Chapter 12

Design and Development of Novel Wrought Magnesium Alloys

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12.1 Introduction

Magnesium alloy has received revived research interest owing to ever increasing demand for lightweight materials in the transportation sector to lower the emission of greenhouse effect gases by weight reduction. However, there are only a few applications of magnesium alloys such as cast alloys for engine blocks. If wrought magnesium alloys can substitute some of the structural components in automotive bodies, further reduction of weight is expected. However, there are limited applications of wrought alloys due to their poor mechanical properties, low corrosion resistance, flammability, and high cost of processing. Therefore, the development of novel wrought alloys is essential to broaden the applications of magnesium alloys to automotive bodies. This chapter discusses the requirements to make wrought magnesium alloys industrially viable through a brief review of their mechanical properties. A new concept to achieve improved mechanical properties is presented along with examples of novel heat treatable wrought magnesium alloys.

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12.2 Requirements for Wrought Magnesium Alloys

The majority of structural components in transportation vehicles consist of steel and aluminum alloys. If wrought magnesium alloys are to substitute some of these materials, the best target materials would be Al–Mg–Si-based (6XXX series) alloys, which are used as body panels, door frames, and space frames.

Certain magnesium wrought alloys have equivalent or superior mechanical properties compared with those of 6XXX series aluminum alloys as shown in Fig. 12.1 (b). However, applications of wrought magnesium alloys are limited. One main reason for this is the high processing cost that originates from their poor workability and formability. Low corrosion susceptibility and flammability would also limit the applications. However, the poor flammability can be improved by the addition of Ca. The following sections discuss the directions for developing industrially viable wrought magnesium alloys emphasizing the reduction of processing costs.

12.2.1 Extruded Alloys

Figure 12.2 shows an extrusion limit window diagram for various magnesium alloys and AA6063 aluminum alloy (Atwell and Barnett, 2007). This figure shows extrusion temperature ranges and speeds for successful extrusion. Successful extrusion is expected if the extrusion temperature and speed are within the process windows.

Fig. 12.1 Relationship between strength and elongation to failure in 6XXX series aluminum alloys and wrought magnesium alloys. Data points are adopted from Davis (1993); Abedesian and Baker (1999); Kamado et al. (2005)

Fig. 12.2 Extrusion limit window diagram for Mg- x Al-1Zn ($x = 3, 6$) (wt.%) alloys. Reprinted from ref. Atwell and Barnett (2007) with permission from Springer Nature

Mg-6Al-1Zn (AZ61) and Mg-6Zn-0.5Zr (ZK60) are commercial wrought magnesium alloys with yield strengths of ~ 230 MPa, which is comparable with that of the AA6063 alloy. However, AZ61 and ZK60 alloys have poor extrudability compared with AA6063. This means that the processing cost for AZ61 and ZK60 is much higher than that for AA6063. Therefore, the key to make these magnesium alloys industrially viable is to substantially improve their extrudability.

Figure 12.2 also shows that better extrudability may be achieved by lowering the composition of alloying elements; the extrusion limit windows for Mg-3Al-1Zn (AZ31), Mg-2Zn-1Mn (ZM21), and Mg-1Mn (M1) alloys are much larger than those for the AZ61 and ZK60 alloys. However, lowering the content of alloying elements is accompanied by a reduction in the yield strengths (Murai, 2004). Murai et al. reported that the maximum extrusion speed can be increased by lowering the Al content in Mg- x Al alloys from $x = 2.0$ to 0.5. However, the decrease in Al content results in the decrease of the yield strength from 180 to 140 MPa, respectively. The use of precipitation hardenable “dilute” alloy might be a promising approach towards the achievement of an excellent extrudability and high strength simultaneously because the dilute alloy is solution treatable and expected to be extrudable in the single-phase region. The extruded products are expected to be strengthened by subsequent artificial aging. This is the design concept for high-strength magnesium alloys with excellent extrudability.

