Effects of Solute Segregation on Precipitation Phenomena and Age Hardening Response of High-Purity and Commercial AZ91 Magnesium Alloys

Yosuke Tamura1, Yusaku Kida1,* Ayumi Suzuki1,*, Hiroshi Soda2 and Alexander McLean2

1Department of Mechanical Science, Chiba Institute of Technology, Narashino 275-0016, Japan
2Department of Materials Science and Engineering, University of Toronto, Toronto, Ontario M5S 3E4, Canada

In the present study, the continuous and discontinuous precipitation behavior of the commercial AZ91 alloy containing manganese and the AZ91 alloy produced from high-purity elemental components with no manganese addition has been investigated. It was found that for the commercial alloy, the solute manganese segregated within the primary α-Mg dendrites during solidification and played a major role in the initiation of non-uniform distribution of β-precipitates within the matrix grains. In addition, the solute manganese significantly suppressed the growth of discontinuous (lamellar) precipitates. The high-purity alloy also exhibited non-uniform precipitation. However, the precipitation patterns differed from those observed in the commercial alloy due to the inhomogeneous distribution of aluminum, the origin of which was rooted in the solute segregation within the interdendritic regions of the solidification structure. These differences in the precipitation mode caused by the presence or absence of manganese influenced the age hardening of the alloys. The high-purity specimens aged at lower temperatures attained higher peak-hardness owing to greater area fractions of discontinuous precipitation cells.

Keywords: magnesium alloy, solute segregation, precipitation phenomena, age hardening response

1. Introduction

Manganese is added in magnesium-aluminum-zinc (AZ) alloys to offset the adverse effects of iron impurities, which significantly reduce corrosion resistance.1) It also inhibits grain growth during annealing and increases yield strength and hardness.2–4) In commercial grade AZ91 (i.e. casting alloys), the solute manganese exerts significant influence on the precipitation behavior of β-phase during age-hardening treatment.5) The precipitation of the β-Mg17Al12 phase occurs simultaneously in two forms: continuous precipitation (nucleation and growth of isolated precipitate particles within the matrix grains) and discontinuous precipitation (growth in a lamellar mode from the grain boundaries).6,7) It has been noted that non-uniform β-Mg17Al12 precipitation occurred within the grains during aging, causing densely populated areas and leaving large precipitate-free regions. It has been suggested that these geometric patterns are due to the occurrence of continuous precipitation in those areas of the grains that are richer in aluminum.8,9) This was based on the assumption that the aluminum concentration may have remained higher in areas where the eutectic β-Mg17Al12 phase had existed in the interdendritic regions of the as-cast structure even after this phase had completely dissolved into the α-Mg matrix during solution treatments and thus the secondary β-Mg17Al12 phase precipitated preferentially in these regions during aging.9) Kaya et al.9) suggested that this non-uniform precipitation of the β-phase may partially contribute to the poor age-hardening response of AZ91. In commercial alloys, it was found that manganese was responsible for the non-uniform precipitation of the β-phase and the detailed aspects have been reported elsewhere.5) Thus, in order to clarify the effects of precipitation on the age-hardening response, the present paper will deal with the role of solute segregation on the continuous and discontinuous precipitation behavior of commercial AZ91 alloys containing manganese and high-purity AZ91 alloys without manganese. The effects of the precipitation behavior are evaluated in terms of the age-hardening response of the alloys.

