Strong and ductile heat-treatable Mg-Sn-Zn-Al wrought alloys

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Abstract

A newly developed Mg-Sn-Zn-Al based alloy shows substantial strengthening by artificial aging. A Na-doped Mg-5.4Sn-4.2Zn-2.0Al-0.2Mn-0.1Na (TZAM5420-0.1Na) (wt%) alloy exhibited a significant increase in yield strength from 243 to 347 MPa by a T6 treatment due to the uniform dispersion of nanoscale precipitates by aging. The trace addition of Na causes the formation of Sn-Na co-clusters in the early stage of aging, which provides heterogeneous nucleation sites for Mg₂Sn precipitates. However, Na strongly segregates at grain boundaries and this degrades the ductility significantly. To overcome this problem, we developed a Na-free Mg-6.6Sn-5.9Zn-2.0Al-0.2Mn (TZAM6620) alloy, in which nano-scale MgZn₂ precipitates are uniformly dispersed by double aging. Pre-aging caused the formation of Zn-rich Guinier Preston zones, which acted as heterogeneous nucleation sites for the MgZn₂ precipitates. The double-aged TZAM6620 alloy exhibited a very high yield strength of 370 MPa with large elongation of 14%.

1. Introduction

The development of high strength wrought magnesium alloys is strongly desired for transportation vehicles to improve their fuel efficiencies by weight reduction. While the grain refinement by severe plastic deformation and slow-speed extrusion can induce high yield strengths over 300 MPa in various magnesium based alloys such as Mg-Al-Zn (AZ) [1-5], Mg-Zn-Zr (ZK) [6-8] and Mg-Sn (T) based alloys [9-11], the strengthening is achieved at the expense of ductility and formability due to their work hardened nature. On the other hand, precipitation hardenable alloys are formable after a solution treatment if recrystallized microstructure is optimized, and the final product can be strengthened by artificial aging [12]. Such a heat-treatable wrought magnesium alloy was demonstrated in the Mg-Zn based alloy microalloyed with Ag, Ca and Zr, ZKQX6000 [12]. More recently, Bhattacharjee et al. reported an equivalent mechanical properties even without the addition of expensive Ag [13].

The Mg-Sn system is precipitation-hardenable since the solubility of Sn decreases with temperature [14]. However, little work has been done on the precipitation strengthening of Mg-Sn wrought alloys. Unlike the Mg-Al-Zn (AZ) and Mg-Zn-Zr (ZK) alloys [15], the Mg-Sn alloys are softened when artificially aged directly after extrusion since coarse Mg_2Sn particles dynamically precipitate during hot-extrusion [16]. The artificial aging after a solution treatment (T6) does not induce significant strengthening to the Mg-Sn wrought alloy either [17], because the solution treatment above 500 °C leads to a rapid grain growth. To develop heat-treatable Mg-Sn based alloys, the poor age hardening response needs to be improved and the rapid grain growth during the solution treatment must be controlled [17-26].

Recently, Elsayed *et al.* demonstrated the significant age hardening response that reached to a peak hardness of over 100 VHN in a Mg-9.8Sn-3.0Al-1.0Zn-0.1Na (TZA1031-0.1Na) cast alloy [27]. Although such a significant age hardening is expected to strengthen the

extruded sample by the T6 treatment, the Na-doped TAZ1031 extruded alloy exhibited very limited ductility because of the Na segregation at grain boundaries [10]. In this work, we thoroughly investigated the role of microalloyed Na on the mechanical property and microstructure evolution during the T6 treatment of a new series of alloys, Mg-5.4Sn-4.3Zn-2.0Al (TZA542). The TZA542 and similar alloys exhibit the age hardening response as high as the previously reported TAZ1031 alloys [22, 25, 28]. We expected this low Sn alloy would be more suitable as wrought material than the TAZ1031 based alloys. Since it can be solution treated at a lower temperature compared to the TAZ1031 alloy due to the lower Sn concentration, the rapid grain growth during the solution treatment could be controlled [14]. Based on the strengthening mechanism by the Na addition determined by atom probe tomography (APT) and transmission electron microscopy, we have developed a Na-free Mg-Sn-Zn-Al extruded alloy by optimizing the composition and heat treatment process. The newly developed Na-free Mg-6.6Sn-5.9Zn-2.0Al-0.2Mn (TZAM6620) alloy exhibited an extraordinary high yield strength over 370 MPa along with the elongation to failure of 14% by the introduction of duplex aging that induces heterogeneous nucleation sites for precipitates.

2. Experimental Procedure

Alloy ingots were prepared by induction melting using steel crucibles under an Ar atmosphere and casting into iron molds. Table 1 summarizes their alloy nomenclatures and chemical compositions in both wt.% and at.%. Mn was added as a grain growth inhibitor during the solution treatment [29-31]. The cast ingots were homogenized at 450 °C for 24 h in an Ar atmosphere followed by quenching into water. The samples were extruded at 300 °C with the ram speed of 2 and 0.1 mm/s and an extrusion ratio of 20. The extruded samples

were subjected to the T6 treatment consisting of the solution treatment in an electric furnace and aging in an oil bath at various conditions. The age hardening responses were measured by the Vickers hardness tests under a load of 500 g. Mechanical properties were evaluated by tensile tests at an initial strain rate of $1.0 \times 10^{-3} \text{ s}^{-1}$ using round bar specimens with the diameter and gauge length of 4 and 22 mm.