12.2.2 Sheet Alloys

Room temperature formability is one of the important properties required for sheet alloys as a low processing cost is anticipated. Although aluminum alloy and steel sheets are easily processed into final shapes by stamping or other forming

Fig. 12.3 (a) Schematic illustration showing the principle of the Erichsen cupping test. (b) Snapshots of Mg–3Al–1Zn (wt.%) (AZ31) alloy and 6XXX series aluminum alloy sheets after the Erichsen cupping test

processes at room temperature, magnesium alloy sheets need elevated temperature environments of $\sim 300^\circ\text{C}$ for the forming process due to the poor formability at room temperature. The Erichsen cupping test is widely used as an indicator of the formability of sheet alloys. It evaluates the stretch formability in Index Erichsen (I.E.) value, which corresponds to the height required to fracture a cupped sheet metal deformed by a spherically shaped punch (Fig. 12.3 (a)). Figure 12.3 (b) shows snapshots of the samples after the Erichsen cupping test, demonstrating that the AZ31 commercial alloy sheet has a much lower stretch formability than a pure aluminum sheet; the I.E. value for the AZ31 sheet is only 2 ~ 3 mm, which is much lower than that of pure aluminum alloy (8.9 mm).

The poor room temperature formability of the magnesium alloy sheet is attributed to the limited number of slip systems due to the hexagonal close-packed (hcp) structure and the strong (0002) texture that develops during the hot-rolling process. As schematically shown in Fig. 12.4 (a), the [0002] directions (c-axes) of the magnesium grains are strongly aligned to the sheet normal direction (ND) during the hot-rolling process. In such a case, the deformation along the sheet thickness direction is difficult because the slip system is limited to the basal slip at room temperature in magnesium alloys (Fig. 12.4 (b)).

Weakening the basal texture is known to be an effective approach toward improving the poor room temperature formability. For example, the strong (0002) texture is weakened by the addition of trace Ce into a Mg–1Zn (wt.%) alloy (Mackenzie and Pekguleryuz, 2008). Chino et al. showed that the Mg–1Zn–0.2Ce

Fig. 12.4 Schematic illustration of (a) a typical crystallographic texture developed in magnesium alloy sheets and (b) illustration of basal $\langle a \rangle$ slip in magnesium and magnesium alloys

(wt.%) (ZE10) alloy exhibits a high I.E. value of 8–9 mm, which was comparable with that of Al–Mg–Si (6XXX series) aluminum alloys (Chino et al. 2008, 2010a). The development of such weakened texture was also reported following the addition of Ca or rare-earth (RE) elements into Mg–Zn-based alloys (Chino et al. 2009, 2010b, 2011; Wu et al. 2011; Bhattacharjee et al. 2014; Bian et al. 2016; Park et al. 2017), and the optimization of the thermo-mechanical processing route in Mg–Zn and Mg–Al alloys (Chino and Mabuchi 2009; Huang et al. 2009, 2011, 2012, 2015a, b; Suzuki et al. 2015; Yi et al. 2016; Trang et al. 2018).

Figure 12.5 shows the relationship between the yield strengths, σ_{ys} and I.E. values for various magnesium alloys. Some magnesium alloys have comparable stretch formability with that of aluminum alloys. However, there is a trade-off relationship between the I.E. value and the yield strength, σ_{ys} , that is, high I.E. values are achieved at the expense of σ_{ys} . Therefore, because a value of σ_{ys} below 150 MPa is not satisfactory for automobile body applications, another approach is required to achieve excellent room temperature formability and satisfactory strength simultaneously.

To overcome the tread-off relationship between yield strength and stretch formability, the use of a precipitation hardenable alloy is regarded as a promising approach. As shown in Fig. 12.6, a solution treatment is applied to the hot-rolled sheet to form a supersaturated solid solution and recrystallized microstructure. If the recrystallized microstructure shows a weak (0001) texture, the solution-treated sheet may yield a good room temperature formability. The low strength of the solution-treated sample

Fig. 12.5 Relationship between the yield strengths, σ_{ys} and I.E. values for various magnesium alloys. The figure also includes the data for 6XXX series aluminum alloys

Fig. 12.6 Illustration of the processing route of heat-treatable alloys

can be substantially increased by subsequent artificial aging. This is a new design concept for developing formable high-strength magnesium sheet alloys.

