Precipitation Behavior in an Al-Mg Alloy with High Mg Composition

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Abstract We have investigated the precipitation phenomena which occur at high aging temperatures in an Al-Mg alloy with high Mg concentration by means of Vickers hardness (HV) testing, differential scanning calorimetry (DSC), transmission electron microscopy (TEM) and analytical scanning transmission electron microscopy (STEM-EDX). It was found that the hardness and heat changes are closely correlated, and that the size of the exothermic heat peak depends on the quantity of β'-phase formed during isothermal aging prior to the DSC measurements. This implies that the formation of β'-phase precipitates is mainly responsible for the increase in hardness. Our TEM observations showed that β'-phase precipitates are plate-like in morphology and form on matrix {100} planes, whilst stable β-phase precipitates are granular in shape. In-situ TEM using a heating holder revealed that β-phase precipitates grew by consumption of β'-phase platelets. Element-maps obtained by STEM-EDX indicated that the composition of β'-phase platelets was approximately Al-33at%Mg.

Keywords: aluminum-magnesium alloy, precipitation, isothermal aging, Vickers microhardness, differential scanning calorimetry, transmission electron microscopy

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1. Introduction

Aluminum-base Al-Mg alloys are well-known light-weight metallic materials possessing high strength and good corrosion resistance, which make them versatile in various practical applications. As the Mg composition increases, the strength of the alloy increases but the workability decreases. The deterioration of workability causes difficulties in production and usage [1]. Previous studies have claimed that precipitation hardening occurs in Al-Mg alloys with a Mg content more than ~6wt%, while in alloys containing less than ~6wt%Mg the mechanism is solid-solution hardening [2,3]. However, this conclusion is still under discussion, because of insufficient knowledge of how the atomic composition, the annealing temperature and the diffusivity of Mg atoms affect phase decomposition.

A variety of precipitation phenomena have been reported in Al-Mg alloys. Precipitates have been found to form both inside grains and at grain boundaries during high-temperature aging [4,11]. Other structural changes such as the formation of GP zones, and modulated and ordered structures have been reported in alloys annealed at low temperatures [5,6,7]. The crystal structures of stable β-phase and metastable β'-phase have been previously investigated. However, the details of phase decomposition in Al-Mg alloys are still not fully understood [8,9,10]. Since both solid-solution and precipitation strengthening are important in Al-Mg alloys, the mechanisms should be examined in detail. The present work investigates precipitation in an Al-13.7at%Mg aged at 473K.

2. Experimental Procedure

We examined an Al-13.7at%Mg alloy, using a Shimadzu HMV-2000 Vickers hardness tester, a RIGAKU Thermoplus 8230 differential scanning calorimeter (DSC), a HITACHI H-800 transmission electron microscope (TEM) and a JEOL 2100F scanning transmission electron microscope equipped with an energy-dispersive X-ray spectrometer (STEM-EDX).

The samples were homogenized by annealing at 723K in a salt bath (KNO₃: NaNO₃ = 1:1 in molar ratio) for 4320 min. They were then solution-treated at 723K for 60 min and quenched in ice water. Subsequently, the samples were aged isothermally either at 373K or at 473K in an oil bath. The size of samples for HV measurement was 10 mm × 10 mm × 1.5 mm, and the surface was polished slighly with emery #2000 paper. DSC measurements were performed from room temperature to 723 K at a rate of 2K / min. The samples for conventional TEM were punched out as disks with a diameter of 3 mm, and the disks were electro-polished after heat treatments. The samples for STEM-EDX were prepared using an electro-polisher and a focussed ion-beam thinner.
3. Results and Discussion

3.1. Vickers Hardness Tests

Figure 1 shows the changes in the Vickers hardness (HV) due to isothermal aging. At an aging temperature of 373K, the Vickers hardness started to increase after aging for \(2 \times 10^4\) min and continued to increase to the maximum aging time of \(10^6\) min. In the specimen aged at 473K, the hardness increased after only 30 min to reach a peak hardness of \(HV = 138.2\) after 500 min. The hardness then remained close to this value before falling off after about 5000 min due to overaging.