Microstructure characterization was performed by Auger electron spectroscopy (AES), scanning electron microscope (SEM), transmission electron microscope (TEM) and 3D atom probe (3DAP). Auger spectroscopy was done using ULVAC-PHI, PHI 680 operating at 10 kV. The round bar sample with V-notch was fractured at a cryogenic temperature in an ultra-high vacuum atmosphere, and Auger spectra were acquired from the fractured surface. SEM observations with energy dispersive spectroscopy (EDS) were performed using a field emission SEM, FEI Helios Nanolab 650, equipped with Bruker EDS detector. Electron backscattered diffraction (EBSD) analyses were done using a field emission SEM, Carl Zeiss Cross Beam 1540EsB, equipped with a HKL EBSD system and CHANNEL 5 software. TEM observation was carried out using FEI Tecnai 20 and Titan G2 80-200 TEMs. Thin foils for the TEM observation were prepared by punching 3 mm diameter discs, mechanical polishing and ion-milling using a Gatan Precision Ion Polishing System (PIPS). 3DAP analyses or atom probe tomography (APT) were carried out with a locally built laser-assisted wide-angle atom probe (LAWATAP) using a femtosecond laser pulse at a wavelength of 343 nm. Square bars with dimensions of $0.5 \times 0.5 \times 15 \text{ mm}^3$ were cut from bulk samples and electropolished to prepare sharp and needle-like specimens. The 3DAP analyses were performed in an ultra-high vacuum condition ($< 1.0 \times 10^{-8} \text{ Pa}$) at a base temperature of 20 K.

3. Results

Figure 1 (a) shows variations in Vickers hardness values of TZA542, TZAM5420, TZA542-0.1Na and TZAM5420-0.1Na alloys as functions of aging time. After a solution treatment and quenching (T4 treatment), the Vickers hardness values decrease to ~ 55 VHN for all the samples. The hardness starts to increase significantly after 6 h aging at 160°C . While the hardness reaches a peak after 300 h for both TZA542 and TZAM5420, the addition of Mn to the TZA542 alloy decreases the peak hardness from 74.2 ± 1.7 to 65.7 ± 1.8 VHN. The trace addition of Na to the TZA542 and TZAM5420 alloys substantially increases the peak hardness value to 92.2 ± 2.5 and 92.9 ± 2.5 VHN, and the peak aging time was shortened to 100 h.

Figure 1 (b) shows the age-hardening curves of TZA542, TZA562 and TZAM6620 alloys with different solution treatment and aging temperatures. The age-hardening curves for the TZA542 alloy solution treated at 350°C and 450°C for 0.25h shows that the decrease in hardness is suppressed at the solution treatment temperature of 350°C . Hereafter, only the results of the samples solution treated at 350°C are discussed. TZA542 alloy shows the peak hardness of 73.1 ± 1.3 VHN after aging for 100 h at 160°C . The TZA562 alloy that contains a higher amount of Zn by 2wt.%, reaches a higher peak hardness of 81.3 ± 1.8 VHN after 30 h aging at 160°C . This peak aging time is only one third of that of the TZA542 alloy. The peak hardness further increases to 86.2 ± 3.1 VHN with decreasing the aging temperature to 140°C while the time to reach the peak hardness is delayed to 160 h. Interestingly, the double aging consisting of the pre-aging at 70°C for 150 h and the second aging at 140°C lead to a substantial increase in the peak hardness of the TZA562 alloy. After the pre-aging at 70°C for 150 h, the hardness increased to 80.7 ± 1.3 VHN. When this pre-aged sample was double-aged at 140°C , the age hardening response was substantially enhanced compared to the single-aged

sample with the peak hardness of 99.0 ± 1.2 VHN after 30 h aging. The addition of 1 wt.% Sn and 0.5 wt.% Mn to TZA562 alloy, i.e. TZAM6620 alloy, resulted in a slight increase in peak hardness to 89.7 ± 1.0 VHN by single aging at 140°C compared to the TZA562 alloy single aged at 140°C . By double aging the TZAM6620 alloy at 70°C for 150 h and 140°C , the TZAM6620 alloy showed the highest peak hardness of 102.1 ± 1.0 VHN. Note that the hardness exceeding 100 HVN is not commonly observed in magnesium alloys without rare earth elements, suggesting TZAM6620 has potential to show high strength with an optimal heat treatment.