2. Experimental Aspects

To produce a high-purity AZ 91 alloy, high-purity magnesium (>99.99 mass%) was prepared by a distillation technique. A detailed description regarding the generation of high-purity magnesium has been given elsewhere.10) The high-purity magnesium was then melted together with 99.99% pure aluminum and zinc under a gas mixture of carbon dioxide and sulfur hexafluoride at a temperature of about 750 °C in a magnesia crucible coated with magnesium oxide to produce the high-purity AZ 91 alloy. The melt was poured into a cylindrical cavity 20 mm in diameter and 105 mm in length of a cast iron mold. Commercial AZ91E alloy ingot was re-melted in a SUS430 grade stainless steel crucible coated with magnesium oxide powder and poured at 750 °C into a mold of the same dimensions. In an attempt to obtain cast structures with a coarse grain size for ease of micro-structural observations, the melt was poured without grain refinement treatment. This generated microstructures with an average grain size of approximately 250 μm for the commercial alloy and 60 μm for the high-purity alloy. Cast rods were sectioned into 5 mm thick disks and used for solution heat-treatment and subsequent age hardening experiments. The chemical analysis of the high-purity and commercial AZ 91E alloys is shown in Table 1. The specimens were solution heat-treated at 410 °C (683 K) in air for 24h (86.4 ks) in a convection muffle furnace to dissolve the eutectic β-Mg17Al12 phase and to homogenize aluminum throughout the matrix. The specimens were subsequently subjected to age-hardening treatments at 150, 170, 190, 210 and 230 °C (423, 443, 473, 503 and 523 K) for...
durations up to 2520 h (9072 ks) in a silicone oil bath and the results evaluated by measuring hardness as a function of aging time. Micro-structural examination of specimens in the cast and aged conditions was conducted by both optical and scanning electron microscopy after etching with a 2% solution of oxalic acid. The distribution of solute elements was examined using electron probe micro-analysis (EPMA) equipped with a wavelength dispersive spectrometer (WDS). The accelerating voltage and current used were 15 kV and 2.2 × 10⁻⁸ A, respectively. The area fraction of growing precipitate cells was calculated at regular intervals using the image analyzer (Image Plus Pro ver. 5) from micrographs representing an area of 880 µm × 710 µm, which encloses approximately 8 grains. Also the composition of precipitates in the early stage of aging was analyzed using EDS in STEM.

3. Results and Discussion

3.1 Cast structure and solute segregation

Although the segregation of solute elements in cast structures is known and well documented in the literature, since the solute segregation associated with solidification exerts significant influence on precipitation behavior of β-phase during age hardening, the difference in the cast structures of high-purity and commercial alloys will be described briefly to help understand the full extent of the effects of the solute segregation on precipitation. The cast structure of the AZ91 magnesium alloy, which exhibits a dendritic form, is often referred to as a cored structure due to its non-equilibrium solidification as well as its aluminum-rich area and eutectic phase within the interdendritic regions. Owing to the partition coefficient $k_0$ that is less than unity ($k_0 < 1$), the solute aluminum is enriched along the periphery of the growing α-Mg primary dendrites, resulting in the formation of a eutectic β-phase in the last solidifying liquid in the interdendritic regions. The distribution of the eutectic β-phase is influenced by the dendrite arm spacing and dendrite morphology. As shown in Fig. 1, the high-purity and commercial AZ91E materials, which were melted and cast in the same way without grain refining treatments, exhibited distinct differences in grain size and dendrite morphology. The high-purity alloy produced fine grains of approximately 60 µm in average size, while the commercial alloy, produced much coarser grains of about 250 µm, exhibiting well developed dendrites with six-fold symmetry. On the other hand, the dendrites in the high-purity alloy, shown in larger magnification in Fig. 2, exhibited the basic rosette form with elongated petals surrounded by the eutectic β-phase (bright regions) and aluminum rich areas (dark regions). It was found that these differences in dendrite form and size exerted significant effects on precipitation patterns of β-phase during age hardening. As shown in the X-ray elemental mapping of aluminum in Fig. 3, aluminum rich areas exist in the interdendritic regions of the grains for both high-purity and commercial alloys and also more prominently along the periphery of the grains for the high-purity alloy. It should be noted that due to the difference in grain size, the elemental mapping of aluminum of the high-purity alloy covers several grains, while the mapping of

