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Quantitative Analysis of the Vicinity of Grain Boundaries with Precipitate Free Zones in Al-Zn-Mg (-Ag) Alloys

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Abstract

To correlate quantitatively the mechanical properties of Al-4.9mass%Zn-1.8massMg(-0.3mass%Ag) alloys with solute distribution in the vicinity of grain boundaries, corresponding microstructural and compositional characteristics respectively by TEM observation and EDX analysis, tensile test and nanoindentation measurement have been performed. The remarkable decreases in hardness and solute concentrations were observed towards grain boundaries even in the regions just outside precipitate free zone (PFZ). In the Ag-added alloy, the nanoindentation hardness could be maintained up to closer regions to grain boundaries at a level similar to that inside grains, resulting in larger elongations to fracture. Such a modification in solute concentration in the vicinity of grain boundaries could be achieved even by two-step aging treatments, and by which 0.2% proof stress of the ternary alloy increased without decreasing elongation.

1. Introduction

The precipitation process of Al-Zn-Mg alloy system has been extensively investigated by numerous researchers, and the following precipitation sequence is generally accepted [1].

$$\text{Super saturated solid solution } \alpha \rightarrow \text{GP zone} \rightarrow \eta' \rightarrow \eta\ (MgZn_2)$$
$$\rightarrow T((Al,Zn)_{48}Mg_{32}) \qquad (1)$$

The intermediate η' phase mainly contributes to the age hardening of the alloy due to the finer dispersion inside grains in the aging process. However, TEM observation has shown that PFZ is also formed around grain boundaries, regardless of transgranular precipitation being taking place. This suggests 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 nucleation [2, 3], and 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 on the mechanical properties of alloys. Thomas *et al.*[5] reported that microcracks are generated inside PFZ due to the preferential deformation of PFZ, resulting in the decreased elongation to fracture. On the other hand, it was also reported that slip bands and stress concentration are preferentially relaxed in PFZ, resulting in the increased strength and elongation [6]. However the definitive conclusions on the formation mechanism of PFZ and the effects on the mechanical properties have not been established yet.

As for the modification of solute distribution in the vicinity of grain boundaries, two methods have been applied to change the width of PFZ; i.e. (1) microalloying addition and (2) two-step aging treatment. Microalloying addition of Ag was found to exhibit both accelerated and increased age-hardening in Al-Zn-Mg, with the smaller width of PFZ than that of the ternary alloy [8]. Furthermore, it is also known that if two-step aging treatment is applied, fine precipitates are formed even inside PFZ during the first aging [2, 7]. However, no consideration has been given not only to the mechanical properties of the modified PFZ but also to the formation mechanism of the PFZ in Al-Zn-Mg-Ag alloys.

In this work, the mechanical properties were quantitatively correlated with the corresponding micro structural and compositional characteristics of solute concentration in the vicinity of grain boundaries in Al-4.9Zn-1.8Mg(-0.3Ag) (mass%) alloys. The nanoindentation method was successfully utilized to estimate the mechanical properties of such quite small regions as PFZ. Microstructure observation and EDX analysis were also performed inside grains and near grain boundaries to compare with the results obtained by nanoindentaion and tensile tests.

2. Experimental Procedure

Two alloys studied in this work are Al-4.9Zn-1.8Mg and Al-4.9Zn-1.8Mg-0.3Ag (mass%) alloys. The ingots were homogenized at 743K for 172.8ks, then hot- and cold-rolled to 1.3mm thick sheets. Specimens were solution-treated at 743K for 3.6ks in a salt bath ($NaNO_3$:KNO_3=1:1), and were quenched into iced-water and kept for 60s. Aging treatments were carried out in a silicon oil bath at 433K. The nanoindentaion measurement was performed around grain boundaries using ENT-1100a. Micro Vickers hardness was also measured with a load of 500g for 15s. Microstructural observation and EDX analysis were performed using conventional TEM with an EDX system and FE-SEM. To some specimens, furthermore, two-step aging was applied; i.e. aging at 373 or 408K for 1209.6ks after aging at 453K for 10.8ks. Tensile test was carried out with a strain rate of 1mm / min at RT.