Figures 2 (a) and (b) show tensile and compressive stress-strain curves of the TZA542, TZAM5420, TZA542-0.1Na and TZAM5420-0.1Na alloys in the as-extruded and peak aged conditions. Table 2 summarizes their tensile yield strength, σ_{TYS} , ultimate tensile strength, σ_{UTS} , and elongation to failure, ε_T , compressive yield strength, σ_{CYS} , compressive strength, σ_{CS} , and compressive strain, ε_C . While the as-extruded TZA542 and TZAM5420 alloys exhibit similar σ_{TYS} of 184 and 182 MPa, the TZAM5420 alloy shows larger ε of 24% compared to that of the TZA542 alloy, 11% as shown in Fig. 2 (a). In compression, the as-extruded TZA542 and TZAM5420 alloys exhibit σ_{CYS} of 170 and 168 MPa. The extruded alloys show low yield asymmetry of a tension to compression ratio, $\sigma_{CYS}/\sigma_{TYS}$, of 0.9. By the T6 treatment, the TZA542 and TZAM5420 alloys show only a slight increase in σ_{YS} ; the σ_{YS} of the TZA542 and TZAM5420 alloys increase to 228 and 186 MPa at the expense of ε_T . The T6 treated TZAM5420 alloy shows even larger elongation, ε , of 15% compared to that of the T6 treated TZA542 alloy, 6%. However, σ_{CYS} of the TZA542 and TZAM5420 decrease to 141 and 142 MPa resulting in higher yield asymmetry with $\sigma_{CYS}/\sigma_{TYS}$, of 0.62 and 0.76 compared to the as-extruded alloys. The as-extruded TZA542-0.1Na and TZAM5420-0.1Na alloys

exhibit σ_{TYS} of 203 and 243 MPa and σ_{CYS} of 197 and 245 MPa, which are slightly higher compared to those of the as-extruded TZA542 and TZAM5420 alloys. The as-extruded TZA542-0.1Na and TZAM5420-0.1Na alloys also show low yield asymmetry with $\sigma_{CYS}/\sigma_{TYS}$, of 0.97 and 1.01, respectively. The TZA542-0.1Na and TZAM5420-0.1Na alloys exhibit larger increase in σ_{TYS} by T6 treatment compared to the TZA542 and TZAM5420 alloys. TZA542-0.1Na alloy shows the increase in σ_{TYS} from 203 to 257 MPa by a T6 heat treatment. However, the T6 heat treatment results in significant loss of ε_T to only 0.03 for both TZA542-0.1Na and TZAM5420-0.1Na alloys. The T6 treatment also resulted in the increase in yield asymmetry with $\sigma_{CYS}/\sigma_{TYS}$, of 0.78 and 0.65 for TZA542-0.1Na and TZAM5420-0.1Na since σ_{CYS} shows only a slight increase or decrease by the T6 treatment.

Figure 2 (c) and (d) show the tensile and compressive stress-strain curves of as-extruded and peak aged TZA562 and TZAM6620 alloys. Table 3 summarizes their tensile yield strength, σ_{TYS} , ultimate tensile strength, σ_{UTS} , and elongation to failure, ε_T , compressive yield strength, σ_{CYS} , compressive strength, σ_{CS} , and compressive strain, ε_C . The as-extruded TZAM562 alloy exhibits σ_{TYS} and σ_{CYS} of 243 and 234 MPa with low yield asymmetry of $\sigma_{CYS}/\sigma_{TYS}$, of 0.96 as well as the other extruded alloys. Although the σ_{TYS} and σ_{CYS} show only a slight increase to 255 and 237 MPa by the artificial aging at 140 °C for 100h, the double-aging results in a substantial increase in σ_{TYS} and σ_{CYS} to 346 and 277 MPa without significant loss of ductility, $\varepsilon_T=15\%$ unlike Na-containing alloys. The TZA562 alloy keeps low yield asymmetry of $\sigma_{CYS}/\sigma_{TYS}$, of 0.93 and 0.80 after peak aging at 140 °C and double aging. The addition of 1wt.% of Sn and 0.5wt.% of Mn results in further increase in the strength. The as-extruded TZAM6620 alloy exhibits σ_{TYS} and σ_{CYS} of 247 and 253 MPa with low yield asymmetry of $\sigma_{CYS}/\sigma_{TYS}$, of 1.02 as well as the other extruded alloys. As well as the TZA562

alloy, the double-aging results in a substantial increase in σ_{TYS} and σ_{CYS} to 370 and 307 MPa keeping low yield asymmetry of $\sigma_{CYS}/\sigma_{TYS}$, of 0.83 while the artificial aging at 140 °C showed only a slight increase in the strength. Both single aged and double aged TZAM6620 show large ductility, ε_T , of 13 and 14% compared to T6 treated Na-containing alloys.