<table>
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<tr>
<th>Alloy grade</th>
<th>Al</th>
<th>Zn</th>
<th>Mn</th>
<th>Si</th>
<th>Fe</th>
<th>Cu</th>
<th>Mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>High-purity alloy</td>
<td>8.7</td>
<td>0.94</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>—</td>
<td>—</td>
<td>Bal.</td>
</tr>
<tr>
<td>Commercial AZ91E</td>
<td>8.5</td>
<td>0.71</td>
<td>0.23</td>
<td>0.01</td>
<td>0.001</td>
<td>0.001</td>
<td>Bal.</td>
</tr>
</tbody>
</table>

Fig. 1 Optical micrographs showing the cast structure of (a) high-purity alloy and (b) commercial AZ91E alloy, poured into a cast iron mold at 750 °C (1023 K).

Fig. 2 Large magnification (SEM micrograph) of the cast high-purity alloy specimen in Fig. 1(a), showing the dendrite in a rosette form surrounded by the eutectic β-phase (bright regions) and aluminum rich regions (dark areas).
commercial AZ91E covers a single grain under the same magnification (six-fold symmetry dendrite radiates from the center of the photograph). The growth of secondary arms from the six-fold stem in the commercial alloy resulted in a complex geometrical pattern, entrapping aluminum-rich regions between the dendrite arms as clearly seen in the X-ray mapping. Solute zinc concentrates in the same way as aluminum and is also contained in the $\text{C}_12$-phase. However, in addition to the commonly known segregation behavior of aluminum and zinc during solidification, solute manganese in the AZ91E alloy was found to segregate within the dendrite rather than within interdendritic regions. The results of EPMA line analysis with WDS, carried out across several dendrite arms along the line segment marked AB in Fig. 4, clearly shows that manganese concentration is higher in the core of the dendrites and the concentration of aluminum and zinc is higher within the interdendritic regions.

### 3.2 Grain growth during solution heat treatment

Manganese in magnesium alloys restricts grain growth during hot forming or annealing. This was also confirmed for the cast commercial alloy which contains 0.23% of manganese. As shown in Fig. 5, the commercial alloy exhibited only small grain growth during the solution heat treatment at 410°C, almost retaining the initial grain size of the cast material, while the high-purity alloy containing no manganese exhibited considerable grain growth from about 60 μm to 240 μm during the same 48 h time period. Artificially grain-refined commercial AZ 91E alloy with the grain size of about 55 μm also showed almost no grain growth during an 8 h heat-treatment at a temperature of 400°C, indicating the growth inhibiting effect of manganese.

The eutectic $\text{C}_12$-phase (bright areas in Fig. 4) was almost completely dissolved within 3 h for both the high-purity and commercial alloys at 410°C. After approximately 8 h, aluminum segregation was undetectable by X-ray elemental analysis for both alloys. However, in the commercial alloy, it was found that the distribution of manganese remained unchanged even with prolonged heating. Figure 6 shows SEM micrograph and EPMA line scan for aluminum, zinc and manganese of the commercial alloy specimen heated for 24 h. There are no major concentration peaks for aluminum and zinc distribution, but segregation of manganese still remains within the grain.

Shown in Fig. 7 is the temperature-diffusivity diagram from the literature for comparing the diffusivity of various elements in the magnesium. The diffusivity of zinc is higher than that of aluminum while the latter is about the same as the self-diffusivity of magnesium. However, the diffusivity of manganese is at least one order of magnitude lower than that of aluminum. At the solution heat-treatment temperature of 410°C (683 K) or at 1.46 × 10$^{-3}$ (K$^{-1}$), the diffusion coefficients for zinc, aluminum, and manganese are approximately 3.3 × 10$^{-14}$, 6 × 10$^{-15}$ and 1.8 × 10$^{-16}$ m$^2$s$^{-1}$, respectively. Using the equation, $x = 2(Dt)^{0.5}$, where $x$ is...
the diffusion distance, \( D \) is the diffusion coefficient \( (\text{m}^2\text{s}^{-1}) \) and \( t \) is time \( (\text{s}) \), the diffusion distance for zinc, aluminum, and manganese under the present heat treatment condition \((683\, \text{K}, 86.4\, \text{ks})\) can be calculated for comparison. The equation yields the distance of 107, 46, and 8 \( \mu \text{m} \) for zinc, aluminum, and manganese, respectively, indicating the greater difficulty in diffusing manganese into the matrix than aluminum and zinc during the heat treatment.

