak- and over-aged conditions. Note that the size of grain boundary precipitates also gradually increases with aging time.

#### 3.2. Microchemical analysis

To obtain compositional information around grain boundaries, the change in solute concentrations towards a grain boundary was examined by EDX analysis. Fig. 3 shows an example of the ternary alloy aged at 433 K for 259.2 ks. Both of Zn and Mg concentrations are maintained at levels of bulk concentrations in the regions far enough from the grain boundary. On the other hand, it is also obvious that the concentrations of Zn and Mg are lower not only in PFZ but also in the regions just outside PFZ. This suggests that solute atoms migrated to the grain boundary, resulting in the formation of coarsened grain boundary

### Table 1

|    | Zn   | Mg   | Ag   | Cu   | Mn   | Cr   | Si   | Fe   | Al   |
|----|------|------|------|------|------|------|------|------|------|
| Ternary | 4.86 | 1.78 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | Bal. |
| Ag-added | 4.89 | 1.78 | 0.28 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | Bal. |
precipitates with regions of depleted solute concentrations. Note that high solute concentrations were actually detected on the grain boundary if grain boundary precipitates were analyzed by EDX. Fig. 4 shows the changes in Zn and Mg concentrations inside PFZ of the ternary alloys aged at 433 K. The regions analyzed by EDX were almost 150 nm far from grain boundaries. It should be noted that the solute concentrations of Zn and Mg inside PFZ monotonously decrease with aging time. This depletion behavior of solute elements well corresponds to the coarsening of grain boundary precipitates as shown in Fig. 2.

3.3. Nanoindentation hardness

Fig. 5 shows backscattered electron images of the ternary alloy aged at 433 K for 259.2 ks after nanoindentation test. It is clearly seen that some of triangle indents were loaded inside PFZ with brighter contrast.
along a grain boundary. The relationship between nanoindentation hardness and distance from the grain boundary is shown in Fig. 6. Based on the direct observation of nanoindentation marks, the hardness inside PFZ was found to be much lower than those inside grains. It is also obvious that the hardness in the regions just outside PFZ also decreases towards the grain boundary. This tendency is quite similar to the decreasing behavior of solute concentrations in Fig. 3, suggesting that the hardness is mainly attributed to solid solution hardening. Fig. 7 shows the temporal changes in hardness inside a grain and inside PFZ for the ternary alloys aged at 433 K. It is firstly revealed in this work that the hardness inside PFZ monotonously decreases with aging time, although the hardness inside grains increases in the earlier stage of aging.

### 3.4. Effects of Ag addition

Microalloying addition of Ag is well-known to exhibit both the accelerated and increased age-hardening in Al–Zn–Mg alloys [9]. Since such effects could be reconfirmed in this work, consideration has been given not only to the mechanical properties of PFZ but also to the formation mechanism of PFZ even for the Ag-added alloy.

Fig. 8 shows the microstructural change around grain boundaries in the Ag-added alloy aged at 433 K. PFZ is observed with a width much smaller than that of the ternary alloy in Fig. 2. This modification of PFZ by Ag addition well agrees with the result of the previous work [9]. It should be also noted that grain boundary precipitates are not so coarsened compared with those of the ternary alloy. The change in Zn and Mg concentrations across grain boundaries are shown in Fig. 9 for the ternary and Ag-added alloys aged at 433 K for 259.2 ks. The concentrations of Zn and Mg in the Ag-added alloy were found to be much more maintained up to closer regions to the grain boundary than those in the ternary alloy. Fig. 10 shows the relationship between nanoindentation hardness and distance from the grain boundary in the Ag-added alloy. Note that the decrease in hardness towards the grain boundary is much smaller than that of the ternary alloy (Fig. 6).

### 4. Discussion

From the obtained experimental results, it was confirmed that there is a region where precipitates are coarsened and solute concentrations decrease compared with those inside grains. The changes in hardness, solution concentration...
and precipitate density are schematically illustrated in Fig. 11 against the distance from grain boundaries of the ternary and Ag-added alloys. The vicinity of grain boundaries of Al–Zn–Mg(–Ag) alloys seems to be separated into three regions, i.e. “PFZ”, “Transition-area” and “Grain-region”. Transition-area was newly proposed in this work is adjacent to PFZ. Since solute concentrations in Grain-region are kept at levels of bulk concentrations, it is conceivable that finely dispersed precipitates greatly contribute to hardness. On the other hand, in PFZ hardness is only due to the solid solution hardening because there is no precipitate. The lower hardness inside PFZ is therefore attributed to the decreased solute concentrations as a result of the formation of grain boundary precipitates. In Transition-area, furthermore, the hardness decreases due to less effective solid solution hardening and precipitate hardening than those inside grains.

As for the effects of Ag addition, Transition-area and PFZ were found to be much narrower than those in the ternary alloy because precipitates are formed and solute concentrations are maintained up to closer regions to grain boundaries. To understand the reason why the width of PFZ decreases in the Ag-added alloy, our proposed ordering parameters between elements, $V$, were taken into account [10–12]. Fig. 12 shows an ordering parameter map of several microalloying elements X in Al–Zn–Mg alloys. This map systematically indicates how much Zn–X and Mg–X pairs interact each other in Al. For example, a smaller value of $V_{Zn-X}$ (or $V_{Mg-X}$) corresponds to the stronger interaction of Zn–X (or Mg–X), resulting in the formation of co-clusters consisting of those elements. The detailed derivation method of ordering parameters is described in our previous papers [10–12]. From Fig. 12, it is obvious that Ag has the strong interactions with Zn and Mg compared with other elements. Therefore, Ag atoms preferentially trap Zn and Mg atoms migrating to grain boundaries, resulting in the prevention of solute depletion. Maloney et al. [13] reported by using three-dimensional atom probe (3DAP) that Ag promotes co-clustering of Ag...
and Zn atoms, followed by Zn–Mg–Ag rich clusters which accelerate the nucleation of the intermediate \( \eta \) precipitates. Therefore, the systematic prediction of the atomistic behavior of elements based on our uniquely estimated ordering parameters seems to be sufficiently useful to reproduce the formation mechanism of PFZ in Al–Zn–Mg(–Ag) alloys.

5. Conclusions

The nanoindentation method has been effectively applied to analyze the mechanical properties of the regions near grain boundaries in Al–Zn–Mg(–Ag) alloys. TEM observation and EDX analysis have been also performed to correlate the microstructures and solute concentrations with the obtained nanoindentation hardness. The results are summarized as follows.

1. The hardness is lower not only in PFZ but also outside PFZ than those within grains, indicating the existence of the newly proposed Transition-area.

2. The hardness is mainly attributed to precipitation hardening in grains, solid solution hardening in PFZ and less effective solid solution hardening and precipitation hardening in Transition-area, respectively. In PFZ, the hardness monotonously decreases even during age-hardening stage inside grains.

3. In the Ag-added alloy, the hardness was maintained up to closer regions to grain boundaries than that in the ternary alloy. This is due to the strong interactions of Zn–Ag and Mg–Ag, resulting in the formation of narrower regions of PFZ and Transition-area.

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