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Research Paper

Utilization of Microalloying with Rare Earth Elements and Hot Extrusion for Remarkable Grain Refinement and Enhancement of Mechanical Properties of as-Cast Magnesium Alloy

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ABSTRACT

The effects of micro-addition by rare earth (RE) elements (via cerium-based mischmetal) and hot deformation (via extrusion process) on the microstructure and mechanical properties of Mg-0.5Zn-0.5Zr alloy were studied. Optical microscopy, scanning electron microscopy (SEM), energy-dispersive spectroscopy (EDS), and tensile testing were used for characterization of alloys in the as-cast and wrought conditions. It was found that the addition of 0.5 wt% RE combined with the hot extrusion process could remarkably refine the grain size from 1320 µm for the as-cast Mg-0.5Zn-0.5Zr alloy to the recrystallized grain size of 1.3 µm for the extruded Mg-0.5Zn-0.5Zr-0.5RE alloy. Compared to the as-cast counterparts, the ultimate tensile strength (UTS) and total elongation to failure were significantly enhanced by the extrusion process. Quantitatively, the UTS of ~ 300 MPa with the total elongation of ~ 18% was obtained for the extruded Mg-0.5Zn-0.5Zr-0.5RE alloy, which reveals the favorable effects of the ultra grain refinement on the enhancement of the mechanical properties of magnesium alloys.

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1. Introduction

Since magnesium alloys have HCP crystal structure and the number of slip systems in this structure is very few, the formability of Mg alloys is poor at ambient temperature [1,2]. To enhance the mechanical properties; zinc has been frequently used as a major alloying element in magnesium alloys [3-5]. Not only this element improves the strength of Mg alloys, but it also increases their formability, where both grain refinement [6] and solid solution strengthening [7] have been noted. Another critical element is zirconium, which is a grain refiner for Mg alloys [8]. Accordingly, the ZK series of magnesium alloys have gained significant attention [9]. Among the Mg-Zn-Zr alloys, the composition of Mg-0.5Zn-0.5Zr with the incorporation of rare earth (RE) elements has gained considerable attention. For instance, a combination of Gd, Y, Nd, and Er has been extensively added to the Mg-0.5Zn-0.5Zr alloy and the formation and effects of long period stacking order (LPSO) structures have been discussed in detail [10-12]. The effect of Sm addition to the Mg-0.5Zn-0.5Zr alloy has also been investigated, and it has been reported that the resulting intermetallic particles could act as heterogeneous nucleation sites for dynamic recrystallization during hot extrusion via particle stimulated nucleation mechanism (PSN) mechanism for enhancement of mechanical properties and weakening the basal texture in the as-extruded alloys [10,11]. The Mg-2.5Nd-0.5Zn-0.5Zr alloy has shown that the coarse microstructure with a continuous network of intergranular eutectic Mg12Nd phase can be refined by the high strain rate rolling (HSRR) process [12]. Besides these works, the effect of RE in the form of mischmetal addition, due to its lower price [13], to the Mg-0.5Zn-0.5Zr alloy is important in the as-cast and wrought conditions, which needs a systematic investigation. The present work is dedicated to this subject.

2. Experimental procedure

As discussed in the introduction section, based on the previous research works, the Mg-0.5Zn-0.5Zr alloy has gained considerable recent attention. For Mg alloys, rare earth addition at microalloying levels has been shown to be favorable, while high amounts of RE degrade the mechanical properties of Mg alloys [14-17]. As a result, the RE content of 0.5 wt% was used in the present work. Accordingly, the Mg-0.5Zn-0.5Zr and Mg-0.5Zn-0.5Zr-0.5RE alloys (wt%) were considered in this work. Pure Mg, as well as Mg-50Zn and Mg-33Zr master alloys and cerium-based mischmetal (48.7Ce-26.4La-19.6Nd-5.3Pr) were used as the charge materials in an induction furnace with a clay graphite crucible for melting under the protection of a gas mixture containing 95 vol% CO_2+ 5 vol% SF_6 and pouring into a cylindrical metallic mold shown in Figure 1a. While the chemical compositions of the alloys are nominal, based on the careful examination of the master alloys using the inductively coupled plasma (ICP) technique, the reported chemical compositions are reliable. The homogenized ingots (400 °C-12 h) were preheated at the temperature of 250 °C for 1 h, which was followed by extrusion at 250 °C with a ratio of 12:1 as schematically depicted in Figure 1b.