The overall trends seen in these curves - that the maximum value of the HV hardness occurs at longer aging times at the lower aging temperature, but the HV hardness attains a higher value - are commonly observed in precipitation-hardened aluminum alloys. Unlike other Al-base precipitation alloys, however, overaging after the peak condition did not occur rapidly in the Al-13.7at%Mg annealed at 473K: the hardness kept at a high level for a relatively long period. This fact suggests that the diffusion of Mg atoms in the aluminum-rich matrix does not occur easily.

Figure 1. The Vickers hardness vs. aging time curves obtained for Al-13.7at%Mg alloy samples isothermally aged at 373K and 473K, respectively.

3.2. DSC Measurements

DSC thermograms of Al-13.7at%Mg specimens aged for various times at 473K are shown in Figure 2.

Exothermic peaks appearing above the horizontal axis and endothermic peak below the axis represent the formation and dissolution of stable/quasistable phases, respectively. An endothermic peak due to clustering is observed at 320-350K. Exothermic/endothermic peaks appeared around 470-520K are likely due to precipitation of the \(\beta'\)-phase [9,12]. Another exothermic peak corresponding to the precipitation of the \(\beta\)-phase is observed in the vicinity of 560K. The heights of the exothermic peaks due to the formation \(\beta'\)- and \(\beta\)-phases decreased with increasing aging time. This trend suggests that both types of precipitates formed during the isothermal aging prior to the DSC measurements. The reduction of the heat \(\Delta h\) corresponds to the amount of precipitation as was observed in Al-Mg-Si alloys [13]. To estimate the amount of the \(\beta'\)- and \(\beta\)-phases transformations in this Al-Mg alloy quantitatively in a similar manner to the previous work, we separated the two exothermic peaks appearing around 460-600K, using a commercial software package, “Origin”.

Figure 3 shows the relationships between the \(\Delta h(\beta')\), \(\Delta h(\beta)\) and the aging time, respectively. The aging time at which the heat change started to increase coincides with the onset time of the increase in HV hardness. Thus, comparing the heat reductions \(\Delta h(\beta')\) and \(\Delta h(\beta)\) with the Vickers hardness, we conclude that the precipitation of \(\beta'\)- and \(\beta\)-phases were responsible for the increase in hardness, but the precipitation of \(\beta'\)-phase is likely to be more important.

Figure 3. Heats of metastable and stable precipitates estimated from DSC measurements of Al-13.7at%Mg samples aged at 473K for various times.

3.3. TEM Observations

TEM was carried out to investigate microstructural evolution in specimens aged both at 373K and at 473K. Figure 4 shows two TEM micrographs of the same area in a sample aged at 373K for \(1 \times 10^2\) min taken from the \(<001>\) and \(<110>\) zone axes of the aluminum matrix, respectively. In the TEM micrograph taken from the \(<001>\) direction, precipitates appear needle-like with lengths of the order of microns along \(<100>\) directions but with negligible width, while in the micrograph taken from the \(<110>\) direction they seem plate-like with considerable width. These observations are consistent with platelet precipitates lying on matrix \{100\} planes, which are edge-on when viewed from the \(<001>\) direction.

Figure 2. DSC curves of Al-13.7at%Mg samples isothermally aged at 473K for various times.
TEM micrographs of samples aged at 473K for various times from 10 min to 500 min are shown in Figure 5. They show that β’-phase precipitates were formed in the matrix at these aging conditions. Precipitates were initially granular, but transformed into a plate-like precipitates, and finally turned into thick rod-shaped precipitates with increasing aging time.

In order to distinguish the shapes of β’- and β-phases precipitates, we examined the microstructure of samples aged at the condition that the exothermal peak fell down to the horizontal line in the DSC instrument. Figure 6 shows TEM images of the microstructure taken from <100> and <110> zones of the matrix. The TEM observations revealed that β-phase precipitates are thick granules with irregular shapes.