Figure 3 (a) - (d) are inverse pole figure (IPF) maps obtained from the as-extruded TZA542, TZAM5420, TZAM5420-0.1Na and TZAM6620 alloys taken from the planes parallel to the extrusion direction. The as-extruded samples exhibit the bimodal grain structure consisting of fine and equi-axed recrystallized grains, and coarse un-recrystallized grains elongated along the extrusion direction. While the recrystallized grains in the as-extruded TZA542 and TZAM5420 alloys have similar average grain sizes of 4.5 and 4.9 μm , Fig. 3 (a) and (b), the trace addition of Na leads to the refinement of the recrystallized grains to 2.5 μm , Fig. 3 (c). The recrystallized grains in the TZAM6620 alloy have the average size of 1.6 μm , which is finer than those of the TZA542, TZAM5420 and TZAM5420-0.1Na alloys because of the slow extrusion speed as expected from the previous work [10, 11]. The insets to Fig. 3 (a) - (d) show the (0001) pole figures analyzed from the plane normal to the extrusion direction. They show the alignment of [0001] direction to the radial direction of the extruded bars, which is typical for extruded magnesium alloys.

After the solution treatment, the grains are fully recrystallized as shown in the IPF maps of the solution treated samples, Fig. 3 (e) - (h). After the solution treatment at 450 °C, the grains in the TZA542 alloy are coarsened to 89.5 μm , while those in the TZAM5420 and TZAM5420-0.1Na alloys have finer grain structure with the size of 35.5 and 25.3 μm . The TZAM6620 alloy solution treated at 350 °C keeps the finest grain size of 7.8 μm . The textured feature in the solution-treated TZA542 and TZAM5420 alloys were difficult to characterize because of the limited number of grains within the field of view. However, since

the (0001) pole figures analyzed from the solution treated TZAM5420-0.1Na and TZAM6620 alloys show the alignment of [0001] directions to the radial direction of the extruded bars as seen from the inset to Fig. 3 (g) and (h), the typical ring extruded texture observed in the as-extruded conditions still remains after the solution treatment.

Figure 4 (a) is a backscattered electron SEM image obtained from the solution treated TZAM5420-0.1Na alloy. Due to the channeling contrast, individual grains are visible. Secondary phases are located along the grain boundaries as indicated by arrows. The corresponding EDS elemental map of Sn, Al and Mn, Fig. 4 (b), shows that some are enriched in Sn, and others are enriched in Al and Mn. Figure 4 (c) shows a fractured surface of the solution treated TZA542-0.1Na alloy showing brittle fractured feature at the grain boundaries. The Auger spectrum obtained from the fractured surface, Fig. 4 (d), shows a peak corresponding to Na at 993 eV as well as those from Mg, Sn and O, indicating the Na segregation at the grain boundaries. Figure 4 (e) show bright field TEM image taken from the TZAM6620 alloy solution treated at 350 °C. Spherical precipitates with the size of 211.0 ± 18.0 nm are densely observed along the grain boundaries and grain interiors compared to those in TZAM5420-0.1Na alloy solution treated at 450 °C. A micro-beam diffraction pattern taken from one of the spherical precipitates identified them as the Mg_2Sn phase, Fig. 4 (f).

Figure 5 (a) and (b) show the bright field TEM images of the T6-treated TZA542 alloy taken from the zone axes of $[01\bar{1}0]$ and $[0001]$. Precipitates are heterogeneously dispersed within the matrix. As shown in Fig. 5 (b), a part of blocky precipitates are linearly aligned along the $[10\bar{1}0]$ direction, while the others are heterogeneously dispersed within the grain. The blocky precipitates were identified as β_2' phase [28, 32], and their average size was 55.2 ± 3.9 , 41.7 ± 3.2 and 26.0 ± 2.3 nm in length, width and height. The coarse lath shaped precipitates also form on the (0001) plane of the magnesium matrix. They are the Mg_2Sn

phase [14], which grows along the $[11\bar{2}0]$ direction with the size of 190 ± 13.9 , 53 ± 5.2 and 68.3 ± 7.7 nm in length, width and thickness. Figure 5 (c) and (d) show the bright field TEM images of the peak-aged TZAM5420-0.1Na alloy at 160 °C. Note that these images were taken from the zone axes of $[11\bar{2}0]$ and $[0001]$. The precipitates are much finer and uniformly dispersed compared to those in the peak-aged TZA542 alloy. The precipitates are the lath shape with the size of 33.9 ± 6.29 , 14.5 ± 3.0 and 13.7 ± 2.7 nm in length, width and height, and form on the (0001) plane of the magnesium matrix.

As shown in the HAADF-STEM image taken from the zone axis of $[11\bar{2}0]$ (Figure 6 (a)), the two precipitates indicated by arrowhead are in contact with each other in the peak aged TZAM5420-0.1Na alloy. Fig. 6 (b) and (c) are micro-beam diffraction patterns obtained from the two precipitates indicated by black and white arrows in Fig. 6 (a). Note that these patterns were taken from the zone axis of $[10\bar{1}0]$ for easy visualization of diffraction spots. These precipitates were identified as the Mg_2Sn and β_2' phases. However, Fig. 5 (a) does not show whether or not the Mg_2Sn and β_2' phases are indirect contact with each other. To clarify this, 3D atom probe analysis was performed. The 3D atom map (Fig. 5 (d)) and ladder diagram taken from the volume in Fig. 5 (d) (Fig. 5 (e)) clearly confirm these precipitates are in direct contact with each other.

