Effect of Mg$_2$Sn Particles on Microstructure and Mechanical Properties of aged AZ Series Magnesium alloy.

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Abstract. Magnesium alloys have received a considerable research focus in transportation sector due to its lightness and environmental legislation to reduce green-house effects. In this work, a magnesium alloy containing aluminium, zinc and tin as major alloying addition was studied. After casting, the alloy was homogenised and hot-rolled at 400 °C. This temperature was sufficient to promote extensive dynamic recrystallization as evident from microstructure. Texture was obtained as pole figures. The pole figures clearly revealed basal texture which also ensures the rotating of the crystals along the rolling directions. Aging of the alloy was conducted up to 30 hr at 170 °C. Surprisingly, this T5 treatment showed increased mechanical properties with time. This behaviour was studied in scanning electron microscopy. It was found that spherical-shaped Mg$_2$Sn particles were precipitated as both nano-size particles and micron-size particles. These particles were responsible to age-strengthening of the alloy. Since particle stimulated nucleation is size dependent phenomenon, only Mg$_{17}$Al$_{12}$ phase effectively participated in grain refining. Aging response was entirely due to the presence and coarsening of Mg$_2$Sn particles.

1. Introduction

Magnesium (Mg) alloys have drawn a great attention in automobiles and transportations due to their lightweight and low densities. Lightweight automobiles and transports are environment-friendly with higher fuel economy [1,2]. Also lightweight constructions, automotive industries, aerospace industries and other fields widely used Magnesium and their alloys that attract researchers to work with various Mg alloys [3, 4]. The low yield strength, poor ductility at room temperature, higher cost than steels and aluminium alloys however makes their application limited [5-7]. Among various hardening methods, magnesium alloys can be strengthened by solid solution strengthening or by precipitation hardening [8]. This paves a way of strengthening with addition of Sn, Zn, Ca, Ce or some other element to Magnesium or Mg-Al[9,10] or Mg-RE[11-13] binary systems. Mg-Al binary system contains BCC β-Mg$_{17}$Al$_{12}$ phase that influences the mechanical properties of the alloy system [14-16]. In the case of Mg-Sn binary phase diagram, solubility of Sn in α-Mg decreased from 14.85wt% at 561°C to 0.17wt% at room temperature. Sn addition creates stable Mg$_2$Sn phase that has FCC crystal structure with a high melting temperature(770°C). Addition of Sn to the Mg-Al system promotes grain refinement and improves mechanical properties [17,18].
Mg-Al-Zn-Sn alloy system shows a better combination of strength and ductility at room temperature or elevated temperature along with lower cost than other Mg alloys[19-24]. An improved age hardening response of this alloy system attracts researchers to develop new age hardenable alloys. In this work, age hardening behaviour of Mg-5Al-1Zn-2Sn alloy rolled-sheet will be investigated after hot rolling followed by T5 heat treatment. The ability of Sn nano-particles to promote or hinder recrystallization will also be highlighted.

2. Experimental

A plate of dimension 250×120×20 mm is cast from commercially pure Mg, Al, Zn and Sn ingots. The entire alloying elements were melted in an induction furnace at 800°C in an inert atmosphere. A continuous flow of pure argon (99.995%) created the inert atmosphere. After complete melting, the alloying mixture was agitated for 5 minutes and then poured into a metal mould which was preheated to 200°C. The composition was measured by X-Ray Fluorescence (XRF) technique which is given below in Table 1. The cast plates were then machined off and homogenized for 18 hrs at 410°C followed by water quenching. Two thick plate of individual dimension 100×50×13 mm were cut from the homogenized cast plate and hot rolled. Hot rolling was performed at 400°C with a rolling speed of 0.25m/sec. The thickness of the plate was reduced from 13mm to 2.5mm with 80% of total reduction. The reduction rate was 0.66mm per pass. The rolling temperature was made uniform by reheating the plate after every pass. Tensile samples with gauge length of 20mm were prepared. These samples were further T5 heat treated at an aging temperature of 170°C. Aging time of 3hr, 6hr, 12hr, 18hr, 24hr and 30hr were selected for every group of samples. Samples for optical microscopy (OM) and scanning electron microscopy (SEM) were prepared by following standard metallographic techniques. Samples for OM were etched with acetic picral (Picric acid 4.2g, Acetic acid 10mL, Distilled water 10mL, Ethanol 70mL). Optical micrographs were observed with Optical microscope (OPTIKA B-600MET) and the SEM micrographs were observed after aging with Field-Emission Scanning Electron Microscope (JEOL JSM-7600F) with an Energy-Dispersive Spectrometer (EDS). The Texture analysis was carried out with XRD. Tensile tests at room temperature were carried out with a Universal Testing Machine (INSTRON 3369). A FV-800 Vickers hardness tester with pyramidal indenter and 3kg load was used to determine the Vickers hardness at several points of the rolled sheet after aging.

