Simultaneous achievement of high thermal conductivity, high strength and formability in Mg-Zn-Ca-Zr sheet alloy

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ABSTRACT
Lightweight magnesium alloys with good thermal conductance are in demand for structural components in portable devices. This work presents a strategy to achieve excellent thermal conductivity, room temperature (RT) formability and high strength in magnesium sheet alloys. We found that a Mg-1.6Zn-0.5Ca-0.4Zr alloy shows a substantial increase in thermal conductivity to over 130 W/(m·K) due to the reduced supersaturation of solute atoms in the matrix by the precipitation of Guinier-Preston (G.P.) zones while exhibiting excellent RT formability with a large Index Erichsen value of 8.1 mm, and a high yield strength of 227 MPa by peak aging treatment.

IMPACT STATEMENT
This work reports a superiority of heat treatable magnesium alloy in simultaneously achieving high thermal conductivity and excellent mechanical properties through quantitative analysis of the microstructure in atomic scale.

1. Introduction
Lightweight magnesium (Mg) alloys with good thermal conductance and high strength are attractive for structural components in portable devices [1,2]. However, these characteristics are contradictory in commercially available wrought Mg alloys, e.g., Mg-3Al-1Zn (wt.%, AZ31) and Mg-6Al-1Zn (wt.%, AZ61). Because they are strengthened by solution strengthening, the lattice distortion induced by solute atoms leads to the increase in electron scattering and resultant low thermal conductivity [3,4]. For example, the AZ31 sheet alloy shows an adequate yield strength of above 200 MPa, while the poor thermal conductivity of ~86 W/(m·K), which is much lower than 158 W/(m·K) in pure Mg, may not meet the growing requirements [3]. Precipitation hardening is an effective approach to achieve the high strength and thermal conductivity simultaneously as evidenced in aluminum alloys [5]. Among various Mg alloys, Mg-Zn system is age-hardenable and shows a minimal effect on the loss of thermal conductivity; the binary Mg-Zn alloy maintains above 100 W/(m·K) even 8t.% of Zn is alloyed [6]. A Mg-2Zn-Zr (wt.%) alloy exhibits a high thermal conductivity of 132.1 W/(m·K) and yield strength of 196 MPa [7], and these properties are expected to be further improved by the enhancement of age hardenability. The trace addition of Ca into dilute Mg-Zn based alloys can significantly enhance the age-hardening response by the precipitation of Guinier Preston (G.P.) zones; a maximum hardness increment is obtained by the addition of 0.5 wt.% Ca into the Mg-1.6Zn (wt.%) cast alloy [8]. The addition of Ca is also known to weaken the strong basal texture in Mg sheet alloys, which improves the poor RT formability [9]. Zr addition also leads to concurrent achievement.
of excellent RT formability and high strength by the formation of fine dispersion of Mg(Zn,Zr)\textsubscript{2} precipitates in fine-grained structure \cite{10}. 

In this study, we fabricated a Mg-1.6Zn-0.5Ca-0.4Zr (ZZX210, wt\%\textsubscript{\textregistered}) sheet alloy and demonstrate a novel approach to achieve high thermal conductivity, high strength and large RT formability simultaneously. The state-of-the-art aberration corrected high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and three-dimensional atom probe (3DAP) analysis are used to unveil the quantitative correlation between the thermal conductivity and structure of nanoscale precipitates along with solutes distribution, which has been difficult to quantify in dilute alloys. These results are expected to give critical insights into the rational design of thermally conductive magnesium alloys with excellent mechanical properties.