Figure 7 (a) and (b) show the bright field TEM images of the TZAM6620 alloy peak aged at 140 °C. These images were taken along the zone axes of $[01\bar{1}0]$ and $[0001]$. Two kinds of precipitates are observed; one is rod-like precipitates grown along the $[0001]$ direction, and the other is blocky ones on the (0001) plane. The $[0001]$ rods have the average size of 247 ± 16.4 and 12.5 ± 2.8 nm in length and diameter, and they are uniformly dispersed within the matrix phase. The blocky precipitates have the size of 20.1 ± 2.1 and 15.4 ± 1.9 nm in diameter and thickness, and they are heterogeneously dispersed within the matrix. Figure 7

(c) and (d) are microbeam diffraction patterns obtained from a $[0001]$ rod and blocky precipitates. They are identified as β_1' and β_2' phases, which are typically observed in Mg-Zn based alloys. The β_1' phase has the orientation relationship (OR) with the magnesium matrix described as $(2\bar{1}\bar{1}0)_{\beta_1'} // (0001)_{Mg}$, $[0001]_{\beta_1'} // [2\bar{1}\bar{1}0]_{Mg}$, and the β_2' phases have the OR of $(0001)_{\beta_2'} // (0001)_{Mg}$ and $[11\bar{2}0]_{\beta_2'} // [10\bar{1}0]_{Mg}$ as reported previously [32-35]. The double-aging results in the significant refinement of these precipitates as shown in Fig. 7 (e) and (f). The size of the $[0001]$ rod is 24.6 ± 1.3 and 4.8 ± 0.5 nm in length and diameter, and the diameter and thickness of the blocky precipitate is 20.1 ± 2.1 and 15.4 ± 1.9 nm, respectively.

Figure 8 (a) shows HAADF-STEM image of the TZAM5420-0.1Na alloy aged for 6 h at 160 °C. The images were observed along the zone axis of $[11\bar{2}0]$. A lot of brightly imaged dotty contrasts are observed, indicating the enrichment of the alloying elements heavier than Mg, i.e., Zn or Sn, as indicated by black arrows, while there are also a few coarse lath-shaped precipitates as indicated by white arrows. As shown in the magnified HAADF-STEM image in the inset to Fig. 8 (a), the dotty contrast has the diameter of ~ 4 nm with coherent interface with the Mg matrix. Figure 8 (b) shows a 3D atom map obtained from the TZAM5420-0.1Na alloy aged at 160 °C for 6 h. Na-enriched regions are recognized from the density of Na atoms. For better visualization of the Na-enriched regions, one of the Na-enriched regions is displayed using an isoconcentration surface of 0.4 at.% Na. Figure 8 (c) shows a ladder diagram analyzed from a selected volume in Fig. 8 (b). The composition of the Na-enriched volume was calculated as Mg-12.04Sn-0.75Zn-1.1Al-1.9Na (at.%), which means the formation of Sn-Na co-cluster at 6h.

The extended aging for 16 h resulted in the precipitation of lath shaped precipitates as indicated by white arrows in the HAADF-STEM image in Fig. 9 (a). Figure 9 (b) shows

the 3D atom map obtained from the same sample. In addition to the Na-enriched particles, a lot of Sn-enriched regions are observed, and it looks like that they are in contact with the Sn-Na co-clusters. The Sn iso-concentration surface with the concentration of 14.5 at.% visualize one of the Sn-enriched precipitates. Fig. 9 (c) shows the ladder diagram analyzed from the selected volume with light blue. The composition of the Sn-enriched volume is calculated as Mg-31.3Sn-1.3Zn-1.4Al-0.03Na (at.%), which is consistent with the Mg₂Sn phase. Interestingly, the concentration of Zn, Al and Na at a Mg₂Sn/Mg interface is 9.7, 5.0 and 0.0 at.% showing the segregation of Zn and Al. Fig. 9 (d) also shows the ladder diagram including the Mg₂Sn/matrix interface analyzed from the selected volume with pink in Fig. 9 (b), which confirms the Mg₂Sn particle is in direct contact with the Na cluster.

Figure 10 (a) shows the bright field TEM image of the TZAM6620 alloy pre-aged at 70 °C for 150 h taken along the zone axis of [0001]. A number of tiny precipitates are observed. Figure 10 (b) shows a 3D atom map obtained from the TZAM6620 alloy pre-aged at 70 °C for 150 h. Zn-enriched regions are recognized from the Zn map, one of which is displayed using an isoconcentration surface of 6.1 at.% Zn for better visualization. A ladder diagram analyzed from the selected volume in Fig. 10 (c) shows that the Zn-enriched volume has a composition of Mg-1.5Sn-17.8Zn-6.2Al (at.%). The number density of the Zn-rich precipitates was estimated to be $\sim 1.3 \times 10^{23} \text{ m}^{-3}$.