3. Results and Discussion

3.1 Effects of Ag Addition

The microstructural change around grain boundaries is shown in Figure 1 for the ternary and Ag-added alloys aged at 433K. The precipitates inside grains were identified to be η' and/or η from the corresponding diffraction patterns. PFZ is observed along grain boundaries of the ternary alloy with a width less than 500nm. 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 aging conditions. Note that the size of grain boundary precipitates also gradually increases with aging time. In Ag-added alloy, on the other hand, PFZ is observed with a width much smaller than that of the ternary alloy. This modification of PFZ by Ag addition agrees with the result of the previous work [8]. It should be also noted that grain boundary precipitates are not so coarsened in the Ag-added alloy compared with those of the ternary alloy.

Figure 2 (a), (b) shows backscattered electron images of the ternary alloy aged at 433K for 259.2ks after nanoindentation test. The relationship between nanoindentation hardness and distance from a grain boundary is also shown in Figure 2 (c) with the corresponding EDX analysis results. In the ternary alloy, it is clearly seen that some of triangle indents were

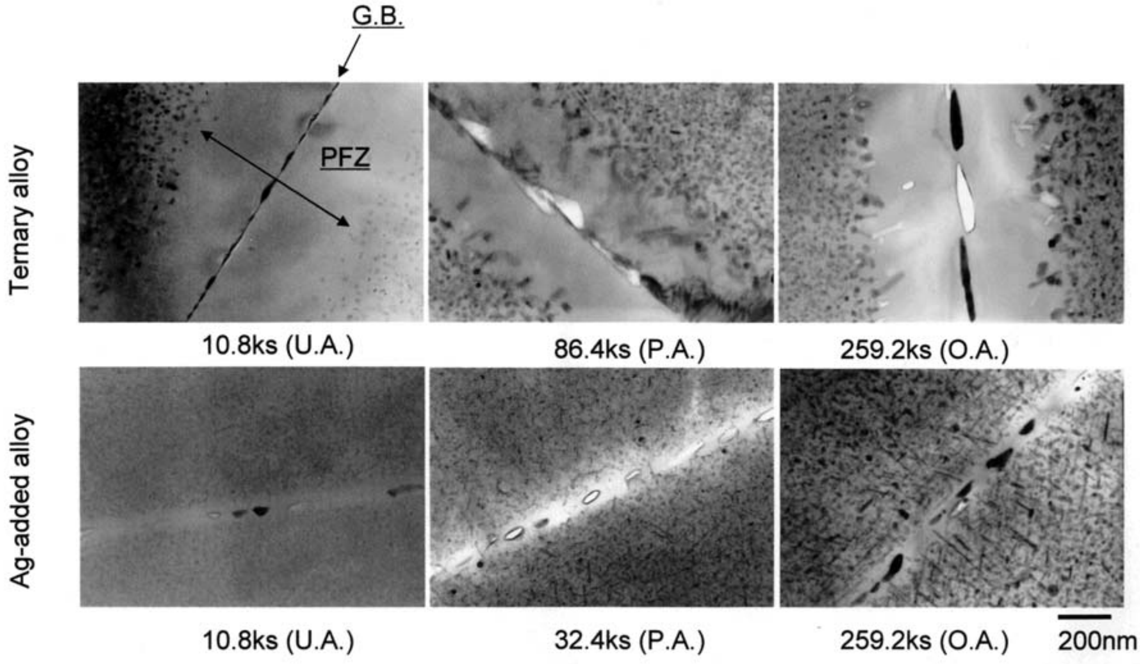

Figure 1: TEM images around grain boundaries in the ternary and Ag-added alloys aged at 433K for various aging times.

loaded inside PFZ with brighter contrast along the grain boundary. Based on the direct observation of indentation marks, the hardness inside PFZ was found to be much lower than those inside grains. Furthermore, it is also clear 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 of Zn and Mg, suggesting that solute atoms migrated to the grain boundary with regions of depleted solute concentrations and decreased nanoindentation hardness. In the Ag-added alloy, on the other hand, the decrease in nanoindentation hardness towards grain boundaries is much smaller than that of the ternary alloy (Figure 2 (d)).Note that Zn and Mg are also much more remained up to closer regions to grain boundaries in the Ag-added alloy, resulting in the same hardness as those inside grains.

