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研究課題名（和文）Development of precipitation-hardenable magnesium sheet alloys with strong and rapid age-hardening response

研究課題名（英文）Development of precipitation-hardenable magnesium sheet alloys with strong and rapid age-hardening response

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研究成果の概要（和文）：Age-hardening response of Mg-Ag-Ca, Mg-Li-Al and Mg-In-Gd alloys has been evaluated to clarify whether the mixing enthalpy value and the atomic size of solute elements are important factors to determine the formation of precipitates.

研究成果の学術的意義や社会的意義
Precipitation has not been widely adopted in commercial magnesium alloys due to their poor and sluggish age-hardening response. This project aims to provide a knowledge platform that can provide us valuable insight into the formation mechanism of the precipitates in magnesium alloys.

研究成果の概要（英文）：This project successfully developed new types of precipitation-hardenable Mg wrought alloys with quick age-hardening response. In addition, this project demonstrated that the mixing enthalpy value between the solute elements and the atomic radius of solute atoms are important factors in designing Mg alloys with fast aging kinetics. However, the hardness increment is rather low. Further work is required to enhance the hardness increment by the short-time artificial aging in order to compete with 6000 series Al alloys.

研究分野：金属材料工学

キーワード：マグネシウム合金　時効硬化　混合エンタルピー　原子半径　析出物

１．研究開始当初の背景

Solid-state precipitation is one of the most effective methods to strengthen various engineering alloys, particularly in 6xxx series aluminum alloys, as shown in Fig. 1. However, the same approach has not been widely adopted in commercial magnesium (Mg) alloys due to their poor and sluggish age-hardening response [1]. For example, the hardness increment for a commercial AZ31 (Mg–3Al–1Zn in wt.%) alloy is only about 5 HV after artificial aging, as shown in Fig. 1. In contrast, a commercial ZK60 (Mg–6Zn–0.4Zr in wt.%) alloy shows a slightly higher hardness increment of 15 HV [2]. However, it needs more than 200 h to reach the peak hardness condition at 160 °C, which is apparently too long for practical applications. Recently, Mg–Ca–Zn and Mg–Ca–Al alloy systems have been received considerable attention due to their rapid age-hardening response [3-5]. As can be seen from Fig. 1, Mg–0.5Ca–1.6Zn (wt.%) and Mg–0.5Ca–0.3Al (wt.%) alloys can reach the peak hardness condition within 2 h at 200 °C. Detailed microstructure observations reveal that monolayer Guinier-Preston (GP) zones on the basal planes are responsible for the age-hardening, as shown in Fig. 2a.

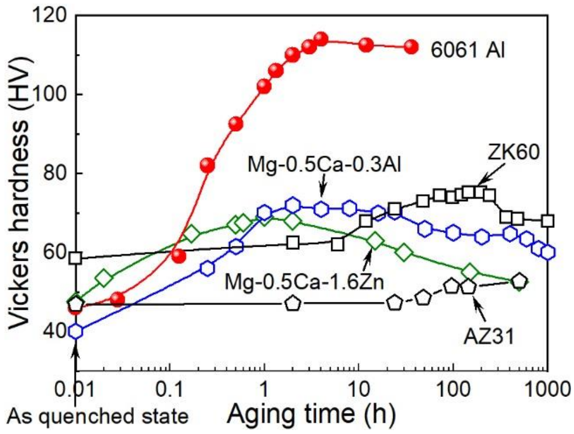

Fig. 1. Comparison of age-hardening response of commercial AZ31, ZK60 and experimental Mg–0.5Ca–1.6Zn and Mg–0.5Ca–0.3Al alloys with 6061 Al alloy [1-5].

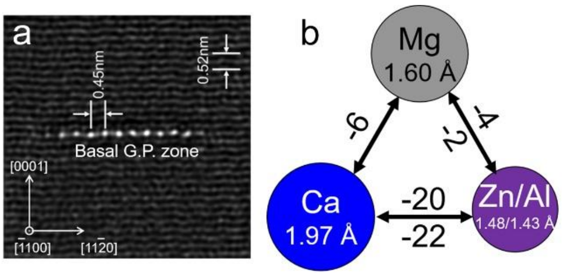

Fig. 2. (a) Mono-layer GP zones formed on the basal plane of Mg–0.5Ca–1.6Zn alloy [4]. (b) The relationships between the atomic size and mixing enthalpy values of the constituent element and main element in Mg–Ca–Zn/Al alloy systems [6].