3.3 Effect of manganese on discontinuous precipitation

The precipitation treatments were carried out at various temperatures between 150 and 230°C for specimens that were solution heat-treated for 24 h. Within this temperature regime, both continuous and discontinuous precipitations occur competitively from the early stage of aging.\(^{16, 17}\) The discontinuous precipitation, which originates from the grain boundaries, involves cell formation with a lamellar-type structure of \( \beta \)-phase and an aluminum-depleted \( \alpha \)-Mg matrix phase, while the continuous precipitation involves the formation of isolated particles of \( \beta \)-phase within the matrix grains.\(^7\) These precipitations were monitored at regular time intervals by optical microscopy. The micrographs in Fig. 8 show the growth of discontinuous precipitation cells in the high-purity and commercial alloy specimens after heat-treatment at 210°C for 1 h. A pronounced growth of the discontinuous precipitation cells (dark regions) was observed along the grain boundaries in the high-purity specimen, while only a small amount of cells was detected in the commercial alloy. The growth of discontinuous precipitation cells involves the advancement of newly formed matrix-cell boundaries towards the interior of the grains, and the cell growth behavior during age-hardening was comparable to the grain growth behavior during the solution heat treatment. The growth of discontinuous precipitation cells was considerably suppressed in the manganese-containing alloy. Shown in Fig. 9 are the percentages of cell areas, obtained from the image analysis of micrographs (e.g. Fig. 8) of the specimens annealed at 150, 170, 190, 210, and 230°C for various time periods. The growth rate of the cell before reaching the maximum was calculated using the following relation\(^{18}\) between the fraction of the precipitated cell and the growth rate, assuming the cell grows unidirectionally from the grain boundary inward:

\[
 f = 1 - (1 - G t a^{-1})^3
\]

where \( G \) is the growth rate \( (\text{cm} \cdot \text{s}^{-1}) \), \( f \) is the area fraction of cells observed in a micrograph at 100 times magnification, \( t \) is the aging time \( (\text{s}) \) and \( a \) is the side length of the cell when it was assumed to be a cubic form and approximately represented by \( 1/N^{0.5} \) where \( N \) is the number of grains per unit area. The results are given in Table 2.\(^{19}\) These results clearly indicate that the precipitate cells in the high-purity alloy containing no manganese grew at higher rates and thus, occupied much larger areas than in the commercial alloy.

Since the continuous and discontinuous precipitations occur competitively, the growth of precipitation cells eventually ceased after some time had elapsed during aging. This occurs when the continuous precipitation, taking place within the grains depletes the matrix of solute, removing the
chemical driving force for the growth of discontinuous cells. The area fraction of the precipitated cells appears to decrease gradually with time once the maximum value was reached. However, this may be caused by the difficulties with the image analyzer in identifying the cell boundary areas in which the $\beta$-phase within the discontinuous precipitation cells tended to exhibit rod morphologies rather than lamellar morphologies. The average values of the area fraction of precipitate cells at plateau regions in Fig. 9 are also plotted against aging temperatures in Fig. 10. This indicates the area fraction of cells is approximately 20% higher in the high-purity alloy than the commercial alloy and decreases with an increase in aging temperature for both high-purity and commercial alloy specimens.

