Enhanced Electromagnetic Interference Shielding of Mg–Zn–Zr Alloy by Ce Addition

Xian-Hua Chen · Li-Zi Liu · Juan Liu · Fu-Sheng Pan

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Abstract The effects of Ce addition on microstructure and electromagnetic interference (EMI) shielding response of Mg–6Zn–0.5Zr (ZK60) alloy have been investigated. Ce addition resulted in grain refinement and higher density of Mg–Zn–Ce and MgZn₂ intermetallic particles in the alloy. In particular, this was substantially remarkable as the addition of Ce was up to 1.0 wt%. It is interesting to note that as-extruded ZK60 alloy with 1.0 wt% Ce addition exhibited an EMI shielding effectiveness (SE) exceeding 70 dB at the frequency range of 30–1,500 MHz, which was significantly higher than that of ZK60 alloy without Ce addition and reached the requirement of high protection. The superior SE was probably related to the increased reflection and multiple reflection of electromagnetic radiation induced by Ce addition. Direct artificial aging at 150 °C for 25 or 50 h led to a further increase of 7–10 dB in the SE of the alloy with 1.0 wt% Ce addition. The advantages of excellent shielding capacity and favorable mechanical strength make the Mg–Zn–Zr–Ce alloy an attractive shielding candidate material for a variety of technological applications.

KEY WORDS: Magnesium alloys; Ce; Shielding effectiveness; Electromagnetic interference; Intermetallic particles

1 Introduction

With the rapid development of electrical and communication industry, there is an increasing interest in electromagnetic interference (EMI) shielding [1–3]. Metallic materials are by far the common candidates for EMI

shielding applications, which possess high shielding effectiveness (SE) because of their high conductivity and/or magnetic permeability [1, 4, 5]. Nevertheless, traditional shielding metals, such as copper, nickel, steel and permalloy, suffer from their heavy weight. Hence, the conductive polymer-matrix composites have been developed to replace or supplement traditional shielding metals [6, 7]. In spite of their lightweight and easy control of conductivity, most of polymer-matrix composites are not suited to structural applications due to poor mechanical strength [3, 5]. It is still a challenge to develop the shielding materials with low density, favorable mechanical strength and excellent EMI SE to prevent electromagnetic radiation effectively.

It is well known that magnesium is the lightest engineering structural metal with a low density of 1.73 g/cm³ and has high specific strength and good EMI shielding capacity [8, 9]. This leads to the expectation that high-strength magnesium alloys may have the potential to be

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X.-H. Chen (✉) · L.-Z. Liu · J. Liu · F.-S. Pan
College of Materials Science and Engineering, Chongqing
University, Chongqing 400045, China
e-mail: xhchen@cqu.edu.cn

X.-H. Chen · F.-S. Pan
National Engineering Research Center for Magnesium Alloys,
Chongqing University, Chongqing 400045, China

F.-S. Pan
Chongqing Academy of Science and Technology,
Chongqing 401123, China

developed as EMI shielding materials. Unfortunately, typical high-strength alloys, such as Mg–Zn–Zr system, have evidently lower EMI SE compared with pure magnesium [10], limiting their applications for EMI shielding in aerospace and military industries where SE over 60 dB is generally required [11]. Such a case is mainly due to that these alloys usually contain a high content of alloying elements. Some alloying elements are solutionized in α -Mg matrix, which is detrimental to their electrical conductivity and consequently lowers reflection attenuation [10]. It is thus significant to enhance the EMI SE of high-strength magnesium alloys obviously, but without impairing their mechanical strength.

Until now, the studies on EMI shielding properties of magnesium alloys are very limited in the literature. Our previous investigation showed that the SE of magnesium alloys could be improved by the precipitation of second-phase particles after heat treatment [12, 13]. Ce is a typical rare earth element, the solid solubility of which in magnesium solid solution is extremely low, i.e., the maximum value is about 0.5 wt% (0.09 at.%) at 592 °C [14, 15]. The precipitation of abundant Ce-containing intermetallics is expected even at low Ce contents in magnesium alloys [15], which may be beneficial to electrical conductivity and shielding properties. In the present study, Ce was added to Mg–Zn–Zr magnesium alloy that resulted in substantially enhanced shielding characteristics and retained high tensile strength.

