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Grain refinement and mechanical properties enhancement of AZ91E alloy by addition of ceramic particles

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Abstract Improved mechanical properties and structural uniformity of Mg-based alloys can be achieved by use of grain-refining additives prior to casting. Ceramic particles of α-Al_2O_3 and SiC can serve as such additives to refine the microstructure of Mg–Al-based alloys. However, direct introduction of ceramic particles into Mg matrix is limited by the poor wetting of those particles by liquid Mg and their massive agglomeration. Mg/α-Al_2O_3 and Mg/SiC master alloys were prepared using a method based on the insertion of the ceramic particles into a molten Mg bath through a Mg-nitride layer formed on the surface of the molten bath. The mixture of Mg/ceramic particles was cooled to room temperature under a nitrogen atmosphere. Mg-15%Al_2O_3 and AZ91E + 10%SiC master alloys were obtained. These master alloys were used to refine AZ91E alloys by introducing various amounts of ceramic particles to manufacture AZ91E + 1%Al_2O_3, AZ91E + 1%SiC, and AZ91E + 3%SiC alloys. These were cast using high-pressure die casting and gravity die casting. The alloy AZ91E + 1%Al_2O_3 was grain refined to ~20 μm and the alloys AZ91E + SiC were grain refined to ~50 μm as against 110 μm in non-refined counterparts. The mechanical properties of the modified alloys are substantially better than those of a non-refined AZ91E alloy which is the result of a combination of grain refinement and reinforcement of the matrix by ceramic particles. Alloy AZ91E + 1%Al_2O_3 exhibited the best mechanical properties.

Introduction

Magnesium alloys have received much attention over the last two decades, as a material for lightweight structural applications, especially in automotive and aerospace industries, because of their good-specific properties such as density, strength, and stiffness [1]. Among the various Mg alloys, Mg–Al-based alloys have shown the best combination of castability, mechanical strength and ductility [2]. Further improvement of components made from this alloy can be achieved by increasing its tensile properties, and particularly the yield stress. It is well-established that the yield strength is directly related to the grain size, so it is essential to reduce the grain size of the cast alloy to obtain higher tensile properties. Grain refinement of Mg–Al-based alloys was discussed in detail in the 1960 s by Emley [3]. A renewed interest in magnesium alloys in recent years has resulted in significant efforts in grain-refining of these commercially important alloys. The grain refining methods reported for Mg–Al-based alloys are carbon inoculation [4], melt superheating [5], ultrasonic vibrations [6], minor addition of alloying elements such as Sr, RE, Th, Si, Ca, and B [7, 8], rapid cooling and other means. Carbon inoculation is currently the only grain refining approach used commercially, however, its effectiveness is limited [7]. The additives of ceramic particles were also used to refine the microstructure of Mg–Al-based alloys [9, 10]. Grain refinement by the addition of ceramics has the additional advantage of strengthening due to the fine dispersion of ceramic particles in the matrix and grain boundaries, referred to hereafter as “composite strengthening”. It is therefore an attractive grain-refining approach for magnesium alloys. However, the introduction of ceramic particles into the Mg matrix is a challenging task because of their poor wetting by liquid Mg. The presence

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of a native oxide film on the particles' surface is assumed to be the main reason for the poor wetting. Intensive mixing for the purpose of introducing the ceramic particles into the liquid magnesium resulted in high gas-porosity and poor mechanical properties. In this study, the refined alloys were prepared by using a two-stage procedure. At the first stage, master alloys containing Mg and ceramic particles (α-Al_2O_3 or SiC) were prepared using a nitrogen-induced wetting of these particles by liquid Mg. At the second stage, these master alloys were used to refine the AZ91E alloy.

Experimental procedure

The casting system for introducing the ceramic particles into molten Mg is schematically presented in Fig. 1. The crucible (3) used for the introduction of alumina particles was prepared from alumina by the slip-casting technique (Fig. 2a), while for the introduction of SiC particles, a cellular aluminum crucible was used (Fig. 2b). α-Al_2O_3 particles (mostly α phase-rhombohedral R$\bar{3}$c [11], containing ~5–10% γ phase-cubic Fd3m [12]) of about 30 nm in size were placed in a porous alumina crucible (3). In order to improve the penetration of the molten magnesium into the crucible, bores with a diameter of 0.8 mm were drilled in the walls of the crucible (Fig. 2a).