![Fig. 8 Optical micrographs showing the growth of discontinuous precipitation cells (dark areas) from the grain boundaries of (a) high-purity and (b) commercial alloy specimens aged at 210°C (483 K) for 1 h (3.6 ks).](image)

![Fig. 9 Percentage of areas occupied by discontinuous precipitation cells for the specimens aged at various temperatures. The open symbol is for high-purity alloy and the closed symbol for commercial alloy. Each value represents the average of 5 measurements. The A.Q. data are the results for the as-quenched specimen.](image)

![Fig. 10 Average area fraction of discontinuous precipitation cells at plateau regions in Fig. 9.](image)

![Table 2 The growth rate of discontinuous precipitation cell for the high purity and commercial AZ91E alloys.](image)
Miki et al.\textsuperscript{21) investigated the effects of small additions of elements on both the growth of the discontinuous precipitation cells and the grain growth in Cu-2\%Be alloy and found a clear correlation in which the small additional elements that restricted the grain growth exerted the same retarding effect on the growth of precipitation cells. The present results for the high-purity and commercial AZ91E alloys are consistent with their results.

3.4 Effects of solute segregation on continuous precipitation

The optical micrographs in Fig. 11 show the continuous precipitation of the $\beta$-phase in progress within the high-purity and commercial alloys. Larger magnifications are shown in Fig. 12. Both alloys exhibited entirely different precipitation patterns. For the commercial alloy, the precipitation preferentially occurred in the form of a distinct geometric six-fold symmetry dendrite within the grain and the form is similar to the as-cast dendrite structures (Fig. 1(b)), indicating a close association with solute segregation that remained within the grains even after long solution heat treatment.

Figure 13 shows the results of EPMA line scan carried out across the precipitated dendrite arms of the commercial alloy. The results clearly indicate the locations of concentration peaks for aluminum and zinc have shifted from those of the as-cast state (Fig. 4) and the new concentration peaks now coincide with those of manganese, indicating that the $\beta$-phase containing aluminum and zinc precipitated preferentially in the regions of the grains that were richer in manganese. Thus, the precipitation must have been aided by manganese segregation that occurred during the solidification stage and remained in the grains even after aluminum and zinc diffuse well into the matrix with solution heat treatment (Fig. 6).

Kamado et al.\textsuperscript{8) also noted that the dendrite form of continuous precipitates within the matrix grains was more pronounced in specimens solidified with higher cooling rates. Their observation is consistent with the present finding that the precipitation pattern is related to solute segregation during solidification.

In the high-purity alloy containing no manganese, the precipitates did not form the dendrite patterns as observed in the manganese-containing alloy, indicating that the precip-
itation in the high-purity alloy is driven by other solute elements such as aluminum and zinc. Aluminum and zinc segregate in the same manner during solidification. Since the diffusivity of zinc is much higher than aluminum, zinc will have a better chance to diffuse homogeneously into the matrix during solution heat treatment. However, the minute differences in aluminum concentration, originating from the initial solute segregation in the cast structure (e.g. Figs. 2 and 3(a)), may still persist within the matrix even after prolonged heat treatment and the concentration differences become undetectable by EPMA line analysis (e.g. Fig. 6). If the non-uniform precipitation patterns (Figs. 11 and 12) in the high-purity specimens are related to the aluminum segregation retained in the matrix, similar patterns can be replicated from the X-ray mapping of the aluminum for the as-cast specimen, shown previously in Fig. 3(a). Figure 14(a) is an image produced from Fig. 3(a) with the aid of Adobe Photoshop by simply changing the image contrast and highlighting the areas that were richer in aluminum concentration. Thus, the brighter areas in Fig. 14(a) correspond to the peripheries and interdendritic regions of the rosette dendrites in Fig. 2, which are richer in aluminum and the dark regions in Fig. 14(a) belong to the inner parts of the dendrites. The pattern that emerged is strikingly similar to the actual precipitated image shown for comparison in Fig. 14(b) and also in Fig. 12. The dark regions in Fig. 14(b), some of which still resemble rosette form, are sparsely precipitated areas and the brighter regions are densely precipitated areas. From this comparison, it can be deduced that for the high-purity alloy containing no manganese, the continuous precipitation was even found to be sensitive to the minute differences in the supersaturation of aluminum in the matrix, and it occurred preferentially at the interdendritic regions and peripheries of the underlying rosette grains of the original solidification structure which solely existed as undetectable levels of concentration differences in the matrix after solution heat treatment, while for manganese containing alloys, segregation of manganese overrode the differences in minute aluminum concentration and the continuous precipitations occurred preferentially in the core of the original dendrites of the solidification structure that were richer in manganese.