| Table 1 |
The chemical composition of the investigated alloys (%wt).

|     |     |     |     |     |
|-----|-----|-----|-----|-----|
| Al  | Zn  | Sn  | Si  | Fe  | Mg  |
| 5.033 | 0.993 | 2.617 | >0.025 | >0.025 | Bal. |

3. Results and discussion

3.1. Microstructures of the as-cast and homogenized alloy

Fig.1a Show the as-cast microstructure of the Mg-5Al-1Zn-2Sn alloy taken from the middle of the cast plate. The optical microstructure shows coarse dendrites of primary α-Mg with discontinuous second phase at the inter-dendritic region, Fig. 1b. After 18hrs of homogenization treatment all the second phases were dissolved and the coarse dendritic structure turned into a coarse grain structure with distinct grain boundary (Fig. 1c).
3.2 Texture of the Alloy

The pole figures of the rolled alloy were constructed from XRD data. For hexagonal metals, the texture is commonly represented by the orientation of the $\{0001\}$ plane. The texture obtained for basal $\{0001\}$, prismatic $\{10\overline{1}0\}$ and pyramidal $\{10\overline{2}0\}$ planes are shown in terms of pole figures in Fig. 2. A strong basal texture is observed. Most of the poles are aligned parallel to the sheet thickness. It implies that the c-axis, $<0001>$, direction of the hcp magnesium crystals lies perpendicular to the rolling direction (RD). No splitting of the texture in the rolling direction, as sometimes observed in magnesium alloy sheet was detected.
3.3. Microstructures of hot rolled alloy

Dynamic recrystallization (DRX) was observed during hot rolling of the homogenized thick plate. Fig. 3 shows the microstructure of the rolled sheet with a rolling reduction of 25% showing dynamic recrystallization. Initiation of new grains along grain boundaries were observed with increasing rolling reduction. Final microstructure after 80% rolling reduction consists of fine equiaxed grains uniformly distributed over the structure (Fig. 3b). Deformation modes in the normal direction during rolling were associated mostly with grain boundaries as grain boundary sliding, bulging of grain boundary and grain boundary separation (Fig. 3a). Twinning contributes slightly in this direction though it is the main deformation modes along the surface, parallel to rolling direction (Fig. 3c).

Figure 3. Optical microstructure after hot rolling at 400°C a) showing dynamic recrystallization, b) equiaxed microstructure after 80% reduction c) twinning at the surface of the sheet after 80% reduction.

3.4. Microstructures after aging

Aging effect of the rolled sheet can be seen from the Fig. 4 after aging at 170°C for different amount of aging time. SEM micrographs show small amount of second phase particles embedded over the matrix after 3hr aging. The spherical bright particle reveals Mg2Sn phase after EDS analysis also the irregular particles reveals as Mg17Al12. Particle coarsens, and new particles appear with aging time. Irregular Mg17Al12 particles and bright spherical Mg2Sn particles precipitate along the grain boundaries and some of them precipitate inside grains. Spheroid like Mg2Sn precipitates along grain boundaries mainly produces pinning effect.
With increasing aging time, the volume fraction of second phase particles was also increased; new particles formed along grain boundaries and interior of the grains. Microstructure after 24hr aging shows new bright Mg₂Sn particles formation, these particles also appeared associated with Mg₁₇Al₁₂ phase after 30hr of aging.

3.5. Mechanical behaviour after aging

Mechanical behaviour of the alloy after T5 heat treatment depends on the degree of precipitation hardening. So the size, shape and distribution of the precipitate determine the mechanical behaviour of AZT512 alloy after aging. The variation of yield strength, ultimate tensile strength and ductility with increasing aging time is shown in Fig. 5.

Yield strength (YS) of the alloy increases from an initial value of 164.2MPa to a peak value of 184.5MPa corresponding with an aging time of 18hrs. YS then decreased slightly with aging time. Ultimate tensile strength (UTS) decreases from an initial value of 228.3MPa to 214.6MPa and then increases gradually with aging time, and holds a peak value of 265.2MPa for 30hrs of aging. This can be simply associated with the increasing number of precipitates with increasing aging time. From Fig. 5, it is obvious that the amount of spherical Mg₂Sn particles increased with aging time. According to
Nie [25, 26], spherical precipitates are effective in blocking dislocation gliding on basal, prismatic, and pyramidal planes.

![Image](image.png)

Figure 6. Embryo of Mg$_2$Sn particle embedded in $\alpha$-Mg matrix.

Fig. 6 shows an embryo of Mg$_2$Sn particle embedded in the $\alpha$-matrix. These embryos help in cluster formation and the spherical Mg$_2$Sn particle cause pinning of the dislocation in the grain boundary during plastic deformation. As a consequence, the difference between YS and UTS increases with time. Ductility changes merely with aging time.

