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INVESTIGATION OF MECHANICAL PROPERTIES AND DEFORMATION BEHAVIOR OF CaO ADDED Mg-6Zn-1.2Y SHEETS

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Abstract

Recently, CaO added Mg-Al alloy sheets exhibited improved strength and elongation due to the effects of dispersion hardening and grain-refining by intermetallic compounds such as Al_2Ca and $(Mg,Al)_2Ca$ and improved melt cleanliness. However, there is little study on these effects in Mg-Zn alloy system. In this study, as-cast ingots were prepared by melting Mg, Zn, Mg-25Y master alloy and Mg-3CaO master alloy in an electric resistance furnace under SF_6+CO_2 atmosphere. Sheet specimens were prepared by hot rolling process after indirect extrusion. The mechanical properties of CaO added Mg-6Zn-1.2Y specimens varied significantly with annealing process while the variation of mechanical properties of Mg-6Zn-1.2Y specimen was small. In addition, the texture of specimens with CaO (Ca in ICP analysis) was different from that of specimen without CaO. Therefore, we discussed the effect of microstructure and texture on mechanical properties and deformation behavior of CaO added Mg-6Zn-1.2Y sheet.

Introduction

There are some limitation to apply magnesium alloys to structural parts, although magnesium alloys have attractive properties such as low density, high specific strength (ratio of strength to density), excellent castability, good machinability and so on [1]. Therefore, many researches on the development of magnesium alloys with not only high strength, but also high ductility have been occurred to overcome the drawbacks of magnesium alloys.

One of these researches is on ECO-Mg alloy. The concept of ECO-Mg alloy was to simply introduce CaO particles as an ingredient into conventional magnesium alloys. The surface oxide layer of molten magnesium alloy changed from porous oxide film to dense and complex oxide films. Therefore, they have been possible (1) non-SF6 process, (2) Be elimination, (3) improved melt cleanliness, (4) ensured original process adjustability for casting, forming, joining as well as surface treatment, (5) improved mechanical property by grain refinement and internal soundness, (6) ensured safety during manufacturing and application by raising oxidation and ignition resistances of machined chips and products, and (7) improved recyclability [2]. In the case of extruded alloys, the CaO added magnesium alloys had good surface quality and the surface roughness decreased with CaO contents [3, 4]. Moreover, the as-rolled CaO added AZ31 alloy exhibited higher strength than as-rolled conventional AZ31 alloy due to the effects of dispersion hardening and grain-refining by intermetallic compounds such as Al_2Ca and $(Mg, Al)_2Ca$ and improved melt cleanliness [5]. However, there is little study on these effects in Mg-Zn alloy system.

Quasicrystals are isotropic and posse specially ordered lattice structure called the quasiperiodic lattice structure [6]. When an alloy possesses quasicrystals as a second phase, they are stable against coarsening at high temperatures due to the low interfacial energy of quasicrystals [7], providing the improved bonding properties in the I-phase/matrix interface. Therefore, to increase both strength and ductility, many researches on magnesium alloys reinforced with quasicrystalline icosahedral phase (I-phase) particles have been performed because magnesium alloys reinforced with I-phase particles, especially Mg-Zn-Y alloys, have been reported to exhibit a good combination of elongation and strength [8-10].

This study has been carried out to investigate microstructures and mechanical properties of CaO added Mg-6Zn-1.2Y sheets with annealing process and understand the effect of the addition of CaO in Mg-Zn-Y alloys.

Experimental procedure

As-cast ingots were prepared by melting commercial purity Mg, Zn, Mg-25Y master alloy and Mg-3CaO master alloy in an electric resistance furnace under SF_6+CO_2 atmosphere, followed by pouring the melt into the steel mold of cylindrical cavity with the dimension of 50 mm in diameter and 200 mm in height. Chemical compositions of as-cast alloys were analyzed by ICP-mass spectrometer and the results were listed in Table 1.