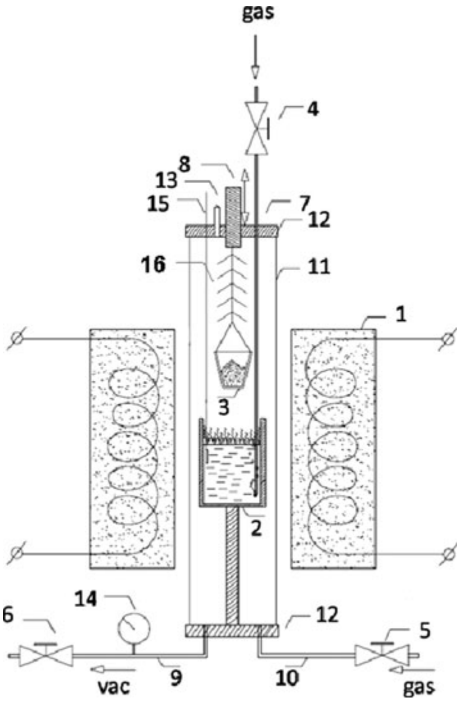

Fig. 1 Nitrogen activated casting system for insertion of alumina particles into Mg: *1* furnace, *2* stainless steel crucible, *3* porous crucible, *4,5,6* valves, *7,10* nitrogen supply, *8* manipulator, *9* connection to vacuum line, *11* quartz or iron tube, *12* covers, *13* safety valve (opens when the pressure reaches 1 atm), *14* vacuum control, *15* thermocouple, *16* stirrer

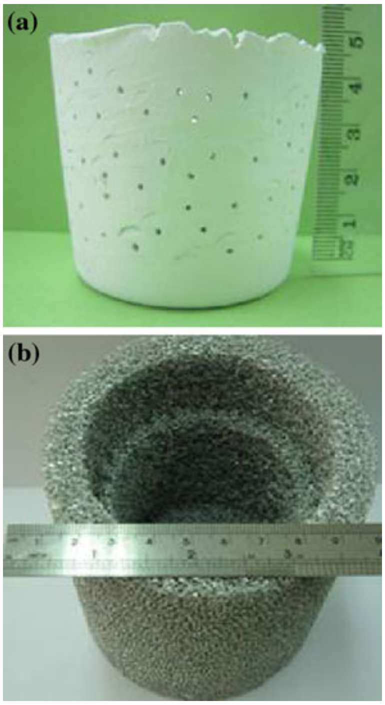

Fig. 2 **a** Alumina crucible prepared by the slip-casting technique. Bores with a diameter of 0.8 mm were drilled in the walls of the crucible, **b** cellular aluminum crucible

Stainless steel crucible (2) with pure Mg and the alumina crucible with alumina nanoparticles were heated to 700 °C for 1 h at 10^{-1} torr vacuum created in the quartz tube (11). After melting the magnesium, nitrogen gas was bubbled for 3 min through the molten Mg, thereby forming a Mg_3N_2 layer on top of the molten bath. Simultaneously, the alumina crucible (3) was lowered into the molten Mg, which penetrated through the porous walls of the crucible to react with the alumina nanoparticles. After that, the crucible with the Mg–alumina mixture was raised and cooled to room temperature under nitrogen atmosphere. The Mg master alloy obtained in the crucible was found to contain 15% Al_2O_3 particles by volume.

SiC particles of different sizes (1 and 3 μm) were used for the preparation of AZ91E–SiC pre-alloys. The SiC particles were etched with KOH prior to their introducing into the molten Mg in order to increase the melt/SiC contact surface. Aluminum pieces, etched SiC particles, Zn, and Mn were placed in a porous aluminum crucible (3) made of cellular aluminum. Pure Mg, placed in a stainless steel crucible (2), was melted under Ar gas atmosphere at 700 °C, then 10^{-1} torr vacuum was created in the iron tube (11) and nitrogen gas was supplied into the liquid Mg. The

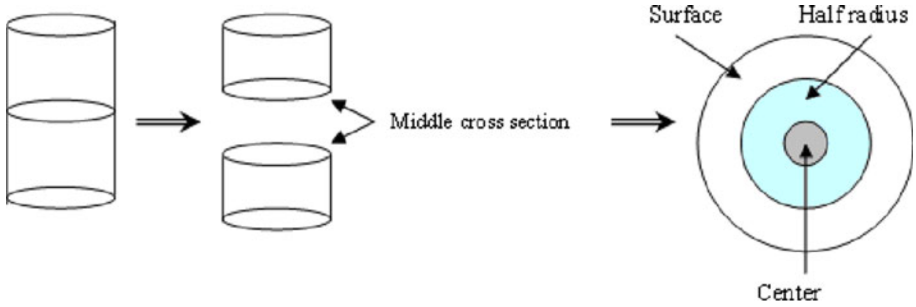

Fig. 3 The different regions of the middle cross-section of the ingot, investigated by optical microscopy

porous aluminum crucible was lowered into the molten Mg, the aluminum crucible melted and in this way the SiC particles were introduced into the liquid Mg. The temperature was raised to 800 °C and the Mg–Al–Zn–Mn–SiC mixture was intensively stirred for 5 min. Finally, the AZ91E/SiC mixture was rapidly cooled by immersing the iron tube in cold water. The master alloy composition was analyzed by SEM + EDS and was found to be Mg–9%Al–1%Zn–0.3%Mn–10%SiC.