2 Experimental

The nominal compositions of the studied alloys were Mg–6Zn–0.5Zr– x Ce (hereafter, referred as ZK60– x Ce, $x = 0, 0.5$ and 1.0, in wt%). The actual chemical compositions of these alloys analyzed by APL4460 direct reading spectrometer are listed in Table 1. The alloys with variable Ce levels were produced using low-pressure casting in a steel crucible under the protection of SF₆ and CO₂ mixed gas. Commercial pure Mg and Zn were used, and Zr and Ce

were added in the form of Mg–30 wt% Zr and Mg–30 wt% Ce master alloys, respectively. The casting ingots were homogenized at 400 °C for 10 h and then hot-extruded into plates with cross section of 13 mm $\times$ 125 mm at 390 °C. Extrusion ratio was calculated to be about 11.5:1. Direct artificial aging treatment was performed on the ZK60–1.0Ce alloy at 150 °C for 4–50 h and cooling in air.

Microstructure characterization was carried out using optical microscopy (OM), scanning electron microscopy (SEM, TESCAN VEGA II LMU) and transmission electron microscopy (TEM, ZEISS LIBRA20D). The volume fraction of intermetallic particles was counted by an Image ProPlus software, and grain size was measured by the linear intercept method. Analysis of second-phase composition was carried out using energy-dispersive spectroscopy (EDS). Specimens for OM and SEM observations were chemically etched with a mixture of 1.5 g picric acid, 25 mL ethanol, 5 mL acetic acid and 10 mL water. Thin-foil specimens for TEM observation were prepared by ion milling.

EMI SE (attenuation upon transmission) was measured using the standard coaxial cable method in accordance with ASTM D4935-2010 in the frequency range of 30 MHz–1.5 GHz. The setup consisted of a DN 1015A SE tester with its input and output connected to an Agilent 8753ES network analyzer. The testing ZK60– x Ce samples were in a disk form with 115 mm in diameter and 2 mm in thickness. Electrical conductivity was measured with a conductivity meter (Sigmascope SMP10) at 20 °C. Mechanical properties of the extruded alloys were evaluated by tensile tests on a CMT5105 material test machine with a strain rate of 10^{−3}/s at ambient temperature. Tensile specimens of 5 mm gauge diameter and 50 mm gauge length were used for tensile tests.

3 Results

Figure 1 illustrates XRD patterns of as-extruded ZK60– x Ce alloys. It can be seen that the phase composition of ZK60 alloy contained α -Mg and MgZn₂, while the addition of Ce induced Mg–Zn–Ce new phase in the Ce-containing alloys. It is obvious that the intensity of Mg–Zn–Ce diffraction peaks increased with increasing Ce content. When the Ce addition went up to 1.0 wt%, these Mg–Zn–Ce diffraction peaks were easily detected in the as-extruded ZK60–1.0Ce alloy.

The optical longitudinal microstructures of as-extruded alloys are shown in Fig. 2. The ZK60 alloy exhibited a bimodal grain structure composed of fine recrystallized grains of about 2–10 μ m and coarse unrecrystallized grains of several tens of microns. The ZK60–0.5Ce alloy still showed such a bimodal grain structure, while had a higher

Table 1 Chemical compositions, average grain size (d), volume fraction of intermetallic particles (V_f) and relative conductivity (σ_r) for ZK60– x Ce alloys

Alloy	Composition (wt%)			d (μ m)	V_f (%)	σ_r (%)
	Zn	Zr	Ce			
ZK60	5.8	0.52	0	6.1	3.6	28.4
ZK60–0.5Ce	5.6	0.49	0.45	4.6	5.7	28.8
ZK60–1.0Ce	5.8	0.51	1.16	2.9	8.2	29.4

Relative conductivity is obtained by the ratio of electrical conductivity of the alloys to pure copper

Fig. 1 XRD patterns of as-extruded ZK60-*x*Ce alloys: **a** ZK60; **b** ZK60-0.5Ce; **c** ZK60-1.0Ce

volume fraction of fine recrystallized grains compared to the ZK60 alloy. It is interesting to note that fully recrystallized microstructure with most of fine grains as small as several microns were present in the ZK60-1.0Ce alloy, indicating Ce addition promotes dynamic recrystallization during hot extrusion. Statistical measurement result of grain size indicated that the addition of 1.0 wt% Ce induced a remarkable decrease of mean grain size from 6.1 to 2.9 μm , as listed in Table 1.