From the experimental results, it was confirmed that there is a region where precipitates are coarsened and solute concentrations decrease compared with those of grains. Therefore, we propose that the vicinity of grain boundaries of Al-Zn-Mg(-Ag) alloys can be separated into three regions; i.e. “PFZ”, “transition area” and “grain”. The transition area was newly detected in this work between grain and PFZ. Since solute concentrations in grains are kept at levels of bulk concentrations, it is conceivable that finely dispersed precipitates greatly contribute to the hardness. On the other hand, it is considered that in PFZ hardness is only due to the solid solution hardening because of no precipitates. Therefore, the lower hardness inside PFZ attributes to the decreased solute concentrations as a result of the formation of grain boundary precipitates. In transition area, furthermore, solute concentrations slightly decrease and precipitates are coarsened. Therefore, the transition area can be defined as the region where the hardness decreases due to the less effective solid solution hardening and precipitate hardening than those inside grains. In the Ag-added alloys, the transition area and PFZ become much smaller because solute concentrations are maintained up to closer regions to grain boundaries. This modification in solute concentration in the vicinity of grain boundaries by the addition of Ag is reasoned in refs. [9, 10].

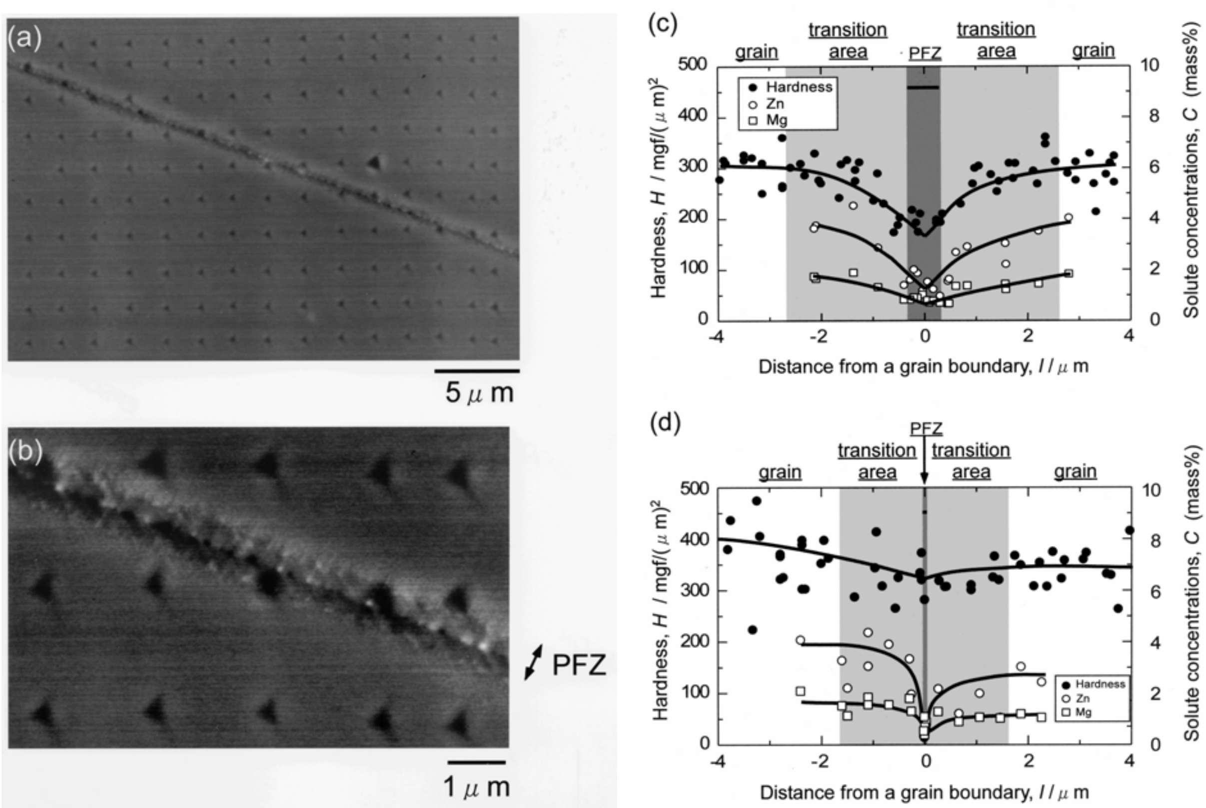

Figure 2: Backscattered electron images of nanoindentation marks around a grain boundary of the ternary alloy aged at 433K for 259.2ks. Some of nanoindentation marks are located inside PFZ with bright contrast. (a) Low magnification, (b) high magnification. Nanoindentation hardness and solute concentration changes across the grain boundary are also shown for the ternary (c) and Ag-added (d) alloys.