2. Materials and methods

The ZZX210 alloy ingot was prepared by induction melting using a high-purity pure Mg, ZK60 (Mg-5.5Zn-0.5Zr, wt.\%), Mg-30 wt.%Ca and Mg-34 wt.%Zr master alloys in a steel crucible under an Ar atmosphere. 10-mm-thick plates machined from the cast ingot were first homogenized at 300 \degree\textdegreeC for 4 h and then slowly heated to 450 \degree\textdegreeC (\textapprox{} 7.5 \degree\textdegreeC/h) maintaining for 6 h, followed by water quenching. The homogenized plates were primarily rolled to \textapprox{} 5 mm thick at 300 \degree\textdegreeC with \textapprox{} 15\% thickness reduction per pass. The 5 mm thick plate were further fine-rolled to \textapprox{} 1 mm thick sheet at 100 \degree\textdegreeC in \textapprox{} 23\% thickness reduction per pass along with reheating at 450 \degree\textdegreeC for 5 min between each pass. The as-rolled sheets were solution-treated at 450 \degree\textdegreeC for 1 h, water quenched and subsequently aged at 170 \degree\textdegreeC in an oil bath. For reference, Mg-1.6Zn-0.4Zr (wt.\%, ZK20) and Mg-5Zn-0.5Ca-0.4Zr (wt.\%, ZK510) alloys were also prepared by the similar process. The age hardening response was studied on the reference, Mg-1.6Zn-0.5Ca-0.4Zr (wt.\%, ZXK510) alloys were also prepared by the similar process. The age hardening response was studied on the reference, Mg-1.6Zn-0.5Ca-0.4Zr (wt.\%, ZXK510) alloy showing noticeable age hardening but takes approximately 45 h to reach the peak hardness with the thermal conductivity of \textapprox{} 130.2 \pm 0.4 W/(m·K). The ZXK510 alloy shows noticeable age hardening with the thermal conductivity of \textapprox{} 130.2 \pm 0.4 W/(m·K).

3. Results and discussion

Figure 1(a) shows the EBSD inverse pole figure (IPF) map and (0002) pole figure obtained from the solution-treated ZZX210 alloy. Note that the IPF map was taken along the transverse direction (TD) of the sheet and reconstructed so that grain orientations from the normal direction (ND) are observed. The solution-treated ZZX210 alloy has an average grain size of \textapprox{} 6.6 \pm 2.8 \mu\textmu m. The (0002) poles are mainly tilted by \textapprox{} 40° towards TD with intensity of 3.3 mrd, which means the development of a TD-split texture. The development of the TD-split texture is distinct feature in the ZZX210 alloy as described in supplementary information and Figure S1; (0002) poles are tilted towards the rolling direction in the ZK20 alloy, which consists of equi-axed grains with a similar grain size of \textapprox{} 7.5 \pm 3.5 \mu\textmu m, while the ZXK500 alloy shows a typical strong basal texture with a coarse grain size of \textapprox{} 13.6 \pm 6.3 \mu\textmu m. Figure 1(b) shows variations in Vickers hardness and thermal conductivity during aging at 170 \degree\textdegreeC. The solution-treated ZZX210 alloy has a hardness of 52.8 \pm 1.6 HV. The hardness rapidly increases to the peak hardness of 66.1 \pm 1.5 HV in 4 h (T6), and then decreases to 52.3 \pm 1.3 HV after 1000 h (over-aging). The thermal conductivity of the solution-treated sample increases from 123.3 \pm 0.8 to 128.6 \pm 0.5 W/(m·K) by the T6 treatment, and further increase to 135.8 \pm 0.6 W/(m·K) by over-aging, Figure 1(b) and Table 1. In contrast, the ZK20 alloy shows little age hardening with the thermal conductivity of \textapprox{} 130.2 \pm 0.4 W/(m·K). The ZXK510 alloy shows noticeable age hardening but takes approximately 45 h to reach the peak hardness with the thermal conductivity increment from 113.9 \pm 1.1 to 123.7 \pm 1.2 W/(m·K), Figure S2a and b.

Figure 1(c) shows nominal tensile stress–strain curves stretched along the RD with snapshot of the solution-treated sample after the Erichsen cupping test in the inset. Table 1 summarizes the mechanical properties loaded along both RD and TD. The solution-treated ZZX210 alloy exhibits an average tensile yield strength (\sigma\textsubscript{YTS} = \frac{\sigma\textsubscript{UTS} + \sigma\textsubscript{TYS}}{2}) of 160 MPa and ultimate tensile strength (\sigma\textsubscript{UTS}) of 255 MPa with an elongation to failure (\epsilon\textsubscript{T}) of 27.3\% with a large I.E. value of 8.1 mm at RT. The T6-treatment results in remarkable increments in the average \sigma\textsubscript{TYS} and \sigma\textsubscript{UTS} to 202 and 278 MPa at a slight expense of \epsilon\textsubscript{T} to
Figure 1. (a) The IPF map and (0002) Pole figure of the solute-treated ZXK210 alloy. (b) Variations in Vickers hardness and thermal conductivity as functions of aging time. (c) Nominal tensile stress-strain curves for solution-treated, T6-treated, and over-aged samples along the RD. Inset to Figure 1(c) is a snapshot of solution-treated sample after Erichsen cupping test at RT.