12.3 Development of Industrially Viable Precipitation Hardenable Alloys

As most binary magnesium alloys are based on systems with potential for precipitation hardening, selection of the alloys that exhibit precipitation hardening is relatively simple. However, most precipitation hardenable alloys reported in the literature are not industrially viable because of their sluggish precipitation kinetics and poor age hardenability. Figure 12.7 (a) shows the variation in Vickers hardness (VHN) as a function of aging time for various binary magnesium alloys. For comparison, the age-hardening curves for Al–Cu–Sn alloy are also shown (Ringer et al. 1995; Nie et al. 2005; Sasaki et al. 2006; Mendis et al. 2007; Oh-ishi et al. 2009). Binary magnesium alloys show very sluggish kinetics for age hardening and demonstrate a relatively small hardness increment by artificial aging compared to Al–Cu–Sn alloys. Most magnesium alloys take tens of hours to reach their peak hardness through artificial aging. Thus, for making the precipitation hardening usable in heat-treatable wrought alloys, the kinetics for precipitation hardening must be substantially accelerated.

In most of the binary magnesium alloys, precipitates form on the (0002) plane (basal plane) of the magnesium matrix. Since the basal slip is the main deformation

Fig. 12.7 (a) Variations in Vickers hardness as functions of aging time for various binary magnesium alloys and Al–Cu alloy. (b) Bright-field TEM images obtained from various magnesium alloys at their peak aged conditions. Reprints from ref. Ringer et al. (1995); Nie et al. (2005); Sasaki et al. (2006); Mendis et al. (2007); Oh-ishi et al. (2009), Copyright 2012, with permission from Elsevier

mechanism in magnesium alloys, the dispersion of the fine plate-like precipitates forming on the prismatic planes of the matrix is expected to be the most effective for precipitation strengthening (Nie, 2003). However, the precipitation of the “prismatic plate” is limited to magnesium–rare earth elements (Mg–RE) systems (Nie, 2012). Since the precipitates observed in the peak-aged binary alloys are coarse and heterogeneously dispersed (Fig. 12.7 (b)), a practical approach to achieve the high peak hardness would be to refine the precipitates via micro-alloying, double aging, or stretch aging. Recent studies on precipitation hardenable magnesium alloys showed that micro-alloying is effective to increase the precipitation hardening response substantially, and very high peak hardness values of ~ 100 VHN were achieved in Mg–Sn and Mg–Zn-based alloys (Fig. 12.8) (Mendis et al. 2007; Elsayed et al. 2013; Sasaki et al. 2015).

However, excellent extrudability or room temperature formability may not be anticipated from these alloys as they contain a high content of alloying elements. In search of precipitation hardenable RE-free alloys, Oh-ishi et al. reported that the age-hardening response of dilute Mg–Ca alloys can be substantially enhanced by the trace addition of Zn and Al because the strengthening phase changes from the equilibrium Mg_2Ca phase, which precipitates heterogeneously with an incoherent interface, to fully coherent Guinier Preston (G.P.) zones (Oh-ishi et al. 2009). The formation of the G.P. zone in the Mg–Ca system was first reported by Oh et al. (Oh et al. 2005). They reported that the trace addition of Zn in the Mg–0.5Ca (wt.%) alloy resulted in the formation of the monolayer G.P. zone enriched with Ca and Zn. Later, Oh-ishi et al. thoroughly investigated the effect of the Zn content on the age hardening response in the Mg–Ca–Zn alloy (Oh-ishi et al. 2009), reporting that the highest age-hardening response is achieved by the addition of 1.6 wt.% of Zn, and the addition of excess Zn results in the change of the precipitate phase. Oh-ishi et al. also identified the structure of the monolayer G.P. zones using atomic resolution high angle annular dark-field scanning transmission electron microscope (HAADF-STEM) observations, as presented in Fig. 12.9 (a). In the G.P. zone, Ca or Zn occupies the nearest-neighbor Mg site at intervals of two Mg atoms, resulting in the ordered structure as shown in Fig. 12.9 (b).

Fig. 12.8 Variations in Vickers hardness as functions of aging time for various magnesium alloys. Data points adopted from ref. Mendis et al. (2007); Oh-ishi et al. (2009); Elsayed et al. (2013)

Fig. 12.9 HAADF-STEM image obtained from the peak aged Mg–0.5Ca–1.6Zn alloy (a) and Schematics of the ordered G.P. zone formed on a single basal plane of the Mg (b). Reprinted from ref. Oh-ishi et al. (2009), Copyright 2012, with permission from Elsevier

Fig. 12.10 Relationship between atomic radii and enthalpy of mixing among alloying elements and magnesium in Mg–Ca–Zn and Mg–Ca–Al alloys

Figure 12.10 shows the relationship between atomic radii and the enthalpy of mixing among Mg, Ca, and Zn. These elements have a negative enthalpy of mixing, and the atomic radius of Ca is larger than that of Mg, and that of Zn is smaller than that of Mg. This leads to the internal order of atoms within the monoatomic layer of the basal plane as shown in Fig. 12.9. In addition to Zn, Al also has a large negative enthalpy of mixing with Ca with a smaller atomic radius. Thus, Al was also expected to work to induce the precipitation of ordered G.P. zones.

