Enhancement of Stretch Formability at Room Temperature by Addition of Ca in Mg-Zn Alloy

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The stretch formability of a rolled Mg-1.5Zn-0.1Ca alloy sheet was investigated at room temperature. The Mg alloy showed a large Erichsen value of 8.2. This is due to a reduction in intensity of basal plane texture and a spreading of the basal poles towards the transverse direction. It is suggested that solid solution of Ca atoms into Mg plays a critical role in the unique texture formation. Activation of non-basal slips by dilute Ca addition was hypothesized to be related to the unique texture formation. [doi:10.2320/matertrans.M2009385]

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Magnesium alloys are promising structural light materials because of their high specific strength, high specific stiffness and so on. The use of Mg alloys is expanding, particularly in automobile industry and consumer electronics industry. For their greater applicability, high formability Mg alloy sheets should be developed. However, (0002) basal planes are aligned parallel to the rolling direction (RD) and the intense basal plane texture is formed during rolling, results in poor formability at room temperature in rolled Mg alloy sheets.

Recently, Mg alloy sheets showing high stretch formability at room temperature have been developed through two means. One is improved rolling technologies such as differential speed rolling,^{1–3)} cross rolling⁴⁾ and high temperature rolling.^{2,3,5,6)} The intensity of basal plane texture is reduced by the improved rolling methods, and therefore, the stretch formability of the rolled Mg sheets is enhanced. Huang *et al.*²⁾ showed that a large Erichsen value of 9.5 is obtained in AZ31 Mg alloy produced by differential speed rolling at high temperature of 823 K. Addition of special elements such as Ce, Y, Gd and La is another route for enhancement of stretch formability at room temperature in Mg alloys.^{7–9)} For example, it has been reported that a rolled Mg-1.5 mass%Zn-0.2 mass%Ce alloy sheet shows a large Erichsen value of 9.0 at room temperature.⁷⁾ Addition of the special elements gives rise not only to a reduction in intensity of basal plane texture, but also to a spreading of the basal poles towards the RD or the transverse direction (TD).^{8–14)} Such unique texture by the addition of special elements is obtained during extruding as well.^{15–18)} However, these additional elements are rare and high cost materials. This is a big problem for commercial applications.

The present paper describes enhancement of stretch formability at room temperature by very low Ca addition of 0.066 mass% to Mg-1.52 mass%Zn alloy. The rolled Mg-Zn-Ca alloy exhibited a large Erichsen value of 8.2 at room temperature, while a rolled Mg-Zn alloy showed a low Erichsen value of 3.4 at room temperature. This finding of the enhanced stretch formability by the Ca addition is very

interesting in terms of both commercial and scientific aspects.

An extruded Mg-1.52 mass%Zn-0.066 mass%Ca alloy (Mg-1.5Zn-0.1Ca alloy) with 50 mm in length, 60 mm in width and 5 mm in thickness was prepared as an as-received specimen. The specimen was heated at 663 K or 1.2×10^3 s in a furnace, and a unidirectional rolling was conducted at a rolling reduction of 20%, where the temperature of roll surface was held at 353 K. The heating and rolling treatments were repeated, and the sheet was rolled to a thickness of 1 mm. The rolling direction was perpendicular to the extrusion direction. Finally, the rolled specimen was annealed at 623 K for 5.4×10^3 s. As a reference, the rolled Mg-1.50 mass%Zn alloy (Mg-1.5Zn alloy) was processed by the same manner with the rolled Mg-Zn-Ca alloy. The chemical compositions of Mg-Zn and Mg-Zn-Ca alloys are listed in Table 1.

Figure 1 shows microstructures of the as-extruded Mg-Zn and Mg-Zn-Ca alloys of the ED–ND plane, where the ED and ND are the extrusion and normal directions, respectively. The as-extruded specimens exhibited a duplex microstructure composed of recrystallized fine grains and un-recrystallized coarse grains. It is noted that the recrystallized grains of the Mg-Zn-Ca alloy exhibited finer grain size compared with those of the Mg-Zn alloy. The (0002) pole figures of the extrusions are shown in Fig. 2. The ring fiber texture with the (0002) basal planes parallel to the extrusion direction was observed in both the alloys. The Mg-Zn-Ca alloy showed weaker texture intensity compared with the Mg-Zn alloy.

Microstructures of the rolled and subsequently annealed Mg-Zn and Mg-Zn-Ca alloys were shown in Fig. 3. The grain

Table 1 Chemical compositions (mass%) of the Mg-1.5Zn and Mg-1.5Zn-0.1Ca alloys.

Specimen	Zn	Ca	Cu	Ni	Fe
Mg-1.5Zn	1.50	0.0003	0.0038	<0.0005	0.0050
Mg-1.5Zn-0.1Ca	1.52	0.0660	0.0032	<0.0005	0.0047

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Fig. 1 Optical micrographs of the as-extruded Mg alloys, where the ED-ND plane is observed: (a) Mg-1.5Zn alloy and (b) Mg-1.5Zn-0.1Ca alloy.

Fig. 2 (0002) pole figures of the as-extruded Mg-1.5Zn alloy (a) and Mg-1.5Zn-0.1Ca alloy (b).