![Image](image.png)

Figure 7. Age hardening curve of the alloy aged at 170°C

Fig. 7 shows the hardness variation with aging time of the alloy. 68HV is the initial hardness value obtained with 3hr of aging; same value of hardness obtained with 6hr of aging and then increase gradually to 70HV for 12hr, 73HV for 18hr and 78HV for 24hr and decrease to 76HV for 30 hr of aging time. The peak hardness value obtained is 78HV correspond to 24hr of aging, 10HV larger than initial value. According to sasaki et al. [27], increase in the hardness value with aging is apparently attributed to the homogeneous distribution of Mg$_2$Sn precipitates and increase in number of precipitates. The micrographs confirm a uniform distribution of fine precipitates of the spherical Mg$_2$Sn after aging (Fig. 4) and also observed an increase in the amount of precipitate with increasing aging time.
3.6 Effects of Sn on Recrystallization

Addition of Al and Sn has profound effect on developed microstructure after rolling. As-cast and homogenized microstructure has an average grain size of 200 µm, whereas after hot rolling, the grain size was reduced to 10 µm. In the microstructure, it is evident that a few grains have grown abnormally to a size comparable to as-cast structure. However, most grains were less than 40 µm in size. This implies that after recrystallization of the alloy during hot rolling, grains were extensively refined. Only a few grains were observed to grow to a larger size.

Second phase particles of size larger than 1 µm is typically considered to promote recrystallization by particle stimulated nucleation (PSN). Fig. 4 confirms such presence of particles—Mg_{17}Al_{12} and Mg_{5}Sn. They are the obvious candidate for favourable condition of grain refining. In Fig. 6, one nano-size Mg_{5}Sn particle is shown. It is believed that these particles will hinder growth of grain boundary and thus retard grain growth. However, they will not be suitable for grain refinement. Recrystallization was favoured by twinning and Mg_{17}Al_{12} particles. Mg_{5}Sn particles can act as nucleation sites for new grains. However, it is more likely that nano-size Mg_{5}Sn particles will delay recrystallization due to pinning effect as they are more likely to be positioned in the prior grain boundaries.

3.7 Effects of Sn on Aging

Mg_{5}Sn particles act as pinning particles as they are nucleated on grain boundaries. Mg_{17}Al_{12} phase is apparently not sufficient to restrict deformation after aging. In contrast, the size of Mg_{5}Sn particles has increased considerably during aging. These particles still provide enough hindrance to dislocation movement. This is confirmed through strength and hardness data. With aging, the particles were coarsened. These coarsened particles were mostly Mg_{5}Sn. They have grown from the tiny nano-size to micron-size level and yet effective to block dislocation movements.

4. Conclusion

The cast, homogenised, rolled and aged microstructure and the mechanical properties after aging of AZ series alloy with 2 wt % Sn addition was studied and following conclusion could be deduced.

a. Addition of 2% Sn to an AZ series Mg alloy is sufficient to promote grain refinement by dynamic recrystallization during hot rolling at 400°C.

b. Increasing aging time coarsen the spherical Mg_{5}Sn particles that improves the mechanical properties of the alloy. Ductility of the alloy varies slightly with aging time. Vickers Hardness increases with the increasing amount of Mg_{5}Sn precipitate and also uniform distribution of precipitate.

c. The best combination of mechanical properties was obtained by aging for 18hr. YS of 184.5MPa and UTS of 257MPa along with 3% ductility.

d. Nano-size Mg_{5}Sn particles were confirmed in the microstructure which is effective in blocking dislocation motions. These particles were coarsened during aging and yet provide strong influence on hindrance of dislocation movement.

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6. Reference

[1] Pan H, Ren Y, Fu H, Zhao H, Wang L, Meng X, Qin G. Recent developments in rare-earth free wrought magnesium alloys having high strength: a review. Journal of Alloys and Compounds. 2016 Apr 5;663:321-31.

[2] Bettles C, Gibson M. Current wrought magnesium alloys: strengths and weaknesses. Jom. 2005 May 1;57(5):46-9.

[3] Sasaki TT, Elsayed FR, Nakata T, Ohkubo T, Kamado S, Hono K. Strong and ductile heat-treatable Mg–Sn–Zn–Al wrought alloys. Acta Materialia. 2015 Oct 15;159:176-86.

[4] Zhang J, Guo ZX, Pan F, Li Z, Luo X. Effect of composition on the microstructure and mechanical properties of Mg–Zn–Al alloys. Materials Science and Engineering: A. 2007 May 15;456(1-2):43-51.

[5] Jung JG, Park SH, Yu H, Kim YM, Lee YK, You BS. Improved mechanical properties of Mg–7.6 Al–0.4 Zn alloy through aging prior to extrusion. Scripta Materialia. 2014 Dec 15;93:8-11.