Jayaraj et al. proved that the G.P. zone also forms by adding a trace amount of Al into the Mg–Ca system. As shown by the variation in the Vickers hardness as a function of the aging time (Fig. 12.11), micro-alloying Al into the Mg–0.5Ca alloy results in a substantial increase in the peak hardness along with a kinetics acceleration (Jayaraj et al. 2010). While the Mg–0.5Ca alloy shows only a small hardness increment, the Mg–0.5Ca–0.3Al alloy shows the higher peak hardness of 72 VHN in only 2 h of aging at 200 °C. As shown in a bright-field (BF) TEM image of the peak-aged Mg–0.5Ca–0.3Al alloy (Fig. 12.11 (b)), the ordered G.P. zone is precipitated as evident from the diffraction contrasts and the streaking feature in

Fig. 12.11 (a) Variations in Vickers hardness as functions of time for Mg–0.5Ca– x Al ($x = 0.1, 0.3, 0.5$, and 1.0) alloys during artificial aging at $200\text{ }^{\circ}\text{C}$, (b) Mg–0.5Ca–0.3Al alloys, (c) 3D atom map of Al and Ca taken from the Mg–0.5Ca–0.3Al alloy. Reprinted from ref. Jayaraj et al. (2010), Copyright 2012, with permission from Elsevier

the selected area diffraction (SAD) pattern. A 3D atom map of the peak-aged Mg–0.5Ca–0.3Al alloy shows that Al and Ca are enriched in the G.P. zones (Fig. 12.11 (c)).

12.4 Examples of Heat-Treatable Wrought Alloys

12.4.1 Extruded Alloys

Following the fundamental work on the age-hardening responses in dilute Mg–Ca–Al and Mg–Ca–Zn alloys, Nakata et al. demonstrated that the Mg–Ca–Al–Mn-based alloys are extrudable at speeds as high as those used in 6XXX aluminum alloys (Nakata et al. 2015). As shown in the snapshots of Mg–0.3Al–0.15Ca–0.2Mn (AXM0301502) and AZ31 alloys extruded at 60 m/min (Fig. 12.12), the AXM0301502 extruded alloy shows a crack-free surface even at a die-exit speed of 60 m/min, while many cracks appear perpendicular to the extrusion direction on the surface of the AZ31 extruded alloy.

Fig. 12.12 Surface appearance of Mg–0.3Al–0.15Ca–0.2Mn (AXM0301502) and AZ31 alloys extruded at 60 m/min. Reprinted from ref. Nakata et al. (2015), Copyright 2012, with permission from Elsevier

Fig. 12.13 Nominal stress–strain curves for AZ31 (a) and as-extruded and T5 treated AXM0301502 alloys. Note that the T5 treatment stands for the artificial aging to the peak hardness right after the extrusion. Nominal stress–strain curves for a T6-treated 6N01 Al alloy (b) and solution treated and T6-treated Mg–1.3Al–0.33Ca–0.46Mn (AXM10304) alloys. Reprinted from ref. Nakata et al. (2015, 2017a), Copyright 2012, with permission from Elsevier

The artificial aging for only 3 h immediately after extrusion leads to an increase in the yield strength from 170 to 207 MPa, which is higher than that of the AZ31 alloy due to the precipitation of the G.P. zones (Fig. 12.13 (a)). The yield strength was further increased to 290 MPa by composition optimization into Mg–1.3Al–0.33Ca–0.46Mn (wt.%) (AXM10304) and subsequent T6 treatment consisting of solution treatment and artificial aging (Fig. 12.13 (b)). Although the yield strength of 290 MPa is higher than that of the 6N01 aluminum alloy, such high strength is achieved at the expense of extrudability. The AXM10304 alloy is extrudable at 24 m/min, which is slower than the extrusion speed of AXM0301502 alloy, 60 m/min. However, Nakata et al. demonstrated that the excellent extrudability and the high yield strength can be simultaneously achieved by the optimization of the homogenization process prior to the extrusion; a Mg–1.6Al–0.2Ca–0.9Mn alloy can be extrudable at 60 m/min by and exhibits a high yield strength of 284 MPa (Nakata et al. 2017b).