Microstructure observations were carried out using optical microscopy and scanning electron microscopy (SEM, TESCAN VEGA II XMU) equipped with an energy dispersive X-ray spectroscopy (EDS) detector for elemental analysis. Phase analysis was based on the X-ray Diffraction (XRD) using a Philips diffractometer with Cu-kα radiation. A solution containing 4.2g picric acid, 70 ml ethanol, 10 ml acetic acid, and 10 ml distilled water was used for chemical etching. The grain size was measured using the standard intercept method according to the ASTM E112-96. Room temperature tensile tests (using a SANTAM STM-20 universal testing machine) were performed using ASTM-E8 round tensile specimens (Figure 1c) at a crosshead speed of 1mm/min. The tests were repeated once, and it was revealed that the reproducibility of results is in the valid range. Hardness measurements were based on the Vickers hardness (using a Wilson Tukon 1202 hardness tester) with a load of 5 kg and a dwell time of 10 s.

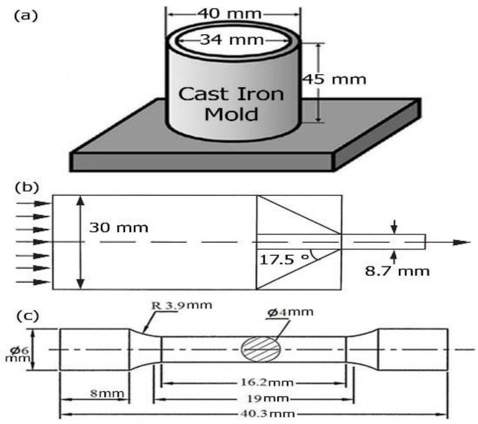
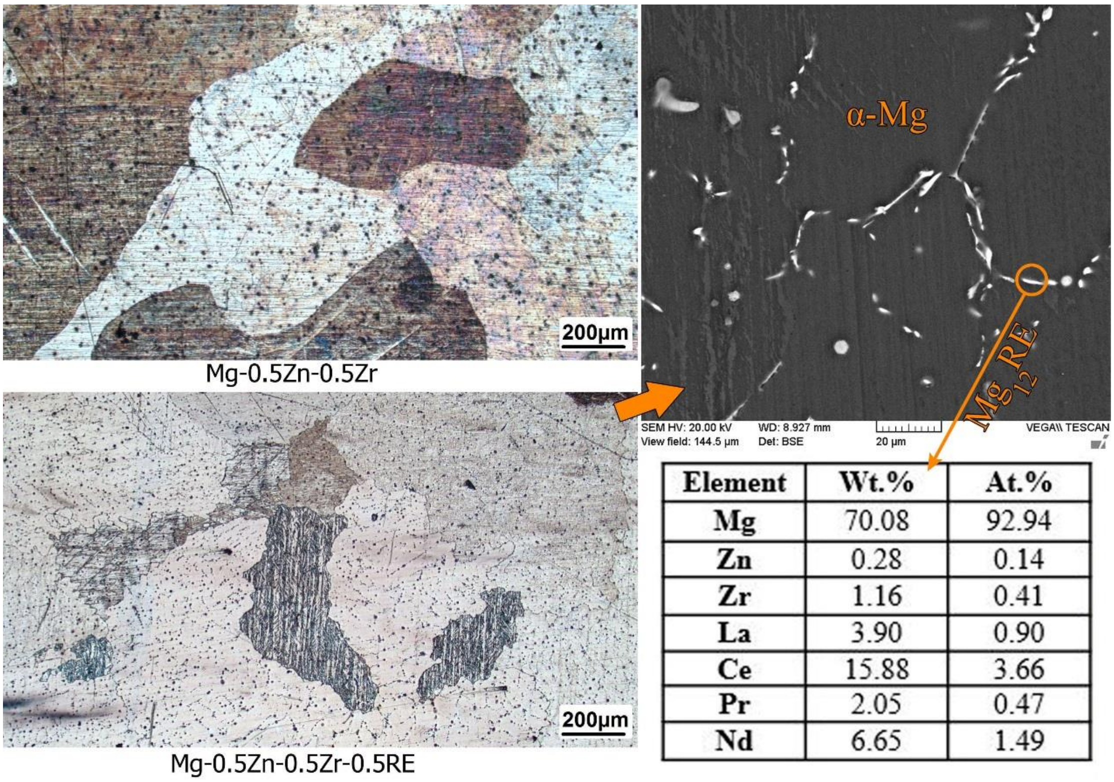


Fig. 1. Details of (a) metallic mold (b) extrusion die, and (c) tensile specimen.