A common feature of these dilute alloys is that the mixing enthalpy value between the solute elements is negatively large. The mixing enthalpy values of Ca–Zn and Ca–Al are -20 kJ/mol, -22 kJ/mol [6], respectively, which are several times larger than the other combinations, as shown in Fig. 2b. A closer look at the atomic radius we can find that the Zn (1.48 Å) or Al (1.43 Å) atoms that are undersized, while the Ca (1.97 Å) atom is bigger than Mg (1.60 Å) atom. Since substituting Mg by Al, Zn and Ca leads to negative lattice misfits (0.106 by Al or 0.169 by Zn) and a positive lattice misfit (0.231 by Ca), the formation of G.P. zones with undersized Al or Zn atoms and oversized Ca atoms is believed to reduce overall elastic strains originated from solute atoms. If this finding that the mixing enthalpy values and atomic size of the solute elements are the important factors to determine the formation of precipitates is correct, then it opens up a possibility of developing a new type of precipitation-hardenable Mg sheet alloy.

２．研究の目的

The purpose of this project is to develop a new type of precipitation-hardenable Mg wrought alloy with strong and rapid age-hardening response. Unlike the conventional trial-and-error method employed for the alloy development, this project proposes three alloy systems based on the mixing enthalpy value and atomic radius of solute atoms. The three alloy systems are Mg–Ca (calcium)–Ag (silver), magnesium–In (indium)–Gd (gadolinium) and Mg–Li (lithium)–Al (aluminum). The mixing enthalpy values between the solute elements in each alloy system, *i.e.* Ca–Ag, In–Gd and Li–Al, are substantially larger than the other combinations. In addition, the alloy systems proposed by the applicant have different combinations of atomic radius of solute atoms, which are (i) a combination of oversized Ca and undersized Ag, (ii) a combination of oversized In and Gd, and (iii) a combination of undersized Li and Al.

３．研究の方法

The ingots of Mg–Ag–Ca, Mg–In–Gd and Mg–Li–Al based alloys with different compositions (all in wt.%) were cast by an induction melting furnace under the protection of an argon atmosphere. The cast ingots were extruded, homogenized and thermomechanically processed under different rolling conditions. The rolled sheets were solution treated at different temperatures to dissolve solute atoms as much as possible, and then water quenched. The water quenched samples were then aged at lower temperatures to form precipitates. The age-hardening response of developed alloys was evaluated using Vickers hardness test at room temperature. A comprehensive microstructure characterization by scanning electron microscope (SEM), electron backscatter diffraction (EBSD), transmission electron microscopy (TEM) was done on the samples prepared under different processing conditions throughout the full period of the project.

４．研究成果

Fig. 3a shows the age-hardening response of T4-treated Mg–xAg–0.1Ca rolled sheets (x = 1.5, 6 and 12) during isothermal aging at 170 °C. The 1.5Ag containing alloy sheet shows a low Vickers hardness value of 41.4 HV in the initial condition (T4: 450 °C for 1 h), and it exhibits a negligible age-hardening. Increasing the Ag content not only leads to a higher hardness value in the T4-treated condition but also enhances the age-hardening response. The 6Ag containing alloy sheet and the 12Ag containing alloy sheet show hardness values of 51.1 HV and 67.0 HV, respectively, in the T4-treated condition. After aging for 336 h, the hardness value of the former is increased to 57.4 HV, and that of the latter is enhanced to 80.0 HV.