4. Discussion

This work has demonstrated the high yield strength of 350 MPa in the peak-aged TZAM5420-0.1Na extruded alloy (Fig. 2 (a)), which is exceptionally high for magnesium wrought alloys that do not contain any rare earth elements. However, the addition of Na caused significant embrittlement due to the segregation of Na at grain boundaries. To

overcome this problem, we have developed the Na-free TZAM6620 alloy. The TZAM6620 alloy exhibited the extraordinary high yield strength over 370 MPa along with the satisfactory ductility up to 14% by double-aging (Fig. 2 (d)). This combination of high strength and ductility is outstanding for wrought magnesium alloy that was processed by ingot metallurgy and subsequent wrought processes. The microstructure characterization suggested that the key for the extraordinary high strength was 1) the inhibition of the grain growth by the Mn_2Sn precipitates during the solution treatment and 2) uniform dispersion of fine nano-scale Mg_2Sn and MgZn_2 (β_2') precipitates by double-aging.

In the TZAM5420-0.1Na alloy, Mn and Na addition contributed to the inhibition of the grain growth during the solution treatment at 450°C (Fig. 3). The BSE SEM image and EDS elemental map in Fig. 4 (a) and (b) have shown that the Sn-rich and Al-Mn enriched particles were located along the grain boundaries, suggesting that these particles pinned the grain boundaries and suppressed the grain coarsening. The Auger spectrum of the TZA542-0.1Na alloy in Fig. 4 (c) and (d) has shown the grain boundary segregation of Na after the solution treatment. Thus, the grain boundary segregation of Na may also contribute to the inhibition of the grain growth by solute-drag like effect during the solution treatment.

Na also caused the significant precipitate refinement as reported previously [20, 27]. Na has positive enthalpy of mixing with Mg [36], and they are virtually immiscible. Since Sn and Na has negative enthalpy of mixing, there is a large driving force to co-segregate as Sn-Na co-clusters when Na precipitate out from the matrix prior to the precipitation of Mg_2Sn phase. The HAADF-STEM and 3DAP results in Fig. 8 (a) – (c) have shown that Na forms co-clusters with Sn with the size of ~ 4 nm and the number density of $6.25 \times 10^{23} \text{ m}^{-3}$ after 6 h of aging at 160°C. The Sn-Na co-clusters act as heterogeneous nucleation sites for the Mg_2Sn precipitates, as evidenced by the atom probe tomography in Fig. 9. In contrast, the Na-free

Mg-Sn-Zn alloys, which forms coarse precipitate microstructure upon aging [37, 38], the Mg_2Sn phase nucleates at the tip of sparsely dispersed MgZn_2 type rod-like β_1' phase with ~ 30 nm in length [37, 38]. The number density of the Sn-Na co-clusters is much higher than that of the β_1' phase [37, 38]. Therefore, the extremely refined precipitate microstructure in the peak aged TZAM5420-0.1Na alloy (Fig. 5 (c) and (d)) is attributed to the formation of a high number density of Sn-Na co-clusters in the early stage of aging, Fig. 8.

Although Na-doped TZAM5420-0.1Na alloy showed extraordinary high-strength in the T6 condition, the sample was brittle because of the grain boundary segregation of Na. A similar phenomenon was reported in the Na-doped TZA1031-0.1Na as-extruded alloy [10]. Thus, we designed a Na-free alloy slightly richer in Sn and Zn to enhance the precipitation kinetics by increasing the supersaturation, TZAM6620. In order to suppress the grain growth during the solution heat-treatment, we adopted a lower solution treatment temperature, 350°C , which is 100°C lower than that of TZAM5420-0.1Na alloy. In this case, the spherical Mg_2Sn particles that dynamically precipitated during the extrusion were not fully dissolved as shown in Fig. 4 (e)). These spherical Mg_2Sn precipitates worked as a grain growth inhibitor during the solution heat-treatment (Figure 4 (e)), and fine-grained structure was kept in the solution treated TZAM6620 (Fig. 3 (d)).

The TZAM6620 alloy solution treated at 350°C can be precipitation strengthened by β_1' and β_2' type precipitates since Zn was fully dissolved into the matrix. Oh-ishi et al. [32] reported the formation of Zn-rich Guinier Preston (G.P.) zones in a Mg-Zn alloy aged at 70°C for 50 h. The G.P. zones acted as nucleation sites for β_1' and β_2' phases causing the substantial refinement of the precipitate microstructure. Following this work, we pre-aged the TZAM6620 alloy at 70°C for 150 h, and we confirmed that the TZAM6620 alloy shows moderate age hardening in this condition (Fig. 1 (b)), and the Zn-enriched spherical G.P. zone

are uniformly dispersed as shown in Fig. 10 (b). The number density of the G. P. zones was estimated to be $\sim 1.3 \times 10^{23} \text{ m}^{-3}$, which is equivalent to that of the Na-Sn clusters observed in the TZAM5420-0.1Na. These zones act as nucleation sites for the β_1' precipitates in the 2nd stage aging, which substantially increased the number of the β_1' precipitates as shown in Fig. 7. In our previous study, the fine dispersion of precipitates was reported to be particularly effective in enhancing the yield strength [36], and the double aged TZAM6620 lead to an extraordinary high yield strength of 370 MPa. Since this alloy does not contain Na that causes the embrittlement of Mg alloys, the newly developed TZAM6620 showed both high strength and good ductility.