The ingots preheated at 300~320 °C for 60 min. were extruded with a reduction ratio of 20:1 and the cross-sectional area of the extruded strips was 25*4 mm^2. The extruded strips preheated at 350 °C for 30 min. were rolled with a reduction ratio of 10 % to 28 % per pass to final thickness of 1.3 mm. After hot rolling, sheets were annealed at 250~350 °C for 15~60 min. Uniaxial tensile tests were carried out on dog-bone specimens (specimen gauge length of 25 mm in length, 6 mm in width, and 1.3 mm in thickness) machined from annealed sheets at room temperature with initial strain rate of 10^{-3} /s.

Table 1. ICP analysis results of as-cast ingots

Alloy No.	Description		Chemical composition (wt.%)			
			Mg	Zn	Y	Ca
1	ZW61	Nominal	92.8	6	1.2	
		Analyzed	Bal.	5.93	1.16	
2	ZWO6103	Nominal	92.5	6	1.2	0.3
		Analyzed	Bal.	6.09	1.11	0.33
3	ZWO6107	Nominal	92.1	6	1.2	0.7
		Analyzed	Bal.	6.20	1.13	0.72

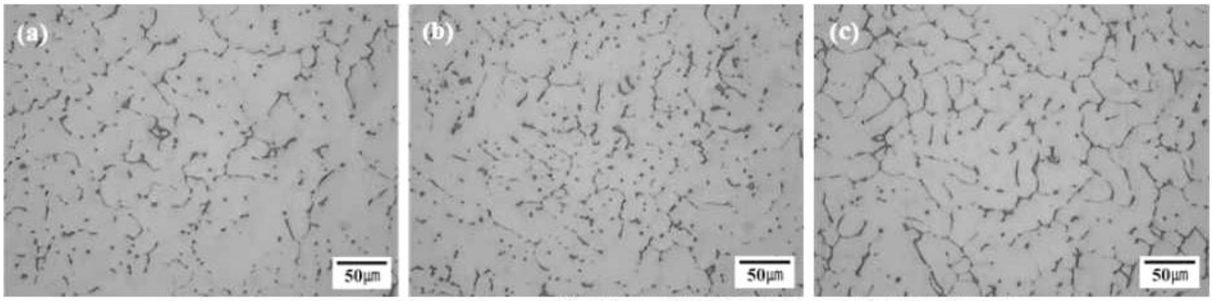

Fig. 1. Optical microstructures of as-cast (a) ZW61, (b) ZWO6103, and (c) ZWO6107 alloys

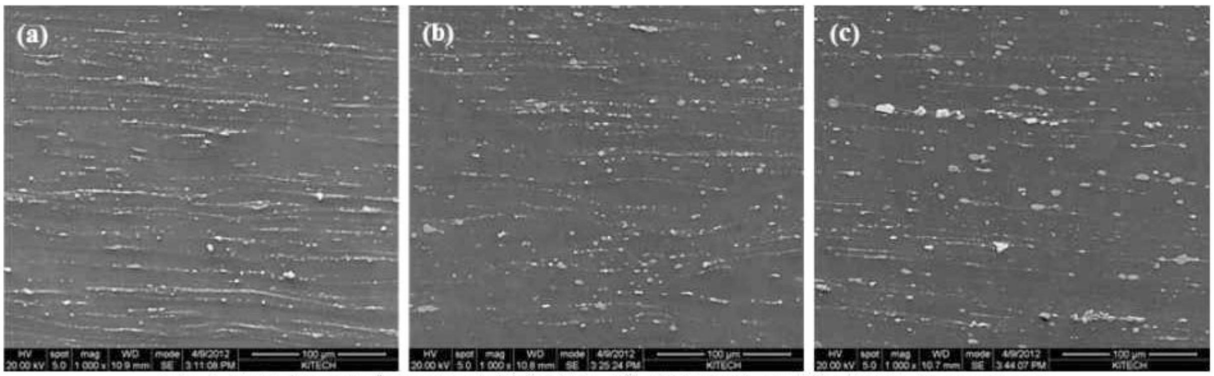

Fig. 2. SEM images of as-extruded (a) ZW61, (b) ZWO6103, and (c) ZWO6107 specimens

For microstructure observation, specimens for an optical microscope were etched with acetic picral etchant or 2 % nital etchant and for an EBSD were ion-milled.