In these TEM images, two types of precipitates may be seen: small needle-like particles, densely distributed; and large precipitates with irregular shapes. The large precipitates were observed to grow, and nearby small precipitates to shrink, so that precipitation-free zones formed around the large precipitates. These observations strongly suggest that the large precipitates grew and coarsened by absorbing solute atoms released by the small particles. We conclude that the small and large precipitates are the β’- and β-phases, respectively, and that the β’- and β-phases are independent from each other with respect to crystallographic structure and thermal stability.

3.5. STEM-EDX Observations on β’-phase Precipitates

Several quasi-stable precipitates with different structures and compositions may form during the phase decomposition of Al-Mg alloys, depending on the aging temperature. In this section, we describe results obtained using STEM-EDX. Since TEM samples were prepared by combination of electro-polishing and ion-beam thinning, β’-phase precipitates often protruded from the sample edge of the thin-film region. Figure 8 shows protruding platelets of β’-phase precipitates in an Al-13.1at%Mg sample aged isothermally at 473K for 1000min. The matrix effect was thus minimized in the composition analysis in this area.

To investigate the structural sequence of the β’- and β-phases, we conducted in-situ TEM heating experiments on as-quenched samples. Figure 7 shows two TEM images of the same area of a sample receiving (a) aging at 473 K for 80 min, and (b) after further in-situ aging at 473 K totally for 500 min.

In these TEM images, two types of precipitates may be seen: small needle-like particles, densely distributed; and large precipitates with irregular shapes. The large precipitates were observed to grow, and nearby small precipitates to shrink, so that precipitation-free zones formed around the large precipitates. These observations strongly suggest that the large precipitates grew and coarsened by absorbing solute atoms released by the small particles. We conclude that the small and large precipitates are the β’- and β-phases, respectively, and that the β’- and β-phases are independent from each other with respect to crystallographic structure and thermal stability.

3.4. In-situ TEM Observations of Microstructural Evolution in an Al-Mg Alloy Aged at 473 K

To investigate the structural sequence of the β’- and β-phases, we conducted in-situ TEM heating experiments on as-quenched samples. Figure 7 shows two TEM images of the same area of a sample receiving (a) aging at 473 K for 80 min, and (b) after further in-situ aging at 473 K totally for 500 min.

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Figure 8. β’-phase precipitates of an Al-13.7at%Mg sample isothermally aged at 473K for 1000 min.

Figure 9 (a) and (b) show STEM-EDX compositional maps of this area for Al and Mg, respectively. These maps confirm that Mg is concentrated in the β’-phase. Quantitative analysis shows that the average Mg
concentrations were 33 at% for the precipitates and approximately 7% for the matrix. This result may be feasible, since it is intermediate between the stable β-phase of Al₃Mg₂ (Mg: 40 at%) and GP zones of Al₃Mg (Mg: 25 at%).

Figure 9. STEM-EDX element maps of Al-13.7 at%Mg alloy sample aged at 473K for 1000 min. The left and right images were Al-K and Mg-K spectral maps, respectively.

In section 3.1 above, we discussed the changes in Vickers hardness during the isothermal aging, and concluded that precipitation in this Al-Mg alloy was relatively slow. The TEM observations here, which show that β'-phase precipitates are subject to Mg diffusion in the matrix, suggest that the slow precipitation is due to low diffusivity of Mg in Al.

4. Conclusions

We have investigated precipitation behavior in an Al-13.7 at%Mg alloy, using Vickers micro-hardness testing, TEM and DSC. The following conclusions were obtained:

(1) The correlation between the hardness changes and heat changes, Δh, in the DSC curves implies that the main contribution to the increase in hardness on aging is β'-phase formation.

(2) TEM observations indicated that β'-phase precipitates form on the {001} planes of the Al matrix and grow along the <001> direction in the early stage of aging at both 373K and 473K. The composition of the β'-phase precipitates is approximately 33 at%Mg.

(3) The relatively slow rate of precipitation in this Al-Mg alloy is caused by low diffusivity of Mg atoms in the aluminum matrix.

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