[6] Qi F, Zhang D, Zhang X, Xu X. Effect of Sn addition on the microstructure and mechanical properties of Mg–6Zn–1Mn (wt.%) alloy. Journal of Alloys and Compounds. 2014 Feb 5;585:656-66.

[7] Zhu SQ, Yan HG, Liao XZ, Moody SJ, Sha G, Wu YZ, Ringer SP. Mechanisms for enhanced plasticity in magnesium alloys. Acta Materialia. 2015 Jan 1;82:344-55.

[8] Callister WD, Rethwisch DG, Materials Science and Engineering: AnIntroduction, 8th ed., 2010. J. Wiley, USA

[9] Clark JB. Age hardening in a Mg-9 wt.% Al alloy. Acta Metallurgica. 1968 Feb 1;16(2):141-52.

[10] Celotto ST. TEM study of continuous precipitation in Mg–9 wt% Al–1 wt% Zn alloy. Acta materialia. 2000 May 1;48(8):1775-87.

[11] Nie JF, Gao X, Zhu SM. Enhanced age hardening response and creep resistance of Mg–Gd alloys containing Zn. ScriptaMaterialia. 2005 Nov 1;53(9):1049-53.

[12] Smola B, Stuliková I, Von Buch F, Mordike BL. Structural aspects of high performance Mg alloys design. Materials Science and Engineering: A. 2002 Feb 15;324(1-2):113-7.

[13] Ping DH, Hono K, Nie JF. Atom probe characterization of plate-like precipitates in a Mg–RE–Zn–Zr casting alloy. Scripta Materialia. 2003 Apr 14;48(8):1017-22.

[14] Leil TA, Hort N, Dietzel W, Blawert C, Huang Y, Kainer KU. Rao KP. Microstructure and corrosion behavior of Mg–Sn–Ca alloys after extrusion. Transactions of Nonferrous Metals Society of China. 2009 Feb 1;19(1):40-4.

[15] Kleiner S, Befort O, Wahlen A, Uggowitzer PJ. Microstructure and mechanical properties of squeeze cast and semi-solid cast Mg–Al alloys. Journal of Light Metals. 2002 Nov 1;2(4):277-80.

[16] Song GL. Effect of tin modification on corrosion of AM70 magnesium alloy. Corrosion Science. 2009 Sep 1;51(9):2063-70.

[17] Hort N, Huang YD, Kainer KU. Intermetallics in magnesium alloys. Advanced Engineering Materials. 2006 Apr 1;8(4):235-40.

[18] NayebAA,Hashemi, ClarkJB, Mg-Sn (Magnesium-Tin), Binary Alloy Phase Diagrams, second ed., T.B. Massalski (Ed.), 1990, 3, 2549-2552.

[19] Kim YK, Sohn SW, Kim DH, Kim WT, Kim DH. Role of icosahedral phase in enhancing the strength of Mg–Sn–Zn–Al alloy. Journal of Alloys and Compounds. 2013 Feb 5;549:46-50.

[20] Mahmudi R, Moeendarbary S. Effects of Sn additions on the microstructure and impress creep behavior of AZ91 magnesium alloy. Materials Science and Engineering: A. 2013 Mar 20;566:30-9.

[21] Elsayed FR, Sasaki TT, Mendis CL, Ohkubo T, Hono K. Compositional optimization of Mg–Sn–Al alloys for higher age hardening response. Materials Science and Engineering: A. 2013 Mar 20;566:22-9.

[22] Wang B, Pan F, Chen X, Guo W, Mao J. Microstructure and mechanical properties of as-extruded and as-aged Mg–Zn–Al–Sn alloys. Materials Science and Engineering: A. 2016 Feb 22;656:165-73.

[23] Yoon J, Park S. Forageability test of extruded Mg–Sn–Al–Zn alloys under warm forming conditions. Materials & Design. 2014 Mar 1;55:300-8.

[24] Kabir AS, Sanjari M, Su J, Jung IH, Yue S. Effect of strain-induced precipitation on dynamic recrystallization in Mg–Al–Sn alloys. Materials Science and Engineering: A. 2014 Oct 20;616:252-9.

[25] Nie JF. Precipitation and hardening in magnesium alloys. Metallurgical and Materials Transactions A. 2012 Nov 1;43(11):3891-939.

[26] Nie JF. Effects of precipitate shape and orientation on dispersion strengthening in magnesium alloys. Scripta Materialia. 2003 Apr 14;48(8):1009-15.

[27] Sasaki TT, Oh-Ishi K, Ohkubo T, Hono K. Enhanced age hardening response by the addition of Zn in Mg–Sn alloys. Scripta Materialia. 2006 Aug 1;55(3):251-4.