Figure 3 reveals that plenty of intermetallic compounds were existent in α -Mg matrix in the three alloys, which should come from broken intermetallic particles formed in cast condition and fine particles precipitating from supersaturated solid solution during hot extrusion [16]. It is quite apparent that the amount of intermetallic particles increased significantly with increasing Ce content. The measured volume fractions of these particles were approximately 3.6, 5.7 and 8.2% for ZK60, ZK60-0.5Ce and ZK60-1.0Ce alloys, respectively. In the meantime, Ce addition changed the type of intermetallic compounds in the as-extruded alloys. According to our EDS analysis, the intermetallic compounds were dominantly MgZn_2 phase in

the ZK60 alloy without Ce, whereas the addition of Ce resulted in the formation of Mg-Zn-Ce phase instead of MgZn_2 phase, as shown in Fig. 3d.

Figure 4 shows the typical TEM images of as-extruded ZK60-1.0Ce alloy. A high density of MgZn_2 and Mg-Zn-Ce precipitates with rod and spherical shapes were observed in the Ce-added alloy. The size of these precipitates was much fine, varying in the range of 10–30 nm. TEM morphology of the relatively large Mg-Zn-Ce phase particles in as-extruded ZK60-1.0Ce alloy is displayed in Fig. 5. The Mg/Zn/Ce atom ratio obtained by TEM is consistent with that measured by SEM. Analysis of selected-area electron diffraction of Mg-Zn-Ce particle (as shown in Fig. 5c) indicated that the Mg-Zn-Ce phase was a orthorhombic structure, which was consistent with the report by Jeong *et al.* [17]. The Mg-Zn-Ce phase has the similar composition to $(\text{MgZn})_{12}\text{Ce}$ phase reported by Kevorkov and Pekguleryuz [15]. $(\text{MgZn})_{12}\text{Ce}$ phase was considered as a continuous substitutional solid solution of Mg_{12}Ce phase by exchanging Mg by Zn while keeping a constant Ce concentration [15]. Mg_{12}Ce , $\text{Mg}_{41}\text{Ce}_5$ and $\text{Mg}_{17}\text{Ce}_2$ phases, observed in Mg-Zn-Zr-Ce alloys in other studies [15, 18, 19], were not found in the present work.

It is well known that the second-phase particles are able to act as nucleation sites for recrystallization during hot deformation, i.e., particle-stimulated nucleation (PSN), which has an effect on grain size and texture of wrought magnesium alloys subjected to rolling, extrusion and forging processes [16, 20]. According to the literatures [21, 22], the large particles above 1 μm could promote recrystallization. Fine particles smaller than 1 μm contribute the retardation of recrystallization by preventing the formation of the lattice curvatures necessary for nucleation via boundary pinning, while, even though the individual particles are below the critical size for nucleation, a cluster of these particles act as PSN like one large particle [21, 22]. As a result, these unbroken large particles as well as clusters of fine particles were believed to promote dynamic recrystallization process that contributed to the finer grains and more homogeneous microstructure in ZK60-1.0Ce alloy compared to ZK60 alloy.

Fig. 2 Typical optical micrographs of as-extruded ZK60-*x*Ce alloys: **a** ZK60; **b** ZK60-0.5Ce; **c** ZK60-1.0Ce

Fig. 3 SEM images showing intermetallic particles in as-extruded ZK60 **a**, ZK60–0.5Ce **b**, ZK60–1.0Ce **c** alloys, and the EDS result of point A **d**

Fig. 4 Typical TEM bright-field image as-extruded ZK60–1.0Ce alloy **a** and the magnified image of the region which is indicated by the frame **b**

The tensile stress–strain curves of as-extruded ZK60 alloys with variable Ce additions are shown in Fig. 6, revealing that Ce addition led to the enhanced tensile

strength and elongation due to the finer grains and more second-phase particles. The as-extruded ZK60–1.0Ce alloy exhibited a relatively good combination of ultimate tensile

Fig. 5 TEM bright-field micrographs showing Mg–Zn–Ce particles in as-extruded ZK60–1.0Ce alloy **a**, EDS results of particle A as indicated in **a** **b**, and SAED pattern obtained from particle A **c**

Fig. 6 Tensile engineering stress–strain curves of as-extruded ZK60– x Ce alloys at room temperature

strength of 316 MPa, yield strength of 250 MPa and tensile elongation of 15%, which were usually enough for most structural applications.