In order to examine the macroscopic mechanical properties, tensile test was performed for the investigated alloys. Figure 3 shows the relationship between 0.2% proof stress and elongation of the alloys aged at 433K for various aging times. Fracture surfaces at maximum proof stresses are also shown for the ternary (aged for 86.4ks) and Ag-added (aged for 32.4ks) alloys. From the results of tensile test, elongation under the same level of proof stress was found to be larger in the Ag-added alloy than that in the ternary alloy. Furthermore, it was also revealed that the mode of fracture remarkably changes from intergranular fracture to transgranular fracture by Ag addition (Figure 3 (b), (c)). This implies that fracture occurs preferentially in the vicinity of grain boundaries with PFZ, strongly suggesting the possibility of the fracture mechanism proposed by Thomas *et al.*[6].

3.2 Effects of Heat Treatment

To examine the effects of two-step aging, the ternary alloy was initially aged at 453K for 10.8ks and then aged at 373K or 408K for 1209.6ks. Figure 4 shows the microstructural change around grain boundaries of the single- and two-step aged alloys. In the specimens single- or two-step aged at 408K, PFZ are observed along grain boundaries without change in the width (Figure 4 (a), (b)). In the specimen two-step aged at 373K, on the other hand, fine precipitates are observed within the initial PFZ formed after the first aging (Figure 4 (c), (d)). Figure 5 shows the corresponding tensile properties of the three alloys and fracture surfaces of the two-step aged alloys. It was found that the similar improvement of mechanical properties could be achieved by two-step aging as is the case of Ag addition (Figure 3); i.e. increased proof stress without decreasing elongation due to the change of fracture mode.

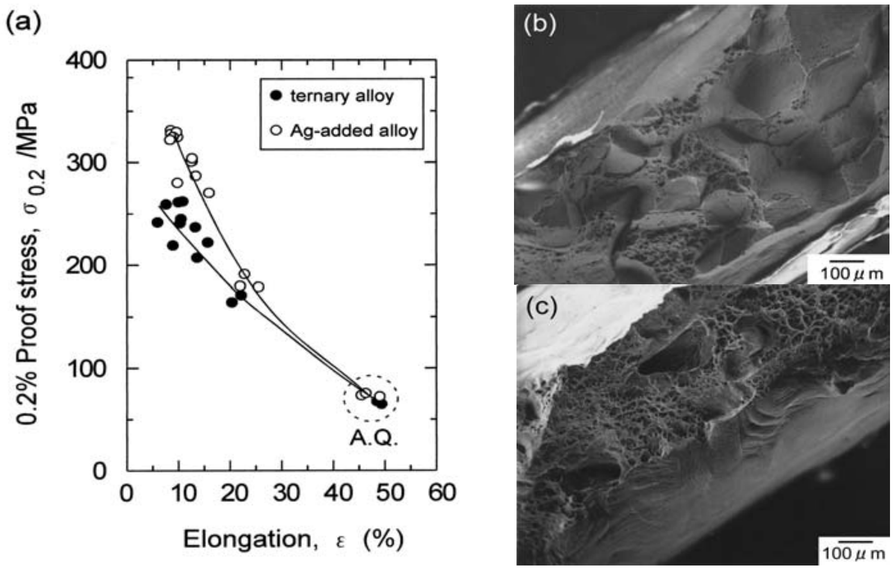

Figure 3: (a) Relationship between 0.2% proof stress and elongation in the ternary and Ag-added alloys aged at 433K. Fracture surfaces at maximum proof stress are also shown for the ternary (b) and Ag-added (c) alloys.