Along with good extrudability and high strength, the dilute Mg–Ca–Al alloys also show an interesting feature. As shown in Fig. 12.13 (b), the dilute Mg–Ca–Al alloy does not show significant loss of ductility by the T6-treatment unlike precipitation hardened Mg–Al, Mg–Zn, and Mg–Sn alloys; the peak aged AXM10304 alloy shows a large elongation of 20%, which is comparable with that of the solution-treated samples.

12.4.2 Sheet Alloys

The large tensile elongation of the Mg–Ca–Al–Mn alloy indicates that the Mg–Al–Ca-based dilute alloy might also exhibit excellent room temperature formability and

Fig. 12.14 Snapshot of the sample after the Erichsen cupping test, inverse pole figure map and (0002) pole figures of the solution treated (a) Mg-1.2Al-0.5Ca-0.4Mn (AXM100) and (b) Mg-1.2Al-0.8Zn-0.4Mn-0.5Ca (AZMX1000) alloys. Reprinted from ref. Bian et al. (2017), Copyright 2012, with permission from Elsevier

satisfactory strength (Bian et al. 2017). However, the solution treated Mg-1.2Al-0.5Ca-0.4Mn (AXM100) alloy sheet shows an I.E. value of only 5.9 mm, which is lower compared with that of the 6XXX series aluminum alloy, Fig. 12.14 (a). An inverse pole figure (IPF) map and (0002) pole figure (Fig. 12.14 (a)) obtained by electron backscatter diffraction (EBSD) indicate that the lack of formability is due to the development of a strong basal texture as discussed in Sect. 12.2.2 (Bian et al. 2016). Bian et al. reported that the poor room temperature formability of the Mg-0.5Ca-0.1Zr (at.%) alloy can be substantially improved by the addition of Zn (Bian et al. 2016). The Mg-1.2Al-0.8Zn-0.4Mn-0.5Ca (AZMX1000) alloy exhibited a high I.E. value of 7.7 in the solution treated condition since the addition of Zn caused the development of a “quadrupole” texture, in which (0002) poles were tilted toward RD and TD (Fig. 12.14 (b)).

The T6-treatment gives rise to the strength of the AZMX1000 alloy sheet (Bian et al. 2017). The AZMX1000 alloy reaches the peak hardness with only 1 h of artificial aging at 200 °C, and the yield strength of the AZMX1000 alloy increases from 177 to 204 MPa (Fig. 12.15 (a)).

In the actual car manufacturing process, body panels made from steel and aluminum alloys are heat treated at low temperatures for short time, e.g. at 170 °C for 20 min for paint curing. The phenomenon that the sheet materials are strengthened during the paint baking process is referred to as “bake-hardening.” The bake-

Fig. 12.15 (a) Nominal stress–strain curves for T4- and T6-treated Mg–1.2Al–0.8Zn–0.4Mn–0.5Ca (AZMX1000) alloys and nominal stress–strain curves for (b) Mg–1.3Al–0.8Zn–0.7Mn–0.5Ca (wt.%) (AZMX1100) and (c) AZ31 alloy before and after inducing 2% strain and artificial aging at 170 °C for 20 min. Reprinted from ref. Bian et al. (2017, 2018a), Copyright 2012, with permission from Elsevier

hardening process corresponds to strain aging, and the descriptions of the bake-hardenability are usually based on uniaxial tensile tests. First, 2% strain is induced into a specimen followed by artificial aging at 170 °C for 20 min. Note that the 2% strain is a typical amount of strain induced into the body materials during stamping, and artificial aging at 170 °C for 20 min simulates the industrial paint-baking process. The pre-strained and artificially aged sheet sample is again subjected to a tensile test. The bake-hardenability is defined as the difference between the maximum stress during pre-straining and the yield stress after baking.

The bake-hardenability in the magnesium alloy was demonstrated for the first time in the Mg–Ca–Al–Zn dilute alloy (Bian et al. 2018a). The AZMX110 alloy exhibits a strength increase of approximately 40 MPa because of the bake-hardening process, while the commercial AZ31 alloy exhibits softening rather than strengthening, Fig. 12.15 (b) and (c) (Bian et al. 2018a). Consequently, the yield strength of the AZMX110 alloy increases from 177 to 238 MPa through the bake-hardening process, which is significantly higher than that of the AZ31 alloy (186 MPa) ((Fig. 12.15 (c))).