3. Results and discussion

The optical micrographs (OM) of as-cast alloys at low magnification are shown in Figure 2. The Mg-0.5Zn-0.5Zr alloy contains huge α-Mg grains with an average size of 1320 µm, and the introduction of 0.5 wt% RE resulted in a slight grain refinement effect in the as-cast condition (1030 µm). It should be noted that a very coarse grain size of ~ 2500 µm has been reported for pure Mg [18], which reveals that the effect of small Zn, Zr, and RE additions are significant. The refinement of grain size by RE addition can be related to the enrichment of RE solutes near the solid/liquid interface during solidification, which enhances the undercooling effect via constitutional undercooling. The backscattered electron (BSE) SEM micrograph of the Mg-0.5Zn-0.5Zr-0.5RE alloy is also shown in Figure 2, where a bright intergranular constituent can be observed. The high brightness implies the presence of elements with high atomic numbers. The EDS analysis of the grain boundary region in Figure 2 reveals the presence of RE (Ce, La, Pr, and Nd) and Zr. This explains the observed brightness due to the high atomic number of these elements. Based on EDS, the atomic ratio of RE/Mg was obtained as ~ 0.07, which is in good agreement with the atomic ratio of 1/12=0.083 for the $Mg_{12}RE$ compound [12]. Phase analysis was also performed by XRD, as shown in **Figure 3**, where the XRD patterns of the Mg-0.5Zn-0.5Zr and Mg-0.5Zn-0.5Zr-0.5RE reveal the presence of α-Mg peaks only. However, the XRD pattern of the Mg-0.5Zn-0.5Zr-1RE alloy with higher RE content (processed similarly) is also shown in Figure 3, where the XRD patterns of the Mg-0.5Zn-0.5Zr and Mg-0.5Zn-0.5Zr-0.5RE reveal the presence of α-Mg peaks only. However, the XRD pattern of the Mg-0.5Zn-0.5Zr-1RE alloy with higher RE content (processed similarly) is also shown in **Figure 3**, where the peaks of $Mg_{12}RE$ compound appear. Therefore, based on the SEM/EDS results, the absence of the diffraction peaks of $Mg_{12}RE$ compound in Mg-0.5Zn-0.5Zr-0.5RE is related to the low amount of this phase.



Element	Wt.%	At.%
Mg	70.08	92.94
Zn	0.28	0.14
Zr	1.16	0.41
La	3.90	0.90
Ce	15.88	3.66
Pr	2.05	0.47
Nd	6.65	1.49

Fig. 2. Optical micrographs of as-cast alloys and the SEM image of the Mg-0.5Zn-0.5Zr-0.5RE alloy and the corresponding EDS point analysis from the intergranular phase..