Table 1. Mechanical properties and thermal conductivity of the ZXK210 alloy. S.T., T6 and O.A. stand for solution-treated, peak-aged and over-aged conditions.

| Condition        | RD        | TD        | Thermal conductivity λ, W/(m·K) |
|------------------|-----------|-----------|-------------------------------|
|                  | σ_TYS, MPa| σ_UTS, MPa| ε_T, %                        |
| S.T. (450 °C/1 h)| 181 ± 1  | 265 ± 2  | 28.2 ± 1.6                   |
| T6 (170 °C/4 h)  | 227 ± 2  | 291 ± 1  | 22.6 ± 1.3                   |
| O.A. (170 °C/1000 h) | 171 ± 1  | 242 ± 1  | 23.8 ± 1.1                   |

21.9%. The over-aging causes substantial decrease of the σ_TYS, σ_UTS and ε_T to 159, 232 MPa and 22%, respectively, Figure 1(c). Compared to the ZXK210 alloy, the Ca-free ZK20 alloy shows a low I.E. value of 6.5 mm, σ_TYS and σ_UTS of 159 and 225 MPa in the solution-treated condition, Figure S2c. The ZK20 is not further strengthened because of no significant age hardening, Figure S2a. Although the ZXK510 alloy shows substantial increase in σ_TYS and σ_UTS from 150 and 264 MPa to 227 and 286 MPa at the expense of ε_T to 15.1% by the T6-treatment, Figure S1c, the ZXK510 exhibits poor RT formability with an I.E value of only 4.5 mm, Figure S2c.

Figure 2 compares the thermal conductivity and yield strength for various Mg sheet alloys [2,3,7,11]. The T6-treated ZXK210 alloy shows the best strength-conductivity balance among various samples. The ZK20 alloy shows a high thermal conductivity of 130.2 W/(m·K) comparable with that of ZXK210 but has a low yield strength of only 159 MPa and poor room temperature formability, Figure S2. The ZXK510 alloy exhibits a high yield strength of 227 MPa and relatively high thermal conductivity of 123.7 W/(m·K), Figure S2b and c. Considering the excellent stretch formability and quick age hardenability, the dilute ZXK210 alloy has a great potential for the development of thermally conductive Mg sheet alloys with excellent mechanical properties.

Figure 3 shows bright-field TEM images of the solution-treated, T6-treated, and over-aged ZXK210 alloys taken from the zone axis of [1120]_α. A number of nanoparticles are observed along grain boundaries and within the grains in the solution-treated sample, Figure 3(a). The nanobeam diffraction patterns taken from the blocky and rod-shaped precipitates indicated by arrows 1 and 2 are identified as Zn_2Zr_3 and Zn_2Zr phases, respectively [12]. For the T6-treated sample, the diffraction contrast indicates a distribution of nanoscale precipitates on the basal plane of the matrix, Figure 3(b). The diffraction patterns taken from the zone axes of [01T0]_α and [0001]_α show continuous streaks along the [0001]_α direction and extra diffraction spots at the 1/3[2110]_α and 2/3[2110]_α positions, indicating the precipitation of ordered G.P. zones on the basal planes of the matrix. A
number of pairs of coarse precipitates with a length of 10-50 nm are formed on the (0001)\(\alpha\) planes in the over-aged samples, Figure 3(c). Since the diffraction patterns are similar to those observed in the T6-treated sample, the coarse precipitates are considered to be evolved from the G.P. zones.