Figure 11 summarizes the yield strengths and elongation to failure of various Mg based wrought alloys fabricated by conventional ingot metallurgy process. The TZAM6620 alloy developed in this work showed better strength-ductility balance compared to previously studied Mg-Sn based alloys and the other commercially available wrought alloys such as Mg-Al-Zn and Mg-Zn alloys. Interestingly, the double aged TZAM6620 alloy exhibits almost the same strength, but larger ductility compared to Mg-RE alloys strengthened by long period ordered structured (LPSO) phase and fine-grained wrought Mg alloys fabricated by severe plastic deformation [2, 5, 6, 46, 47].

This work has demonstrated that the precipitation hardening can be an effective technique to strengthen wrought magnesium alloys without any significant loss of ductility. However, the hot extrudability of the newly developed TZAM6620 and TZA562 alloys is limited; the TZAM6620 and TZA562 alloys could not be extruded at 2 mm/s at 300 °C unlike the TZA542 and TZAM5420-0.1Na alloys. This is probably because the increased amount of Zn reduces the melting temperature, causing the hot cracking during extrusion. Double-aging is also needed to increase the strength substantially by the uniform dispersion of fine

precipitates in the TZAM6620 and TZA562 alloys. They could be a promising candidate as high strength wrought magnesium alloy if the extrudability is improved, and quick and substantial age hardening response is achieved.

5. Summary

We have developed a Mg-Sn-Zn-Al based extruded alloy, which can be significantly strengthened by T6 treatment. The significant strengthening by T6 treatment is attributed to the inhibition to the grain growth during the solution treatment, and the refinement of the precipitate microstructure.

- (1) The trace addition of Na to TZAM542 alloy resulted in the significant yield strength increase from 243 to 347 MPa by T6 treatment due to the uniform dispersion of fine nanoscale Mg_2Sn and β_1' precipitates and the inhibition to the abrupt grain growth during the solution treatment. However, elongation to failure significantly decreased to 3% due to the segregation of Na at grain boundaries.
- (2) The refinement of the precipitate microstructure in Na doped alloy is attributed to the formation of high number density of Sn-Na co-clusters, which provided heterogeneous nucleation sites for the refinement of the Mg_2Sn phase.
- (3) To overcome the embrittlement in Na-doped TZAM541+0.1Na alloy, we have developed a Sn and Zn richer alloy, TZAM6620. Low temperature solution treatment at 350°C remained the Mg_2Sn particles that dynamically precipitate during extrusion undissolved, which inhibit the growth of the grains during solution treatment.
- (4) Pre-aging of the TZAM6620 alloy caused uniform dispersion of Zn-rich Guinier Preston zones. Subsequent artificial aging caused the uniform dispersion of nanoscale β_1' and β_2' precipitates.
- (5) The refined precipitate microstructure lead to the unprecedentedly high yield strength of

370 MPa while keeping relatively good elongation to failure of 14%. This alloy shows the best combination of high strength and ductility among wrought magnesium alloys reported so far.

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Table 1: Alloy nomenclature and compositions of samples used in this work

	wt. %	at. %
TZA542	Mg-5.4Sn-4.2Zn-2.0Al	Mg-1.2Sn-1.7Zn-2.0Al
TZAM5420	Mg-5.4Sn-4.2Zn-2.0Al-0.2Mn	Mg-1.2Sn-1.7Zn-2.0Al-0.1Mn
TZA542-0.1Na	Mg-5.4Sn-4.2Zn-2.0Al-0.1Na	Mg-1.2Sn-1.7Zn-2.0Al-0.1Na
TZAM5420-0.1Na	Mg-5.4Sn-4.2Zn-2.0Al-0.2Mn-0.1Na	Mg-1.2Sn-1.7Zn-2.0Al-0.1Mn-0.1Na
TZA562	Mg-5.4Sn-5.9Zn-2.0Al	Mg-1.2Sn-2.4Zn-2.0Al
TZAM6620	Mg-6.6Sn-5.9Zn-2.0Al-0.2Mn	Mg-1.5Sn-2.4Zn-2.0Al-0.1Mn

Table 2: Tensile properties of as-extruded and T6 treated TZA542, TZAM5420, TZA542-0.1Na and TZAM5420-0.1Na alloys.

Sample	Tensile				Compression			$\sigma_{CYS}/\sigma_{TYS}$
	Condition	σ_{TYS} , MPa	σ_{UTS} , MPa	ϵ_T , %	σ_{CYS} , MPa	σ_{CS} , MPa	ϵ_C , %	
TZA542	As-Extruded	184	311	11	170	451	13.8	0.92
	T6	229	303	6	141	420	14.4	0.62
TZAM5420	As-Extruded	182	324	24	168	419	13.8	0.92
	T6	186	292	19	142	426	14.6	0.76
TZA542-0.1Na	As-Extruded	203	302	11	197	459	12.2	0.97
	T6	257	301	4	200	451	10.4	0.78
TZAM5420-0.1Na	As-Extruded	243	324	10	245	451	10.9	1.01
	T6	347	369	3	225	505.4	11.8	0.65

Table 3: Tensile properties of TZA562 and TZAM6620 alloys. Note that the condition for the double aging condition is 70 °C / 150 h and 140 °C to the peak hardness.