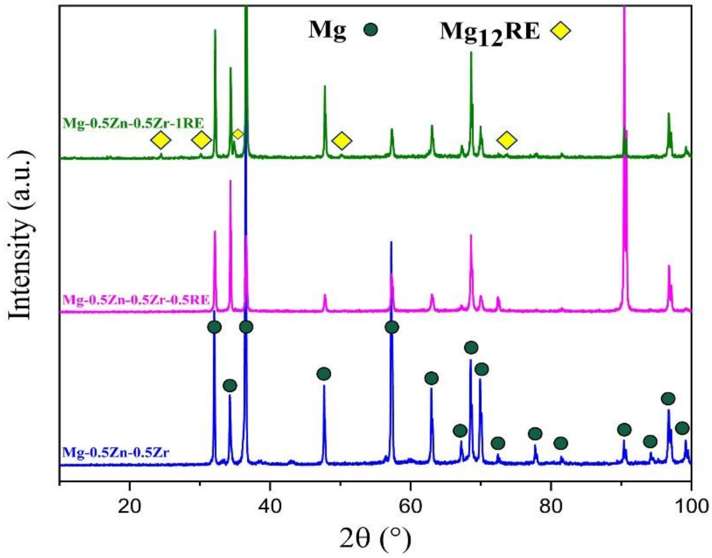
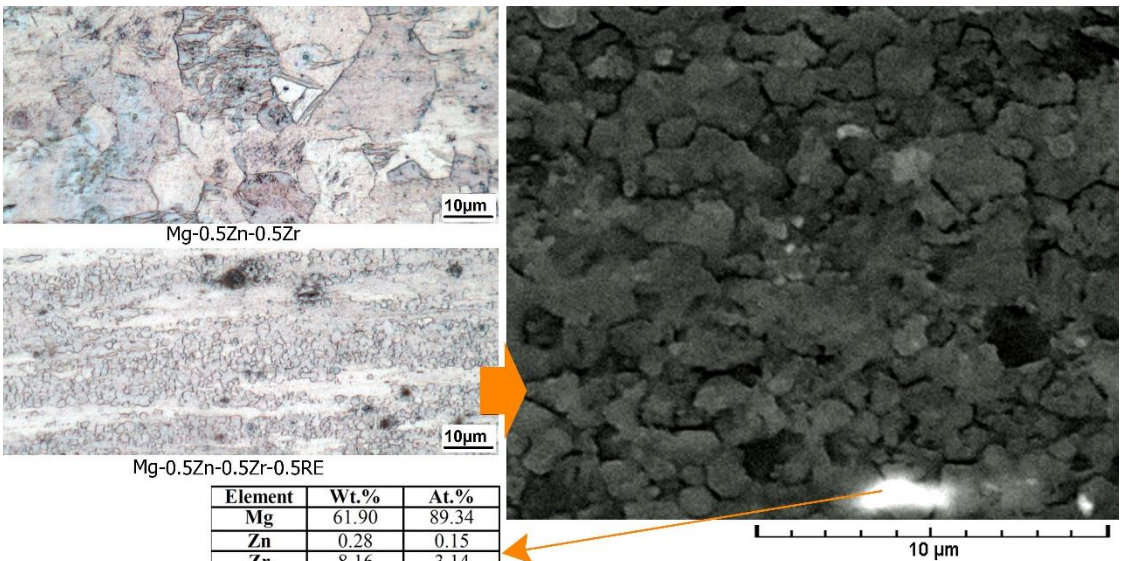


Fig. 3. XRD patterns of as-cast alloys.

The microstructures of the extruded alloys are shown in **Figure 4**. Compared to the as-cast alloys, a remarkable grain refinement can be observed due to the recrystallization processes induced by the hot deformation process [1,5,19-21]. The microstructure of the extruded Mg-0.5Zn-0.5Zr-0.5RE alloy in Figure 4 reveals the necklace type microstructure, which is characteristic of dynamic recrystallization (DRX) [22]. Therefore, the DRX mechanism is responsible for the remarkable grain refinement observed after the extrusion process. As shown in Figure 4, by applying the extrusion process, the grain size has decreased from 1320 µm for the as-cast Mg-0.5Zn-0.5Zr alloy to the recrystallized grain size of 7.5 µm for the extruded alloy, and from 1030 to 1.3 µm for the Mg-0.5Zn-0.5Zr-0.5RE alloy. Although there are some deformed and unrecrystallized grains, the obtained ultrafine grained (UFG) structure of the Mg-0.5Zn-0.5Zr-0.5RE alloy can be seen in the SEM image of **Figure 4**, where second phase particles have been fragmented and dispersed along the extrusion direction. The EDS point analysis of the fragmented particles in Figure 4 reveals the presence of the Mg12RE phase. Therefore, the extruded Mg-0.5Zn-0.5Zr-0.5RE alloy with the UFG microstructure is expected to show huge enhancements in mechanical properties.



Element	Wt.%	At.%
Mg	61.90	89.34
Zn	0.28	0.15
Zr	8.16	3.14
La	3.69	0.39
Ce	15.87	3.97
Pr	2.32	0.58
Nd	7.79	1.89

Fig. 4. Optical micrographs of extruded alloys and SEM image of the Mg-0.5Zn-0.5Zr-0.5RE alloy and EDS point analysis of the shown phase