Fig. 3b shows the age-hardening response of Mg–1.5Ag–yCa rolled sheets (y=0.5, 1 and 2) at 170 °C. The age-hardening curve obtained from the Mg–1.5Ag–0.1Ca rolled sheet was included for the purpose of comparison. As can be seen from Fig. 3b, increasing the Ca content leads to a higher hardness value in the T4-treated condition. The 0.5Ca, 1Ca and 2Ca containing alloy sheets show initial hardness values of 50.5 HV, 52.6 HV and 53.4 HV, respectively. After peak aging, their hardness values increase to 57 HV, 59 HV and 61.8 HV, respectively. A notable feature of dilute Mg–1.5Ag–yCa rolled sheets is that these alloys show much faster age-hardening kinetics compared to concentrated Mg–xAg–0.1Ca alloys, as summarized in Table 1.

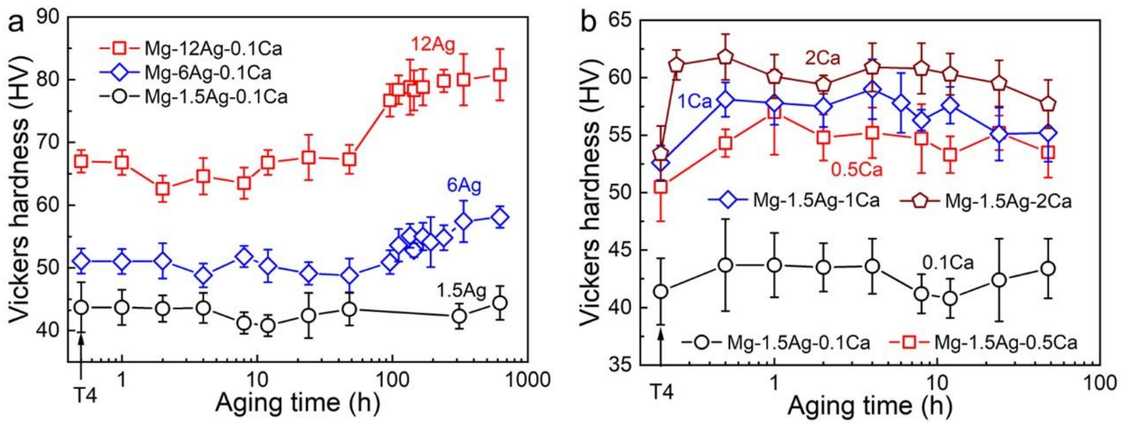

Fig. 3 (a) Age-hardening response of Mg–xAg–0.1Ca (x = 1.5, 6 and 12) and (b) Mg–1.5Ag–yCa (y = 0.1, 0.5, 1 and 2) rolled sheets at 170 °C.

Fig. 4a shows the age-hardening response of Mg–8Li(–xAl) (x = 1, 5) rolled sheets during isothermal aging at 50 °C. The binary Mg–8Li alloy sheet does not show any age-hardening. The addition of 1 wt.% of Al leads to an increase in the T4-treated condition (350 °C for 1 h) from 47.6 HV to 64.2 HV, and results in a minor increase in the hardness (3.7 HV) after only 1 h aging, namely peak aging. Further increase in the Al content to 5 wt.% significantly increases the initial hardness to 90.2 HV, and the resultant alloy shows a peak hardness of 98.5 HV after 2 h aging. Fig. 4b shows age-hardening response of a Mg–4.4In–6Gd extruded plate at 170 °C. The rollability of this alloy is rather poor, and thus it was difficult to produce the material in a sheet form. In this project, the age-hardening of this alloy was evaluated after hot-extrusion followed by high temperature solution treatment at 500 °C for 2 h. The initial hardness of the Mg–4.4In–6Gd alloy is 46.9 HV, and the peak hardness is 51.9 HV after 2 h aging, as summarized in Table 1.