Sample	Tensile				Compression			$\sigma_{CYS}/\sigma_{TYS}$
	Condition	σ_{TYS} , MPa	σ_{UTS} , MPa	ϵ_T , %	σ_{CYS} , MPa	σ_{CS} , MPa	ϵ_C , %	
TZA562	As-Extruded	243	351	21	234	467	11.4	0.96
	Single / 140 °C	255	350	20	237	522	11.9	0.93
	Double aged	346	385	15	277	532	12.4	0.80
TZAM6620	As-Extruded	247	349	16	253	473	11.2	1.02
	Single / 140 °C	267	347	13	248	506	12.6	0.93
	Double aged	370	399	14	307	521	9.8	0.83

Figure Captions

Figure 1: Variations in Vickers hardness as a function aging time at 160°C for (a) TZA542, TZAM5420, TZA542-0.1Na and TZAM5420-0.1Na alloys solution treated at 450 °C, and (b) age-hardening curves for TZA542, TZA562 and TZAM6620 alloys aged at various solution treatment and aging temperatures. Note that Ext., S.T. and P.A. stand for Extruded, Solution Treated and Pre-Aged, respectively.

Figure 2: Nominal stress-strain curves obtained from as-extruded and peak aged samples. (a) TZA542 and TZAM5420 alloys, (b): TZA542-0.1Na and TZAM5420-0.1Na alloys, (c) TZA562 alloy, and (d) TZAM6620 alloy.

Figure 3: Inverse pole figure maps of as-extruded (a) TZA542, (b) TZAM5420, (c) TZAM5420-0.1Na, (d) TZAM6620 alloys, and the solution treated (e) TZA542, (f) TZAM5420, (g) TZAM5420-0.1Na, (h) TZAM6620 alloys. These images are taken from a plane parallel to the extrusion direction. Insets in (a) through (d) and (g) and (h) are the (0001) pole figure analyzed from the normal plane to the extrusion direction.

Figure 4: (a) A backscattered electron SEM image and (b) corresponding EDS elemental map of Sn, Al and Mn obtained from the solution treated TZAM5420-0.1Na alloy. (c) and (d) are the fracture surface and Auger spectrum obtained from the fracture surface obtained from the solution treated TZA542-0.1Na alloy. (e) is a bright field TEM image obtained from the TZAM6620 alloy solution treated at 350 °C. (f) the micro beam diffraction pattern taken from one of the spherical precipitates located along the grain boundary.

Figure 5: Bright field TEM images of the peak aged TZA542 alloy taken from the zone axes of (a) $[10\bar{1}0]$ and (b) $[0001]$. (c) and (d) are the bright field TEM images of the peak aged TZAM5420-0.1Na alloy taken from the zone axes of $[11\bar{2}0]$ and $[0001]$.

Figure 6: (a) is the HAADF-STEM image obtained from precipitates in contact with each other. (b) and (c) are the micro-beam diffraction patterns taken from precipitates indicated by black and white arrows in (a). (d) and (e) are 3D atom map including Sn, Zn, Al and Na and ladder diagram analyzed from the volume indicated in (d).

Figure 7: Bright field TEM images taken from the zone axes of (a) $[10\bar{1}0]$ and (b) $[0001]$ of the peak aged TZAM6620 alloy during single aging at 140°C . (c) and (d) are the microbeam diffraction patterns taken from the lode and blocky shaped precipitates from $[11\bar{2}0]$ zone axis. (e) and (f) are the ones taken from the zone axes of $[10\bar{1}0]$ and (b) $[0001]$ of the peak aged TZAM6620 alloy during double aging.

Figure 8: (a) HAADF-STEM image and (b) 3D atom map of Sn, Zn, Al and Na obtained from the TZAM5420-0.1Na alloy aged for 6 h at 160°C . Inset figure in (a) is the magnified HAADF-STEM image taken from a brightly imaged nanoparticle. (c) is the ladder diagram analyzed from the volume (blue) in (b).

Figure 9: (a) and (b) are the HAADF-STEM images, 3D atom map of Sn, Zn, Al and Na obtained from the TZAM5420-0.1Na alloy aged for 16 h at 160°C . (c) and (d) are the ladder diagram analyzed from the volume with blue and pink in (b).

Figure 10: (a) Bright field TEM image taken from $[0001]$ zone axis. (b) is the 3D atom map obtained from the pre-aged TZAM6620 alloy. Ladder diagram in (c) is analyzed from the selected volume (blue) including Zn-enriched phase in (b).

Figure 11: Yield strength and elongation to failure of various magnesium based extruded alloys. Note that As-Ext. and Aged stand for as-extruded sample, and peak aged sample, respectively. Note that F in legends stands for as-fabricated samples, which means

as-extruded or as-rolled samples.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11

Graphical Abstract