Figure 4 shows HAADF-STEM images obtained from the T6-treated and over-aged ZXK210 alloys taken from the zone axis of [1120]\(\alpha\). The G.P. zones are imaged with bright contrast, indicating that they are enriched with Zn and/or Ca, Figure 4(a,b). The average size of the G.P. zones in the T6-treated sample is \(\sim 3.2 \pm 0.4\) nm, which is much smaller than those in the over-aged sample, \(\sim 35 \pm 10\) nm. The atomic resolution image of the T6-treated sample shows that the G.P. zones are brightly imaged as single atomic columns arranged on the (0001)\(\alpha\) planes, Figure 4(c). No misfit dislocation is observed on the surface or edge of the G.P. zone, suggesting a fully coherent interface with the matrix. In contrast, a pair of basal precipitates with two brightly imaged atomic columns of \(\sim 0.2\) nm distance is observed in the over-aged sample, Figure 4(d). These precipitates have an ABCA stacking sequence along the (0001) planes, indicating the formation of metastable \(\eta^\prime\) phase as reported in Mg-Gd-Zn alloys [13].

Figure 5(a–c) show 3D atom maps of Mg, Zn, Ca and Zr obtained from the solution-treated, T6-treated and over-aged ZXK210 alloys with volumes of 40 × 40 × 200 nm\(^3\). Table 2 summarizes the solute content in the matrix, planar interspace and number density of precipitates in the T6-treated and over-aged samples. The concentration of Zn, Ca and Zr are 0.412, 0.241, and 0.001 at.% in the solution-treated sample. The frequency distribution of 1st-order nearest neighbor (1NN) solute atoms distance shows a consistency between experimental and random distributions, indicating that the elemental distribution in the solution treated sample is uniform, Figure 5(d). The T6-treatment resulted in the depletion of Zn and Ca in the matrix to 0.195 and 0.111 at.% due to the precipitation of fine plate-like G.P. zones with average Zn and Ca concentrations of 17.4 and 16.3 at%, Figure 5(b,e).

The number density and effective planar interspace of the precipitates are calculated to be \(\sim 9.9 \times 10^{23} \text{m}^{-3}\) and \(8.9\) nm based on \(\lambda = \left( \frac{0.953}{\sqrt{f}} - 1 \right) d_i\) [14]. By over-aging, the Zn and Ca elements are further depleted from the matrix, and their contents decreased to 0.071 and 0.003 at.%, respectively. The average Zn and Ca contents in the \(\eta^\prime\) phase are 34.1 and 39.1 at.% and its number density is \(\sim 1.5 \times 10^{23} \text{m}^{-3}\), which is much lower than that of G.P. zones observed in the T6-treated sample, Figure 5(c,f). The low number density leads to a large effective planar interspace of these \(\eta^\prime\) phase is \(\sim 95.1\) nm.

The present work reports an approach to achieve high thermal conductivity, high strength and excellent RT formability simultaneously. The thermal conductivity of the ZXK210 alloy increases from 123.3 to 128.6 W/(m·K) by the T6-treatment, Figure 1(b), due to the precipitation of the G.P. zones, which significantly decrease the Zn and Ca content within the matrix from 0.412 and 0.241 at.% to 0.195 and 0.111 at.%, respectively, Figure 5 and Table 2. Since the thermal conductivity of conductive metals is mainly contributed by electrons rather than phonons, the depletion of solute atoms leads to the
reduced electron scattering, resulting in the improvement of the thermal conductivity [4,15]. The effective planar interspace of precipitates increases to 95.1 nm by over-aging, which is one order larger than that in the T6 treated samples, 8.7 nm, Table 2. Considering the electron mean free path in our alloy should be shorter than that in pure Mg: ∼22 nm at RT [16], the precipitates in the over-aged sample no longer influence the thermal conductivity. Thus, the high thermal conductivity in the over-aged sample is also attributed to the increased planar interspace of precipitates.

The precipitation of the G.P. zones also leads to the substantial improvement of the yield strength from 181 to 227 MPa at 170 °C for 4 h, Figure 1(c), leading to the
excellent strength-thermal conductivity relationship ever reported in the Mg alloy sheets, Figure 2. The solution-treated ZKX210 alloy shows excellent RT formability with an I.E. value of 8.1 mm which is much larger than those of ZK20 and ZKK510 alloys and even comparable to that of 6xxx series Al alloys [17]. The improved formability is predominantly attributed to the weak TD-split texture in which a greater number of grains are favorably oriented for the operation of basal $\{\overline{1}0\overline{1}2\}$ tensile twinning during bi-axial loading in comparison with the RD-texture developed in the ZK20 alloy and strong basal texture in the ZKK510 alloy, Figure 1 and Figure S2 [18,19]. Therefore, we conclude that the heat-treatable dilute ZKX210 alloy is promising to develop strong and formable Mg sheet alloy with high thermal conductivity. However, the large yield asymmetry and strength degradation by over-aging are the issues to be overcome via the texture modification and improvement of age hardening behavior by microalloying.