Figure 7 demonstrates EMI SE as a function of frequency for the as-extruded alloys with different Ce contents. It can be seen that the SE diminished gradually with increasing frequency, which should be mainly ascribed to a decrease in reflection attenuation [1]. The as-extruded ZK60 alloy had the EMI SE value varying from 70 to 54 dB at the testing frequency range of 30–1,500 MHz. Ce addition resulted in a clear increase in the SE, especially a large SE improvement of ~ 17 dB was achieved as the Ce addition is up to 1.0 wt%. It is worth noting that for the as-extruded ZK60–1.0Ce alloy the EMI SE kept as high as 71–81 dB at the whole frequency range, which even meets the military requirement of 60–120 dB [11]. Wen and Chung [23] elevated the EMI SE of cement up to 70 dB by adding stainless steel fibers; however, the thickness of the cement composite was 9.5 mm, which was 4.75 times higher than that of the ZK60–1.0Ce alloys. The EMI SE of

Fig. 7 Variation of EMI SE with testing frequency for as-extruded ZK60– x Ce alloys

as-extruded ZK60–1.0Ce alloy was able to be improved further by direct artificial aging, as shown in Fig. 8. It was found that a remarkable increment of 7–14 dB at the testing frequency range was induced by direct artificial aging at 150 $^{\circ}\text{C}$ for 25 or 50 h.

Table 2 presents a comparison of EMI SE results of the investigated ZK60– x Ce alloys with other common shielding candidate materials. Obviously, the extruded and aged ZK60–1.0Ce alloys possessed excellently competitive properties for EMI shielding, and its shielding capacity was higher than as-cast pure magnesium and AZ31 alloy [10], even comparable to that of 1J50 alloy with high magnetic permeability [24].

4 Discussion

Generally, the EMI wave attenuation arises from three different sources, including reflection (R), absorption (A)

Fig. 8 Variation of EMI SE with testing frequency for ZK60–1.0Ce alloy in the extruded and aged states

and multiple reflection (M). The total EMI SE can be thus written as follows [1, 25]

$$SE = SE_R + SE_A + SE_M. \quad (1)$$

Reflection relying on mobile charge carriers, such as electrons, can be enhanced by higher electrical conductivity. Significant absorption of EMI waves by the shield usually requires electric and/or magnetic dipoles which interact with the electromagnetic fields in the radiation. The electric and magnetic dipoles may be provided by dielectric and magnetic materials, respectively. Multiple reflections require the presence of a large surface area or interface area in the shield.

It is well known that magnesium alloys have relatively low dielectric constant and magnetic permeability, which indicates that absorption attenuation will make a limited contribution to the EMI SE of the studied ZK6– x Ce alloys. The significantly enhanced SE of the as-extruded ZK60 with Ce addition compared to the as-extruded ZK60 could

be intimately correlated with the contributions of reflection and multiple reflections.

Table 1 gives the relative conductivity (relative to pure copper) of the as-extruded ZK60– x Ce alloys, showing that Ce addition resulted in an increase in the conductivity. The elevated conductivity may be due to the following factors: (1) the form of Mg–Zn–Ce phase decreased the amount of Zn in Mg solid solution that could lead to lower electron scattering [26]; (2) Ce addition promoted dynamic recrystallization and induced significantly more uniform microstructure (see Fig. 2), indicating that a considerably lower density of dislocation defects were in ZK60–1.0Ce alloy as compared to ZK60 alloy.