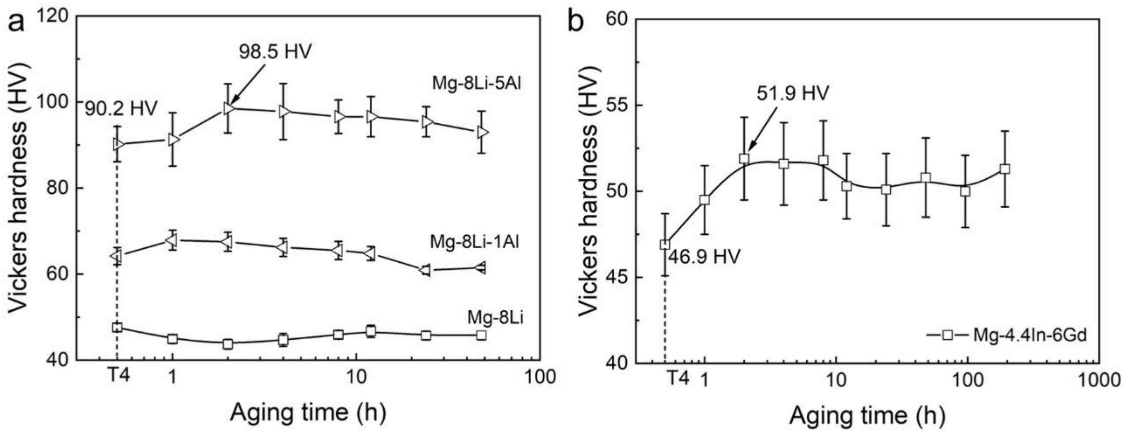

Fig. 4 (a) Age-hardening response of Mg–8Li(–xAl) (x = 1, 5) rolled sheets at 50 °C, and (b) Mg–4.4In–6Gd extruded plate at 170 °C.

Table 1. Initial hardness (T4), peak-hardness, time to reach peak hardness and hardness increment of developed alloys.

Alloy	Initial hardness (HV)	Peak hardness (HV)	Time to reach peak hardness (h)	Hardness increment (HV)
Mg–1.5Ag–0.1Ca	41.4	43.7	0.5	2.3
Mg–6Ag–0.1Ca	51.1	57.4	336	6.3
Mg–12Ag–0.1Ca	67.0	80.0	336	13.0
Mg–1.5Ag–0.5Ca	50.5	57	1	6.5
Mg–1.5Ag–1Ca	52.6	59	4	6.4
Mg–1.5Ag–2Ca	53.4	61.8	0.5	8.4
Mg–8Li–1Al	64.2	67.9	1	3.7
Mg–8Li–5Al	90.2	98.5	2	8.3
Mg–4.4In–6Gd	46.9	51.9	2	5.0

To clarify the reasons for the increase in hardness after aging, the microstructure of the T6-treated Mg–12Ag–0.1Ca sample was observed by TEM. Figs. 5a and b show the bright field (BF) TEM images taken with the incident beam along the $[0001]_\alpha$ and $[10\bar{1}0]_\alpha$ zone axes, respectively. The dispersion of precipitates is homogeneous, and the morphologies of the precipitates seem to consist of rod and polygonal shapes. The rod-type precipitates with a length of 0.5 – 1.5 µm are on the $\{11\bar{2}0\}_\alpha$ plane and their growing direction is parallel to the $<10\bar{1}0>_\alpha$ or $[0001]_\alpha$ directions. It is to be noted that some rod type precipitates lay on the pyramidal plane, as indicated by triangles in Fig. 5b. Fig. 5c shows the high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image with the zone axis of $[0001]_\alpha$, and Fig. 5d shows the high resolution (HR) HAADF-STEM image that is enlarged from the rectangular region in Fig. 5c. Figs. 5e and f are the fast Fourier transform (FFT) patterns generated from the left-hand region and right-hand region of Fig. 5d, respectively. Analysis of these patterns reveals that left-hand region is the α-Mg