Table 2. Electronegativity of elements [12]

Element	Mg	Zn	Y	Ca
Electronegativity	1.31	1.65	1.22	1.00

Results and Discussion

Table 1 showed the results of chemical composition analysis by ICP-mass spectrometer. Although Ca was detected by ICP in alloys, we used "O" as code letter to be distinguished from alloys with metallic Calcium whose code letter is "X".

The microstructures of as-cast alloys were shown in Fig. 1. All alloys were consisted of α-Mg and the secondary solidified phases. According to the EDS analysis results, in CaO added alloys, e.g. ZWO6103 and ZWO6107 alloys, there are two kinds of secondary phases. One consisted of Mg, Zn, and Y, which might be I-phase and the other consisted of Mg, Zn, and Ca, which might be τ_2 ($Ca_2Mg_5Zn_{13}$) phase. Furthermore, with CaO content, the volume fraction of τ_2 phase increased and α-Mg and τ_2 phases composed eutectic pockets. Generally, the greater difference between electronegativity of the elements the more stable compound formation between them [11]. The electronegativity of Mg, Zn, Y, and Ca were listed in Table 2. In Table 2, the electronegativity of Ca is the lowest among elements. Therefore, with increasing CaO or Ca content, the τ_2 phase might be formed easily.

Fig. 2 showed the SEM images of as-extruded specimens. The broken secondary phase particles formed during extrusion from grain boundary networks of as-cast alloys and were distributed as streamlines in parallel to extrusion direction. From the results of EDS mapping, coarser τ_2 phase existed in ZWO6107 strip than ZWO6103 strip. That means with increasing CaO content, the volume fraction of τ_2 phase increased and τ_2 phase is harder than I-phase.

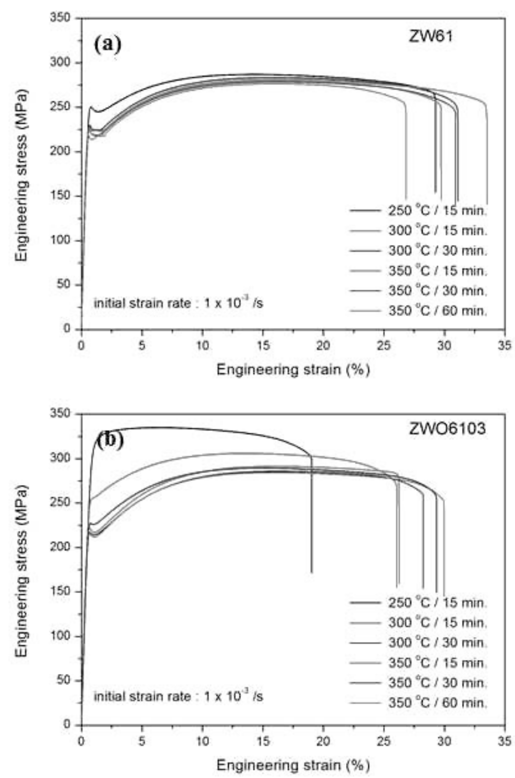

Fig. 3. Engineering stress-strain curves of (a) ZW61 and (b) ZWO6103 sheets

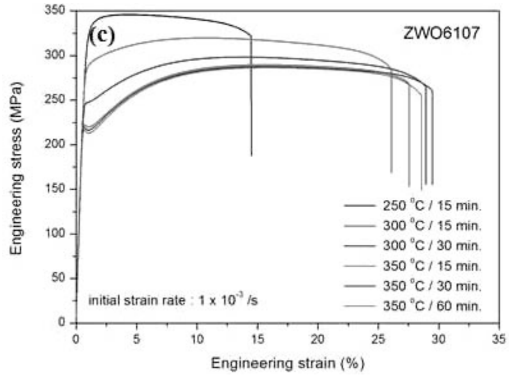

Fig. 3. (*continued*) Engineering stress-strain curves of (c) ZWO6107 sheets

The engineering stress-strain curves of annealed sheets were shown in Fig. 3. In the case of annealed ZW61 sheets, the variation strengths were small in all annealing condition. However, the strengths of annealed ZWO6103 and ZWO6107 sheets varied significantly with annealing times and temperatures. This phenomenon could be explained that the thermal stability of CaO added Mg-6Zn-1.2Y sheet was higher than that of ZW61 alloy sheet. Also, some CaO added specimens which were annealed over 300 °C exhibited the yield phenomenon while the yield phenomenon of ZW61 specimens could be observed in all annealing conditions. J. Koike et al. had reported that the yield phenomenon occurred by the activation of non-basal slip system due to the compatibility stresses in fine-grained microstructures [13]. That is, yield phenomenon could be occurred in fine grains with no or little dislocation. Though CaO added specimens annealed at 250 °C had fine-grained microstructures, there might be many dislocations in grains. Thus deformation mechanism of CaO added specimens annealed at 250 °C was different from that of specimens annealed over 300 °C.