3.5 Role of manganese

The distribution profile of manganese in Fig. 13 is almost identical with that of aluminum, suggesting that the precipitation is directly related to the concentration of manganese, meaning that more manganese concentration leads to more precipitates. It is known that zinc segregates not only to the eutectic $\beta$-phase but also to the precipitate phase substituting for aluminum. The distribution profile in Fig. 13 suggests the same substitution may occur for aluminum with manganese during the precipitation of the $\beta$-phase. If part of the aluminum is substituted with manganese in the $\beta$-phase, the regions of the grains where manganese is concentrated will be able to act as if the regions were richer in aluminum, causing preferential precipitation. There is a report of the $\beta$-precipitates containing a small amount of manganese, the average composition of which is $62.4 \text{Mg}-34.4 \text{Al}-0.1 \text{Mn}-3.1 \text{Zn}$ (in at%) in specimens aged for 24 h at 170°C. However, from this result it is not determinable whether manganese substitutes for aluminum. Thus, in the present investigation, TEM quantitative analysis was also carried out on the particles (Fig. 15) observed in the early stage of aging. Examples of the chemical composition of particles approximately 50 to 200 nm in size observed in the specimen aged for 1 h and 2 h at 210°C are listed in Table 3. The results showed that the $\beta$-precipitates were found to contain a higher proportion of manganese than those in the literature. Particularly, the composition of the particle No. 6 in Table 3, which corresponds to Mg$_{16.8}$Al$_{9}$Mn$_{2.7}$Zn$_{6.5}$, is close to the stoichiometric $\beta$-phase Mg$_{17}$Al$_{12}$ (41.4 at%Al), if the concentrations of aluminum, manganese, and zinc are all summed and taken as aluminum concentration. Thus, it is reasonable to assume that manganese constitutes part of the aluminum in the phase and the regions richer in manganese behave as if the regions are higher in supersaturation,
assisting the formation of nuclei for \(\alpha\)-precipitates. The addition of zinc is known to reduce the solid solubility of aluminum, thus increasing the amount of continuous precipitate phase upon aging.\(^{22}\) However, at the magnesium-rich end of the Mg-Al-Mn system, although it is not clearly defined, the \(\alpha\)-Mg region appears to increase with an increase in manganese concentration,\(^{24}\) suggesting manganese assists the precipitation of the \(\alpha\)-phase differently from zinc.

### 3.6 Age hardening response

Age hardening of AZ91 is solely due to the precipitation and growth of the \(\alpha\)-phase. Many studies have been carried out on the kinetics of precipitation with respect to aging temperature and time, precipitate density, growth orientations, morphologies, as well as numerical modeling.\(^{7,9,16,20,22}\)

In the present work, comparative studies were carried out to evaluate the age hardening response of both commercial and high-purity alloys aged at various temperatures for various time periods. Figure 16 shows the age-hardening curves for the alloy specimens aged at 150, 170, 190, 210, and 230\(^\circ\)C. At higher aging temperatures, both alloys exhibited similar hardening curves, while at lower temperatures, the high-purity alloy specimens exhibited higher peak hardness values than the commercial alloy. In order to evaluate the contributions of continuous and discontinuous precipitates to the overall hardness of the materials, the hardness changes in the discontinuous precipitation cells and matrix grains with continuous precipitates were monitored and the results are shown in Fig. 17. As reported in the literature,\(^{25-27}\) the hardness of precipitated cells was independent of aging time and decreased with an increase in aging temperature. In