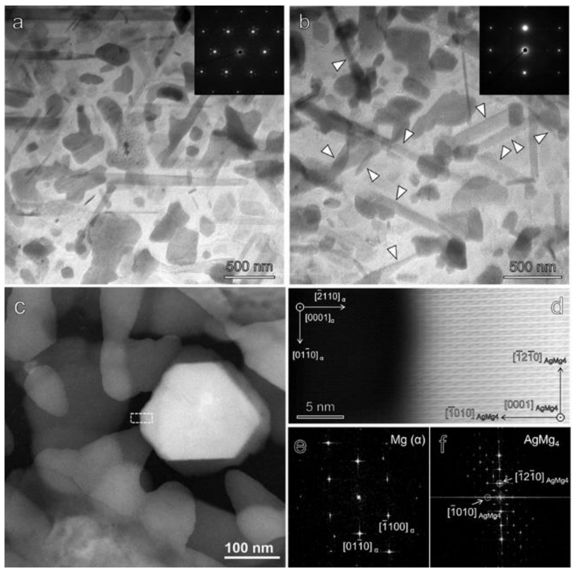

Fig. 5. (a) BF-TEM images showing the microstructure of T6-treated Mg–12Ag–0.1Ca alloy sheet along (a) $[0001]_\alpha$ zone axis and (b) $[10\bar{1}0]_\alpha$ zone axis. (c) HAADF-STEM image recorded along the $[0001]_\alpha$ direction. (d) Enlargement of the marked region in (c). FFT patterns generated from (e) α-Mg matrix and (f) $AgMg_4$ phase showing their orientation relationship.

matrix and the right-hand region is the $AgMg_4$ phase. By further analyzing the FFT patterns, the OR between the α-Mg matrix and $AgMg_4$ is confirmed to be $(0001)_{\alpha} \parallel (0001)_{AgMg4}$, $[\bar{2}110]_{\alpha} \parallel [10\bar{1}0]_{AgMg4}$.

The microstructures of T6-treated Mg–1.5Ag–1Ca and Mg–8Li–5Al samples were also observed. The former was characterized to contain nano-scale particles that are enriched with Ca element, while the latter one was confirmed to contain nano-scale AlLi particles. These nano-scale particles are believed to be responsible for the quick age-hardening response of dilute Mg–Ag–Ca alloys and Mg–Li–Al alloys.

In summary, this project successfully developed new types of precipitation-hardenable Mg wrought alloys with quick age-hardening response. In addition, this project demonstrated that the mixing enthalpy value between the solute elements and the atomic radius of solute atoms are important factors in designing Mg alloys with fast aging kinetics. However, the hardness increment is rather low. Further work is required to enhance the hardness increment by the short-time artificial aging in order to compete with 6000 series Al alloys.

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２．論文標題 Improvement of deep drawing formability of Mg-6Al-1Zn magnesium alloy sheets with high strength utilizing aging precipitation	５．発行年 2022年
３．雑誌名 Scripta Materialia	６．最初と最後の頁 114709～114709
掲載論文のDOI（デジタルオブジェクト識別子） 10.1016/j.scriptamat.2022.114709	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 －

１．著者名 Matsuoka Yusuke、Bian Mingzhe、Huang Xinsheng、Tsukada Yuhki、Koyama Toshiyuki、Chino Yasumasa	４．巻 906
２．論文標題 Simulation-aided analysis on mechanical properties of dilute Mg-Zn-Ca alloy sheets	５．発行年 2022年
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掲載論文のDOI（デジタルオブジェクト識別子） 10.1016/j.actamat.2021.117328	査読の有無 有
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掲載論文のDOI（デジタルオブジェクト識別子） 10.1016/j.msea.2021.141481	査読の有無 有
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1．著者名 Bian Mingzhe	4．巻 50-9
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3．雑誌名 マグネシウム（日本マグネシウム研究会）	6．最初と最後の頁 3-5
掲載論文のDOI（デジタルオブジェクト識別子） なし	査読の有無 無
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掲載論文のDOI（デジタルオブジェクト識別子） 10.3390/met10121632	査読の有無 有
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3．雑誌名 JOM	6．最初と最後の頁 1471-1483
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２．発表標題
溶質偏析による粒界析出の誘起と析出強化型マグネシウム合金の延性への影響

３．学会等名
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４．発表年
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〔図書〕　計0件

〔産業財産権〕

〔その他〕

－

６．研究組織

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７．科研費を使用して開催した国際研究集会

〔国際研究集会〕　計0件

８．本研究に関連して実施した国際共同研究の実施状況

共同研究相手国	相手方研究機関