Figure 12.16 shows the relationship between the yield strength and the I.E. values for various magnesium-based sheet alloys. The AZMX110 alloy showed much

Fig. 12.16 Yield strengths and Index Erichsen values for various magnesium-based alloys. Reprinted from ref. Bian et al. (2018a), Copyright 2012, with permission from Elsevier

higher room temperature formability and yield strength compared with the existing alloys. Therefore, the bake-hardenable AZMX1110 sheet alloy successfully overcame the usual trade-off relationship between formability and strength, which has been hindering the application of magnesium sheet alloy (Bian et al. 2018a).

12.4.3 Toward the Improvement of Room Temperature Formability

The detailed analysis of the microstructure evolution during the stretch forming indicates the direction for the microstructure design to further improve the room temperature formability (Bian et al. 2017, 2018a). Figure 12.17 (a) and (b) shows IPF maps and (0002) pole figures of the AZMX1000 alloy stretch formed to dome heights of 3 and 7.7 mm during the Erichsen cupping test. The (0002) pole figures show that the angular distribution of these (0002) poles gradually becomes narrower toward the ND compared with those of the unstretched sample (Figs. 12.14 (b) and 12.17), indicating that the basal slip mainly operates during the stretch forming.

An EBSD-assisted slip trace analysis also revealed that the activation of the non-basal slip is the key to achieve excellent room temperature formability (Bian et al. 2018b). Note that the EBSD-assisted slip trace analysis initially uses EBSD orientation data to predict the traces generated by the major slip modes such as basal $\langle a \rangle$, prismatic $\langle a \rangle$, and pyramidal II $\langle c + a \rangle$. Then, it compares the predicted traces with the traces detected from the SEM micrograph. The traces observed from the

Fig. 12.17 Inverse pole figure maps and (0002) pole figures obtained from the top and bottom surfaces of the samples after (a) 3 mm and (b) 7.7 mm deformation by Erichsen cupping test. Reprinted from ref. Bian et al. (2017), Copyright 2012, with permission from Elsevier

SEM micrograph (Fig. 12.18 (a)) match well with the predicted trace of the basal $\langle a \rangle$ slip, indicating that these traces were generated by the basal $\langle a \rangle$ slip. The analytical results shown in Fig. 12.18 (b) indicate that the basal $\langle a \rangle$ slip is the dominant

Fig. 12.18 (a) An SEM image and corresponding EBSD IPF map along with slip traces predictions for basal $\langle a \rangle$, prismatic $\langle a \rangle$ and pyramidal II $\langle c + a \rangle$ showing the methodology utilized for slip trace analysis on a stretch deformed grain. (b) SEM micrographs showing traces generated by basal $\langle a \rangle$, prismatic $\langle a \rangle$ and pyramidal II $\langle c + a \rangle$ slips on the surface of the 3 mm stretch formed on Mg-1.2Al-0.3Ca-0.4Mn-0.3Zn alloy. Reprinted from ref. Bian et al. (2018b), Copyright 2012, with permission from Elsevier

deformation mode during the stretch forming of these samples, but Fig. 12.18 also shows the active operation of the prismatic $\langle a \rangle$ slip during the stretch forming.

Since the active operation of the prismatic $\langle a \rangle$ slip was also reported in fine-grained AZ31 and AZ61 alloys during the tensile test by Koike et al. (Koike et al. 2003; Koike and Ohyama 2005), the operation of the prismatic $\langle a \rangle$ slip would be a distinct feature in a magnesium alloy with relatively fine-grained structure. Zheng et al. also reported the enhanced work hardening and large elongation by the operation of $\langle c + a \rangle$ dislocations in an ultrafine-grained Mg–6.2%Zn–0.5%Zr–0.2%Ca (wt.%) alloy subjected to high-pressure torsion (HPT) (Zheng et al. 2019). Recent studies also reported that pure magnesium and magnesium alloys can show super-formability even at room temperature by grain boundary sliding and dynamic recrystallization when the average grain size is down to the micron scale (Somekawa et al. 2017, 2018; Zeng et al. 2017). Therefore, the formation of the fine-grained structure would be a key to further improve the room temperature formability.