Tensile engineering stress-strain curves of the as-cast alloys are illustrated in Figure 5, where the mechanical properties are slightly enhanced by the addition of 0.5 wt% RE due to the slight grain refinement. The tensile stress-strain curves of the extruded alloys are also shown in Figure 5, where it can be observed that both ultimate tensile strength (UTS) and total elongation (%El) were significantly enhanced by the extrusion process. It is comprehensible that these huge improvements are related to grain refinement through the recrystallization mechanism and also the dispersion of fine intermetallics during the extrusion process. On the other hand, the mechanical properties of the extruded Mg-0.5Zn-0.5Zr-0.5RE alloy with UFG microstructure is much better than those of Mg-0.5Zn-0.5Zr alloy with coarser grain size. Quantitatively, the UTS of ~ 300 MPa with the total elongation of ~ 18% was obtained for the Mg-0.5Zn-0.5Zr-0.5RE alloy, which reveals the favorable effects of the ultra grain refinement in the enhancement of the mechanical properties of magnesium alloys. It is well-known that grain refinement usually enhances both strength and toughness of engineering alloys but normally decreases their ductility except in some special circumstances such as superplasticity [23,24]. However, grain refinement might enhance both strength and ductility of Mg alloys, which has been shown in previous research works [25]. The enhancement of strength can be rationalized by Hall-Petch plots, while the enhanced ductility might be explained by the activation of slip systems in the HCP crystal structure, crystallographic texture modifications, and formation of a more homogeneous microstructure as a result of grain refinement [26]. The tensile data and hardness measurements, and the average grain size of the alloys are summarized in Table 1. It can be seen that with the refinement of grain size, the tensile yield stress, UTS, total elongation, and hardness increase.

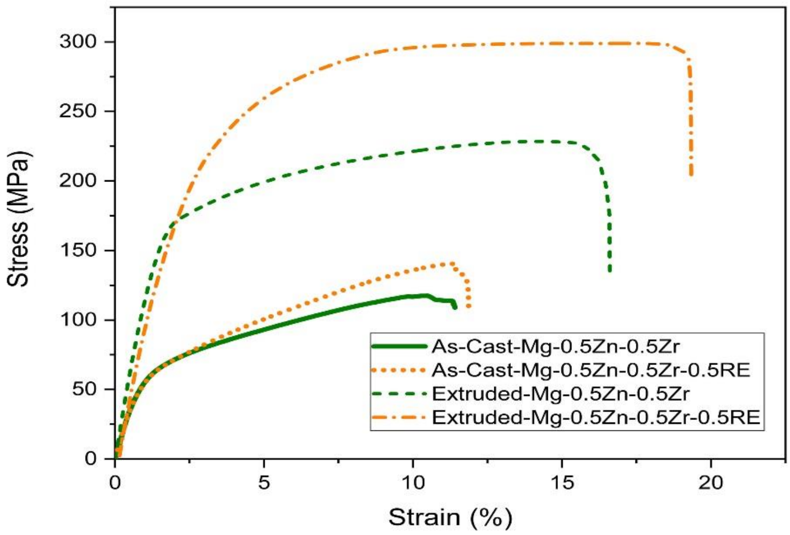


Fig. 5. Representative tensile stress-strain curves.

Table 1. Summary of tensile data, hardness measurements, and the average grain size**.**

Sample	Condition	Grain Size (µm)	Yield Stress (MPa)	Ultimate Tensile Strength (MPa)	Elongation (%)	Hardness (HV)
Mg-0.5Zn-0.5Zr	As-Cast	1320±110	46±12	117±13.8	10.4±2.2	37.7±0.7
Mg-0.5Zn-0.5Zr-0.5RE	As-Cast	1030±80	54±10	140±11.2	10.9±2	38.8±1.7
Mg-0.5Zn-0.5Zr	Extruded	7.5±0.5	186±8	228±12.1	15.6±1.8	43.1±1.5
Mg-0.5Zn-0.5Zr-0.5RE	Extruded	1.3±0.4	197±9	298±8.9	18.3±1.9	61.4±1.7

4. Summary

In summary, the effects of rare earth micro-addition and hot deformation on the microstructure and mechanical properties of Mg-0.5Zn-0.5Zr alloy were studied. It was found that the addition of 0.5 wt.% RE combined with the hot extrusion process could effectively refine the grain size from 1320 µm for the as-cast Mg-0.5Zn-0.5Zr alloy to the ultrafine grained regime (1.3 µm) for the extruded Mg-0.5Zn-0.5Zr-0.5RE alloy. Compared to the as-cast counterparts, the UTS and total elongation values were significantly enhanced by the extrusion process. Quantitatively, the UTS of ~ 300 MPa with the total elongation of ~ 18% was obtained for the extruded Mg-0.5Zn-0.5Zr-0.5RE alloy, which reveals the favorable effects of the ultra-grain refinement on the enhancement of the mechanical properties of magnesium alloys.

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