![Fig. 15 Example of continuous precipitate particles (indicated by arrows) found in a specimen aged for 1 h (3.6 ks) at 210 \(^\circ\)C (483 K) and analyzed for chemical composition.](image)

![Table 3 Chemical composition (in at%) of continuous precipitate particles in specimens aged for 1 h (3.6 ks) and 2 h (7.2 ks) at 210 \(^\circ\)C (483 K).](table)

<table>
<thead>
<tr>
<th>Particle No.</th>
<th>Aged (h)</th>
<th>Mg</th>
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<th>Mn</th>
<th>Zn</th>
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<tbody>
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<td>1</td>
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<td>87.15</td>
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<td>0.93</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
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</tr>
<tr>
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<tr>
<td>6</td>
<td>2</td>
<td>57.98</td>
<td>30.87</td>
<td>9.32</td>
<td>1.82</td>
</tr>
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</table>

![Fig. 16 Age hardening curves for high-purity and commercial alloys at various temperatures. Each value represents the average of 10 measurements. The A.Q. data are the results for the as-quenched specimens.](curve)

![Fig. 17 Age hardening curves for the discontinuous precipitation cells (denoted by circle symbols) and the matrix grains (denoted by triangular symbols). Open symbols are for the high-purity and solid symbols for commercial alloys. Each value represents the average of ten measurements.](curve)
addition, the hardness of cells for the high-purity and commercial alloys was essentially the same. The hardness of the matrix grains on the other hand increased progressively as the continuous precipitation progressed and reached a maximum after some time elapsed. The specimens aged at lower temperature reached almost the same level of hardness as the discontinuous precipitation cells and around this time the peak hardness of the alloys occurred. With the observations of specimens by FE-SEM (Field Emission Scanning Electron Microscopy), the continuous precipitates in the commercial alloy were detected much earlier in the aging process than in the high-purity alloy. It was particularly noticeable for the specimens at lower aging temperatures. This is due to segregation of manganese that instigates the nucleation of the β-phase. This was reflected in the higher hardness values of the matrix grains for the commercial alloy specimens during aging (e.g. solid triangular symbols in Fig. 17 at 150 to 190°C). However, as shown previously in Fig. 9, the areas of the discontinuous precipitation were significantly larger for the high-purity alloy. In addition, the hardness difference between the cells and matrix grains when the area fraction of cells reached maximum was greater at lower aging temperatures. For this reason, the high-purity alloy attained higher overall hardness, particularly at lower aging temperatures (Fig. 16).

4. Summary

High-purity and commercial AZ91E alloys were cast into pencil ingots and the concentration profiles of solute elements in the as-cast, solution heat-treated, and aged specimens were examined. Micro-structural observations by optical and scanning electron microscopy were related to the distribution profiles of the solute elements. Precipitation behavior was examined in terms of the hardening response of the alloys. The results are summarized as follows:

(1) For commercial alloys containing manganese, continuous precipitation was found to occur preferentially in the regions of the grains that were richer in manganese, causing non-uniform precipitation patterns.

(2) Based on the composition of β-precipitates in the matrix grains, manganese was found to be included in the β-precipitates and there is indirect evidence that manganese substitutes for part of the aluminum in the β-phase. For this reason, the regions that are higher in manganese concentration provided a higher driving force for precipitation.

(3) The high-purity alloy containing no manganese also exhibited non-uniform precipitation, caused by the minute differences in solute distribution of aluminum in the matrix grains.

(4) The cause of non-uniform precipitation for both high-purity and commercial alloys is related to the solute segregation in solidification structures.

(5) The high-purity alloy, aged at lower temperatures, attained higher peak-hardness than the commercial alloy specimens, owing to the much higher area fraction of discontinuous precipitation cells.

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REFERENCES