In addition, when specimens were fully annealed (in this case, annealing temperature was 350 °C), ZWO6103 and ZWO6107 sheets exhibited hither ultimate tensile strengths than ZW61 did, although tensile yield strengths of CaO added alloys specimens were slightly lower than those of specimens without CaO. Overall, annealed ZW61 specimens had larger elongation than CaO added specimens due to the dispersion of fine particles.

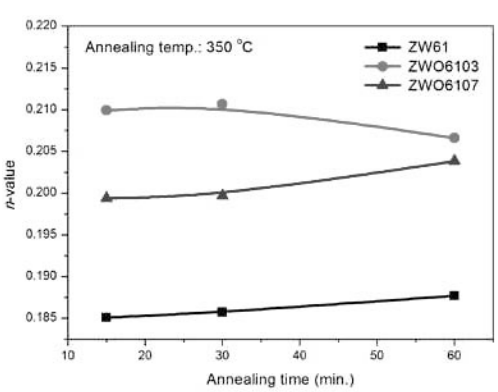

Fig. 4. Variations of strain-hardening exponents (*n*-value) with annealing time

Fig. 4 showed the variations of strain-hardening exponents (*n*-value) with annealing time at 350 °C of the tested specimens, which were measured in the engineering strain range from 5 % to 10 %. As shown in Fig. 4, the *n*-values of ZWO6103 and ZWO6107 sheets were higher than those of ZW61 sheets. When comparing the *n*-values of ZWO6103 and ZWO6107 specimens, ZWO6103 specimens exhibited higher *n*-values than ZWO6107 did. Generally, the strong work-hardening in materials containing non-deforming particles could be deduced from the cutting and bowing process of dislocations. The effective obstacle spacing for a second dislocation to be extruded between the particles was reduced due to the dislocation loops formed by the passage of the first dislocation. Thus, the stress required to generate a second or further loop was increased [14]. In this study, the addition of CaO in Mg-6Zn-1.2Y alloy might reduce the effective obstacle spacing, but when adding 0.7 wt.% CaO, it could be thought that the effective obstacle spacing might increase due to the large τ_2 phase particles.

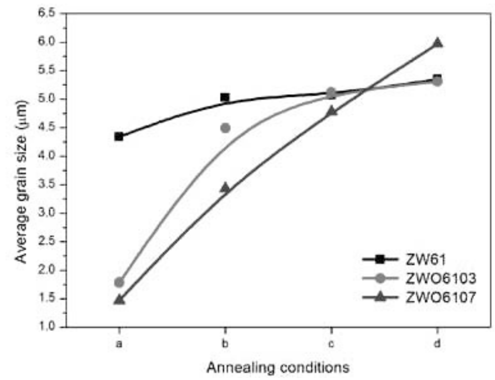

Fig. 5. Comparison of average grain size with different annealing process (a: 250 °C / 15 min., b: 300 °C / 15 min., c: 350 °C / 30 min., and d: 350 °C / 15 min.)

To find the relationship between grain size and yield strength, gain sizes of some tested alloys were measured by EBSD. Fig. 5 showed the average gain sizes of specimens with different annealing process. The variation of grain size of ZW61 specimens was small while the grain sizes of ZWO6103 and ZWO6107 specimens increased with annealing condition. These results corresponded with previous tensile test results.