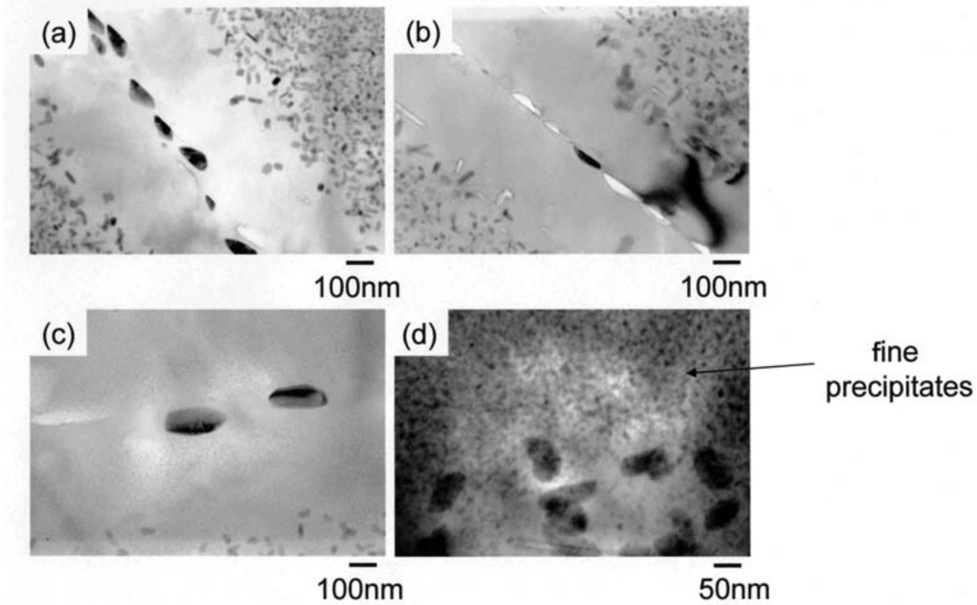

Figure 4: TEM images around grain boundaries in the ternary alloys single aged at 453K (a), two-step aged at 408K (b) and 373K (c) after aging at 453K. Enlarged micrograph of (c) showing fine precipitates inside PFZ of the first aging is also shown in (d).

4. Conclusion

To correlate quantitatively the mechanical properties of precipitate free zone (PFZ) with the corresponding microstructural and compositional characteristics, TEM observation, EDX analysis, tensile test and nanoindentation measurement have been performed for Al-4.9Zn-1.8Mg(-0.3Ag) (mass%) alloys. The obtained results are summarized as follows.

1. The hardness was lower not only in PFZ but also outside PFZ than those within grains, suggesting the existence of newly proposed transition area. Therefore it was found that the hardness is mainly attributed to precipitation hardening in grains, solid solution hardening in PFZ and less effective solid solution and precipitation hardenings in transition area, respectively.
2. 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 modification of solute concentration in the vicinity of grain boundaries by Ag addition. Similar modification could also be achieved by two-step aging.
3. By decreasing the width of PFZ through Ag addition and/or two-step aging treatment, tensile properties of Al-Zn-Mg alloys could be improved quite remarkably.

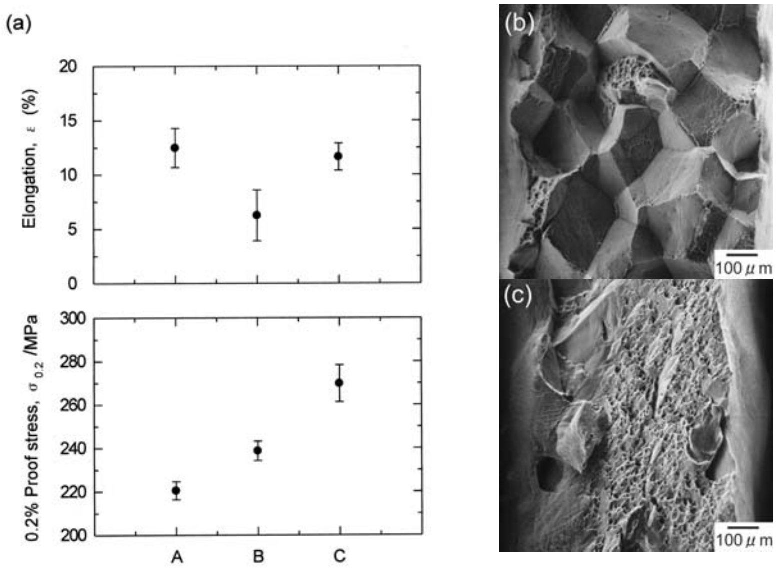

Figure 5: Tensile properties of the single-aged and two-step aged alloys (a) (A: single-aged at 453K for 10.8ks, B: two-step aged at 408K for 1209.6ks after aging at 453K and C: two-step aged at 373K for 1209.6ks after aging at 453K). The corresponding fracture surfaces of the alloys B and C are also shown in (b) and (c), respectively.

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