Fig. 3 Optical micrographs of the Mg-1.5Zn alloy (a) and Mg-1.5Zn-0.1Ca alloy rolled at 723 K and subsequently annealed at 623 K, where the RD-ND plane is observed.

size of the rolled and subsequently annealed Mg-Zn and Mg-Zn-Ca alloy was 63 μm and 32 μm , respectively, indicating that addition of Ca in Mg-Zn promoted grain refinement. Previous studies revealed that dilute addition of 0.1–1.0 mass%Ca to pure Mg¹⁹⁾ and Mg-Zn alloy²⁰⁾ was effective for grain refinement of the as-cast Mg alloys. It is accepted that grain refinement by dilute Ca addition is attained by restriction of grain growth and promotion of nucleation of primary Mg during solidification.^{19,20)} Figures 1 and 3 suggest that dilute Ca addition to Mg-Zn alloy contributes to not only grain refinement during solidification but also grain refinement due to recrystallization during extrusion, rolling and annealing.

The (0002) pole figures of the rolled Mg alloys prior annealing at 623 K are shown in Fig. 4(a) and (b). The intensity of basal plane texture was reduced by the Ca addition in the same manner as the as-extruded Mg-Zn-Ca alloy. Besides, the basal poles were split toward the RD in the Mg-Zn-Ca alloy, on the other hand, the basal pole was slightly tilted toward the RD in the Mg-Zn alloy. The (0002)

Fig. 4 (0002) pole figures of the rolled Mg-1.5Zn alloy (a) and rolled Mg-1.5Zn-0.1Ca alloy (b), rolled and subsequently annealed Mg-1.5Zn alloy (c) and rolled and subsequently annealed Mg-1.5Zn-0.1Ca alloy (d).

pole figures of the rolled and subsequently annealed Mg alloys are shown in Fig. 4(c) and (d). It is of interest to note that the basal poles were tilted toward the TD in the annealed Mg-Zn-Ca alloy, although they were tilted toward the RD prior annealing. This unique texture is the same as that in the rolled and annealed Mg-Zn-Ce alloy.¹⁴⁾ A change in tilt of basal poles from the RD to the TD by annealing points out the importance of static recrystallization during annealing. On the other hand, the basal planes tended to be aligned parallel to the RD more intensely by annealing in the Mg-Zn alloy. Deformation heterogeneities such as shear bands occurred during hot rolling not only in the Mg-Zn-Ca alloy, but also in the Mg-Zn alloy. This indicates that the unique texture formation in the Mg-Zn-Ca alloy is not due to occurrence of deformation heterogeneities such as shear bands.^{12,18)}

The normal stress-strain curves by tensile tests at room temperature are shown in Fig. 5, where tensile tests are carried out at the angle between the tensile direction and the rolling direction of 0, 45 and 90 degrees. The stress-strain relation at the angle of 0 degree for the Mg-Zn-Ca alloy was almost the same as that for the Mg-Zn alloy. On the other hand, at the angles of 45 and 90 degrees, the strength was lower, but the ductility was larger in the Mg-Zn-Ca alloy than in the Mg-Zn alloy. The grain size of the Mg-Zn-Ca alloy was smaller than that of the Mg-Zn alloy. Therefore, the lower strength for the Mg-Zn-Ca alloy is due to the texture softening.¹⁶⁾

The tensile properties at room temperature are summarized in Table 2. The strain-hardening exponent (the n -value) for the Mg-Zn-Ca alloy was larger than or nearly equal to that for the Mg-Zn alloy. Also, the Lankford value (the r -value) for the former was lower than that for the latter. The unique texture for the Mg-Zn-Ca alloy is responsible for the large n -value⁹⁾ and the low r -value.¹¹⁾

Fig. 5 Nominal stress-strain curves for the Mg-1.5Zn and Mg-1.5Zn-0.1Ca alloys at different angles between the tensile direction and the rolling direction: (a) 0 deg, (b) 45 deg and (c) 90 deg.

Table 2 Tensile properties at room temperature of the Mg-1.5Zn and Mg-1.5Zn-0.1Ca alloys rolled at 723 K and subsequently annealed at 623 K (UTS, ultimate tensile stress; TYS, tensile 0.2% yield stress; FE, elongation to failure; n , n -value; r , r -value; r_{ave} , average r -value).

Alloys	Angle	UTS (MPa)	TYS (MPa)	FE (%)	n	r	r_{ave}
Mg-1.5Zn	0	222	84	17	0.32	1.45	
	45	227	117	18	0.29	1.65	1.65
	90	229	131	15	0.25	1.86	
Mg-1.5Zn-0.1Ca	0	220	120	23	0.30	0.84	
	45	211	86	29	0.44	0.80	0.81
	90	209	73	30	0.50	0.79	

The results of the Erichsen tests at room temperature are shown in Fig. 6. The Mg-Zn-Ca showed a large Erichsen value of 8.2 at room temperature. This value is almost the same as those of commercial Al alloys.⁷⁾ It is noted that the high stretch formability is attained by very low Ca addition of 0.066 mass% or 0.024 at%, not by the addition of rare earth metals such as Ce.