4. Conclusion

This study demonstrates that the heat-treatable Mg-1.6Zn-0.5Ca-0.4Zr dilute alloy can achieve an outstanding combination of excellent RT formability, high strength of 227 MPa and high thermal conductivity of 128.6 W/(mK), which has never been reported in other Mg sheet alloys. The simultaneous increase in the strength and thermal conductivity is associated with the precipitation of the G.P. zones enriched with Zn and Ca, resulting in the depletion of solute atoms from the matrix. Such extraordinary properties are achievable only in heat treatable dilute alloys strengthened by the precipitation of G.P. zones.

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Disclosure statement

No potential conflict of interest was reported by the author(s).

References

[1] Luo AA. Recent magnesium alloy development for elevated temperature applications. Int Mater Rev. 2004;49(1):13–30.
[2] Li S, Yang X, Hou J, et al. A review on thermal conductivity of magnesium and its alloys. J Magnes Alloys. 2020;8:78–90.
[3] Avedesian MM, Baker H. Magnesium and magnesium alloys. Ohio (OH): ASM International; 1999.
[4] Madelung O, White GK. Thermal conductivity of pure metals and alloys. Berlin: Springer; 1991.
[5] Lumley RN, Polmear IJ, Groot H, et al. Thermal characteristics of heat-treated aluminum high-pressure die-castings. Scr Mater. 2008;58:1006–1009.
[6] Pan H, Pan F, Yang R, et al. Thermal and electrical conductivity of binary magnesium alloys. J Mater Sci. 2014;49(8):3107–3124.
[7] Li B, Hou L, Wu R, et al. Microstructure and thermal conductivity of Mg-2Zn-Zr alloy. J. Alloys Compd. 2017;722:772–777.
[8] Oh-ishi K, Watanabe R, Mendis CL, et al. Age-hardening response of Mg-0.3 at.% Ca alloys with different Zn contents. Mater Sci Eng A. 2009;526:177–184.
[9] Chino Y, Sassa K, Huang X, et al. Effects of Zinc concentration on the stretch formability at room temperature of the rolled Mg-Zn-Ca alloys. J Japan Inst Metals. 2011;75:35–41.
[10] Homma T, Mendis CL, Hono K, et al. Effect of Zr addition on the mechanical properties of as-extruded Mg-Zn-Ca-Zr alloys. Mater Sci Eng A. 2010;527:2356–2367.
[11] Shin HS, Leon MD. Parametric study in similar ultrasonic spot welding of A5052-H32 alloy sheets. J Mater Process Technol. 2015;224:222–232.
[12] Gao X, Muddle BC, Nie JF. Transmission electron microscopy of Zr-Zn precipitate rods in magnesium alloys containing Zr and Zn. Philos Mag Lett. 2009;89(1):33–43.
[13] Nie JF, Oh-ishi L, Gao X, et al. Solute segregation and precipitation in a creep-resistant Mg–Gd–Zn alloy. Acta Mater. 2008;56:6061–6067.
[14] Nie JF. Effects of precipitate shape and orientation on dispersion strengthening in magnesium alloys. Scr Mater. 2003;48:1009–1015.
[15] Ashcroft NW, Mermin ND. Solid state physics. Orlando (FL): Saunders College; 1976.
[16] Gall D. Electron mean free path in elemental metals. J Appl Phys. 2016;119(8):085101.
[17] Hirsch J. Aluminium alloys for automotive application. Mater Sci Forum. 1997;242:33–50.
[18] Bian MZ, Zeng ZR, Xu SW, et al. Improving formability of Mg–Ca–Zr sheet alloy by microalloying of Zn. Adv Eng Mater. 2016;18:1763–1769.
[19] Suh BC, Kim JH, Hwang JH, et al. Twinning-mediated formability in Mg alloys. Sci Rep. 2016;6:1–8.