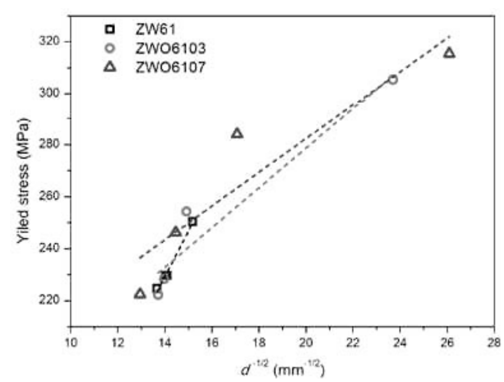

Fig. 6. Relation between yield stress and the inverse square root of the average grain size

Fig. 6 showed the relationship of yield strengths against the inverse square root of the average grain sizes in tested alloys.

Table 3 listed the intercept stress, σ_o and the slope of tested specimens. From data of Fig. 6 and Table 3, it could be noticed that with adding CaO, σ_o increased but k_y decreased. In Hall-Petch relationship, σ_o referred to the average yield strength of a single grain and was determined by all the operative strengthening mechanisms except grain boundary strengthening. And k_y is a complex parameter that determines the effectiveness of grain boundaries in raising yield strength [15]. Therefore, it could be thought that the addition of CaO in Mg-6Zn-1.2Y alloy made average yield strength of a single grain higher but the effectiveness of grain boundaries in raising yield strength lower.

Table 3. Hall-Petch parameters of tested specimens

Alloy	Intercept stress, σ_o (MPa)	Slope, k_y (MPa mm$^{1/2}$)
ZW61	-16.4±17.2	17.6±1.2
ZWO6103	125.7±25.3	7.7±1.5
ZWO6107	152.4±32.9	6.5±1.8

Fig. 7 showed the results of the texture analysis using EBSD obtained from tested specimens annealed at 300 °C for 30 min. Egg-shaped distribution of {0002} pole was observed in annealed ZW61 specimen, which indicated that the strong basal plane texture had been developed during rolling and annealing processes. However, in the case of CaO added specimens, {0002} pole tilted toward the transverse direction (Fig. 7 (b) and (c)). Moreover, the texture intensity decreased from 10.512 (Fig. 7 (a)) to 6.689 (Fig. 7 (c)) with increasing CaO content. This change of texture by adding CaO might contribute to the little reduction of elongation for annealed sheet specimens with high strength.

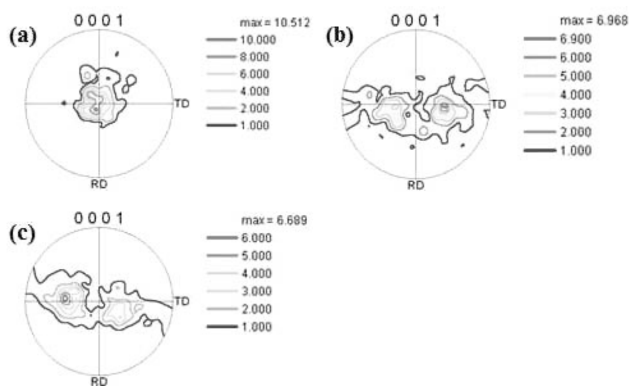

Fig. 7. {0002} Pole figure of tested specimens annealed at 300 °C for 30 min.; (a) ZW61, (b) ZWO6103, and (c) ZWO6107

Conclusion

In the present study, mechanical properties and deformation behavior of CaO added Mg-6Zn-1.2Y sheets were investigated. The conclusions are as follows:

(1) τ_2 ($Ca_2Mg_5Zn_{13}$) phase was formed by addition of CaO in Mg-6Zn-1.2Y alloy.

(2) As-cast structures of icosahedral and τ_2 phases were destroyed by extrusion process and the size of broken τ_2 phase particles was larger than that of icosahedral phase.

(3) In annealed conditions, CaO added Mg-6Zn-1.2Y sheets exhibited higher ultimate tensile strength than ZW61 sheet, but elongation decreased due to the coarser τ_2 phase particles by adding CaO.

(4) The addition of CaO in Mg-6Zn-1.2Y alloy made average yield strength of a single grain higher but the effectiveness of grain boundaries in raising yield strength lower.

(5) Also, the addition of CaO in Mg-6Zn-1.2Y alloy made texture different from ZW61 alloy. And texture change might contribute to the little reduction of elongation for annealed sheet specimens with high strength.

Acknowledgments

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