The higher the electrical conductivity, the greater the vortex electrical current in the shielding alloy; therefore, more energy of the radiation plane-wave field will be dissipated by ohmic electrothermal heat, and a high reverse electromagnetic field will be produced [5, 13], leading to stronger reflection attenuation of electromagnetic radiation based on relevant theories, and thus improved shielding properties in the alloy. After direct artificial aging at 150 °C, the relative conductivity of the ZK60–1.0Ce alloy further increased from 29.4 to ~31.5% due to the precipitation of many second-phase particles. This was dominantly responsible for the obviously enhanced SE in the aged ZK60–1.0Ce alloy, which was consistent with what reported in our previous papers [12, 13].

The skin depth (δ) of a conductive shield is given by [1, 4]

$$\delta = \frac{1}{\sqrt{\pi f \mu \sigma}} \quad (2)$$

where f , μ , σ is frequency, magnetic permeability and electrical conductivity, respectively. Hence, the skin depth decreases with increasing frequency and with increasing conductivity or permeability. For the ZK60– x Ce alloys, δ

Table 2 Comparison of EMI SE results between the ZK60–1.0Ce alloy and other shielding candidate materials

Material	Thickness (mm)	SE (dB)		References
		$f = 200$ MHz	$f = 1,200$ MHz	
Extruded ZK60 alloy	2	67	57	This work
Extruded ZK60–1.0Ce alloy	2	80	71	This work
Aged ZK60–1.0Ce alloy (150 °C/25 h)	2	86	81	This work
Cast pure Mg	2	63	53	[10]
Cast AZ31 alloy	2	68	60	[10]
2,024 Al alloy	2	37	35	[5]
Fly ash/2,024 Al alloy composite	2	53	31	[5]
1J50 magnetic alloy	2	80	68	[20]
Ni fibers/polyethersulfone	2.8	–	58	[1]
Steel fibers/polyethersulfone	2.8	–	42	[1]
Al flakes/polyethersulfone	2.8	–	26	[1]

is approximately 3.2 μm at a frequency of 1.5 GHz in accordance with Eq. (2). The attenuation due to multiple reflection is obvious when the distance between the reflecting interfaces is able to be compared with δ [1, 5]. The as-extruded ZK60–1.0Ce alloy showed the microstructure consisting of fine recrystallized grains and a high density of MgZn_2 and Mg–Zn–Ce intermetallic particles, as observed in Figs. 2 and 3. It is expected that these intermetallic particles and fine grains were capable of contributing to significant multiple reflection to EMI radiation, since most of them had the size in the similar level with δ according to our observations and statistics. Such an effect was similar to the contribution of reinforced particles to the shielding capacity of composites [1]. On the contrary, plenty of coarse unrecrystallized grains and a relatively low density of MgZn_2 intermetallic particles were observed in the as-extruded ZK60 alloy, which indicated that the multiple reflection attenuation was limited. Consequently, it is believed that stronger multiple reflection attenuation occurring in fine grains and phase interfaces played a role in the enhancement of EMI SE induced by Ce addition.

According to what mentioned above, adding Ce enhanced the EMI SE of ZK60 alloy substantially and had a positive effect on mechanical strength at the same time. Moreover, further enhancement of EMI SE could be achieved via artificial aging treatment due to the precipitation of numerous second-phase particles. Our investigation results shed light on the potential to develop lightweight and high-strength EMI shielding magnesium alloys for engineering applications.

5 Conclusions

The effect of Ce addition on microstructure, EMI shielding and mechanical properties of ZK60 magnesium alloy was investigated. Ce addition effectively refined the grain microstructure by promoting dynamic recrystallization and induced a large amount of Mg–Zn–Ce and MgZn_2 intermetallic particles. In the meantime, electrical conductivity was found to be elevated to a certain extent. As a result, considerably enhanced EMI SE of 71–81 dB was achieved at the frequency range of 30–1,500 MHz as 1.0 wt% Ce was added, which should originate from the contributions of increased reflection and multiple reflection. Direct artificial aging at 150 °C for 25 or 50 h resulted in a further increase of 7–10 dB in the SE of the alloy with 1.0 wt% Ce addition. Additionally, it was noted that enhanced mechanical strength was obtained after Ce addition in the alloy. Our findings indicate that the Mg–Zn–Zr–Ce alloy with high shielding capacity and favorable mechanical

strength has great potential in serving as EMI shielding engineering material.

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