It is known that the large strain-hardening exponent leads to a reduction in plastic instability, resulting in enhanced stretch formability. In some works,^{9,21)} the importance of large strain-hardening exponent was pointed out for the enhanced stretch formability of Mg alloys. In the present work as well, the large strain-hardening exponent was obtained in the Mg-Zn-Ca, as shown in Table 2. However, because straining in the thickness direction is essentially required under the biaxial tensile stress state, the stretch formability of Mg with strong plastic anisotropy is mainly dominated by the control of texture.²¹⁾ The grain size is also one of microstructural factors affecting the stretch formability because ductility is increased by decreasing grain size in Mg.²²⁾ However, it was recently reported that the stretch formability at room temperature is enhanced by coarsening of the grain size.²³⁾ Therefore, the enhanced stretch formability for the Mg-Zn-Ca alloy is not due to the larger n -value and

Fig. 6 Specimens after the Erichsen tests at room temperature, (a) Mg-1.5Zn alloy and (b) Mg-1.5Zn-0.1Ca alloy.

Fig. 7 Zinc and calcium images by EPMA for the Mg-1.5Zn-0.1Ca alloy, where the RD-ND plane is observed.

the smaller grain size, but to the unique texture, that is, a reduction in intensity of basal plane texture and a spreading of the basal poles towards the TD.

Recrystallization behavior strongly affects the texture formation. It was suggested that particle-stimulated nucleation (PSN) plays an important role for the unique texture formation in Mg alloys containing rare earth metals.^{15,16)} For PSN, large particles of diameter greater than about 1 μm are required.²⁴⁾ However, such large particles were not observed in the Mg-Zn-Ca alloy, as shown in Fig. 7. Therefore, it is unlikely that PSN is the major contribution to the formation of unique non-basal texture.^{17,18,25,26)}

Spreading of basal poles to the TD is typical of the texture of deformed Zr alloys,²⁷⁾ in which non-basal $\langle c \rangle$ and $\langle c + a \rangle$ slips occurs more readily than basal $\langle a \rangle$ slips. Therefore, it is hypothesized that activation of non-basal slips such as $\langle c + a \rangle$ slips are related to the formation of unique non-basal texture in the Mg-Zn-Ca alloy. The Peierls stress for non-basal slips is decreased with decreasing c/a lattice constant ratio. It was reported that the c/a ratio was decreased from 1.6244 (= c/a ratio of pure Mg²⁸⁾) to 1.6237–1.6213 by the Y addition in Mg-Zn-Y alloys.⁸⁾ On the other hand, no decrease in c/a ratio was obtained in the Mg-Ce alloy due to the small

Table 3 Lattice parameters of the rolled Mg-1.5Zn and Mg-1.5Zn-0.1Ca alloys.

Alloys	<i>a</i> (nm)	<i>c</i> (nm)	<i>c/a</i>
Mg-1.5Zn	3.2072	5.2073	1.6236
Mg-1.5Zn-0.1Ca	3.2080	5.2065	1.6230

addition of 0.035 at%.²⁸⁾ The lattice constants are listed in Table 3 for the Mg-Zn and the Mg-Zn-Ca alloys. A decrease in *c/a* ratio by the Ca addition is not as large as those by the Y addition, and therefore, the active non-basal slips cannot be explained only by a decrease in *c/a* ratio due to the Ca addition.

An increase in stacking fault energy by the Ca addition is another possibility for the active non-basal slips.²⁹⁾ However, the first principle calculation showed that the stacking fault energy is decreased by the Ca addition.³⁰⁾ Therefore, a change in stacking fault energy by the Ca addition is not responsible for the active non-basal slips. Further work is underway to understand the relationships between the Ca addition in Mg-Zn alloy and the activity of non-basal slips.

Stanford *et al.*¹⁸⁾ investigated effects of Al, Sn, Ca, La and Gd additions and they showed no reduction in intensity of basal plane texture and no formation of non-basal texture in the Ca-containing Mg alloy. In their work, many particles were precipitated in the Ca-containing Mg alloy. In the present work, however, the Mg-Zn-Ca alloy is a solid solution alloy containing few small precipitates, as shown in Fig. 7. Therefore, it is suggested that solid solution of Ca atoms into Mg plays a critical role in formation of the non-basal texture. Even a very low Ce addition of 0.035 at% activates the non-basal slip of Mg.²⁸⁾ In the present work, the Ca addition is 0.024 at%. Noted that such low additions drastically affect the deformation behavior of Mg.

In conclusion, the Mg-1.52 mass%Zn-0.066 mass%Ca alloy, rolled at 723 K and subsequently annealed at 623 K, showed a large Erichsen value of 8.2 at room temperature. This is comparable to those of commercial Al alloys. The Mg-Zn-Ca alloy showed the unique texture, that is, a reduction in intensity of basal plane texture and a spreading of the basal poles towards the TD. It is suggested that solid solution of Ca atoms into Mg plays a critical role in the unique texture formation. Activation of non-basal slips by dilute Ca addition is hypothesized to be related to the unique texture formation.

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