12.4.4 Strengthening by G.P. Zones

The cause of the bake-hardenability of the AZMX1110 alloy sheet was investigated through a correlative analysis by TEM and 3D atom probe (3DAP). As shown in Fig. 12.19 (a) and (b), only a uniform imaging contrast can be observed in the BF-TEM image and selected area diffraction patterns obtained from the AZMX1110 alloy, which was artificially aged at 170 °C for 20 min after inducing 2% strain. Although it is difficult to understand the reasons for the bake hardening from the result of TEM analysis, a correlative TEM-3DAP analysis of the bake-hardened

Fig. 12.19 (a) A bright-field TEM image and selected area diffraction patterns taken from the zone axes of $[11\bar{2}0]$, $[01\bar{1}0]$, and $[0001]$. (b) HAADF-STEM image taken from Mg–1.3Al–0.8Zn–0.7Mn–0.5Ca (wt.%) (AZMX1110) alloy after inducing 2% strain and artificial aging at 170 °C for 20 min. Reprinted from Bian et al. (2018a), Copyright 2012, with permission from Elsevier

sample revealed the microstructure features that explain such reasons. Figure 12.20 (a) ~ (c) shows a two-beam BF-TEM image of the 3DAP specimen, the resulting 3D atom maps for the Al, Zn, Mn, and Ca, and the 3DAP map overlaid on the corresponding TEM image obtained from the bake-hardened sample, respectively. Four dislocations (designated as a, b, c, and d) are readily visible in the BF-TEM image (Fig. 12.20 (a)). They are confirmed to be segregated with Ca in the bake-hardened sample (Fig. 12.20 (b)). The 3DAP map overlaid on the corresponding TEM image in Fig. 12.20 (c) clearly shows this feature. The proxigram analyzed from the dislocation indicated by a red arrow shows that the concentrations of Al, Zn, and Ca in the dislocation core are significantly higher than those in the matrix (Fig. 12.20 (d)), which means that Ca, Al, and Zn are segregated along the dislocation cores. A closer look into the 3D atom map in Fig. 12.20 (e) also shows the presence of solute clusters enriched in Ca, Al, and Zn within the matrix. Therefore, Al, Zn,

Fig. 12.20 (a) Bright-field image of a needle-shaped sample before 3DAP analysis, (b) 3D atom map of Mg, Ca, Zn, Al, and Mn, and (c) overlaid bright-field TEM and 3D atom map obtained from Mg–1.3Al–0.8Zn–0.7Mn–0.5Ca (wt.%) (AZMX1110) alloy after inducing 2% strain and artificial aging at 170 °C for 20 min. (d) is proxigrams of local solute concentrations at dislocation lines analyzed from the dislocation indicated by red arrow in (b) and (e) is 3DAP elemental mappings of Mg, solute atoms, and detected Al, Zn, and Ca clusters in the selected region. Reprinted from Bian et al. (2018a), Copyright 2012, with permission from Elsevier

and Ca atoms segregated into dislocation cores are considered to contribute to the bake-hardening effect along with co-clustering of these atoms.

12.5 Summary and Future Outlooks

In this chapter, a heat treatable alloy was introduced as a novel wrought magnesium alloy that would broaden alloy applications in the transportation sector. As a result of the development of precipitation hardenable magnesium alloys, which show substantial age hardening, Mg–Ca alloy micro-alloyed with Zn and/or Al was found to be promising as an industrially viable precipitation hardenable alloy. Mg–Al–Ca–Mn dilute alloy is extrudable at 60 m/min, which is comparable with the extrusion speed of the 6XXX series medium strength aluminum alloys, and the T6-treated sample exhibits higher yield strength (280 MPa) due to the dispersion of G.P. zones. From the Mg–Ca–Al–Zn alloy, a bake-hardenable alloy with excellent room temperature formability was also developed. This is the first time that bake hardenability was observed in magnesium alloys. The bake-hardenable Mg–Al–Ca–Zn–Mn alloy shows a stretch formability of 7.8 mm in I.E. value, which is comparable with that of the 6XXX series aluminum alloys. Bake hardening resulted in the segregation of solute elements along with the dislocation core and the solute cluster formation, and these effects increased the strength to 240 MPa. Although age-hardening phenomena have not been used in conventional wrought magnesium alloys, the optimized alloy shows sufficient age hardening response as observed in many heat-treatable aluminum alloys. Further development of heat-treatable magnesium alloys may reveal wider applications of wrought magnesium alloys.

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