Pure Mg, 9 wt% pure Al, 1 wt%Zn, 0.3 wt%Mn were melted under protective atmosphere 97.7%CO_2 + 0.3%CF_3–CH_2S at 720 °C. Shortly before pouring, the Al_2O_3 or SiC containing master alloy was added into the melt and the mixture was intensively stirred for 10 min. Thereafter, the alloys were gravity die cast in a steel mould (preheated to 300 °C) under CO_2 + Freon 134 protective atmosphere. High-pressure die casting was carried out utilizing Hydrotechnik 200 machine with a steel mould at room temperature to manufacture tensile testing specimens according to Standard Specification for Magnesium Alloys Die Casting ASTM B-94. The refined alloys, AZ91E + 1%Al_2O_3, AZ91E + 1%SiC or 3%SiC (1 or 3 μm), were cast into a cylinder of 30 mm utilizing gravity die casting.

The samples for grain size measurement were cut from the gravity cast rods of 30 mm in diameter. The grain size was determined from optical micrographs by the line intercept method: the number of grain boundaries, n, intercepting line L, determines the average grain size, $d = L/n$; at least five independent readings and at least 100 grains of each specimen were taken into account. The average grain size was measured in three regions of the middle cross-section of the ingot: in the center, in the half radius and in the surface region. The location of the examined regions in the gravity die cast cylinder is presented in Fig. 3. The deviation from the average grain size in different readings was about 10%.

Mechanical properties of the alloys were tested by INSTRON testing machine at 25 °C and relative humidity 60% with a relative error of the load cell of ±0.5%. The results were averaged over five specimens of each alloy, for each measurement.

Results

Microstructure of the master alloys

The microstructure of the AZ91E + 15%Al_2O_3 master alloy was investigated by SEM and TEM. The alumina

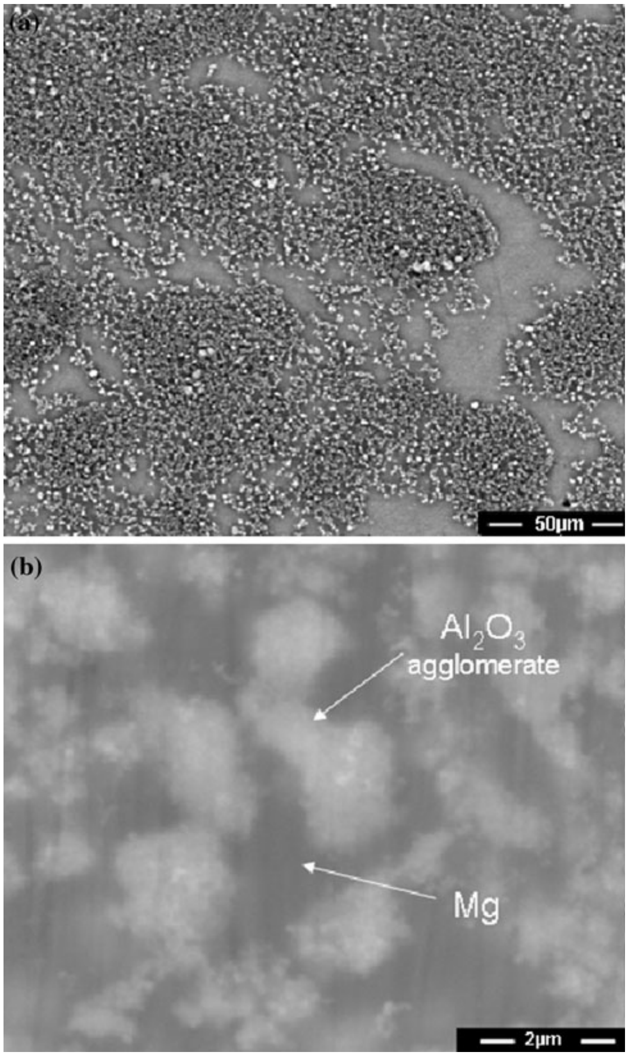

Fig. 4 Microstructure of the AZ91E + 15%Al_2O_3 master alloy: **a** distribution of ~1 μm Al_2O_3 particles in the Mg matrix, **b** close image of alumina agglomerates

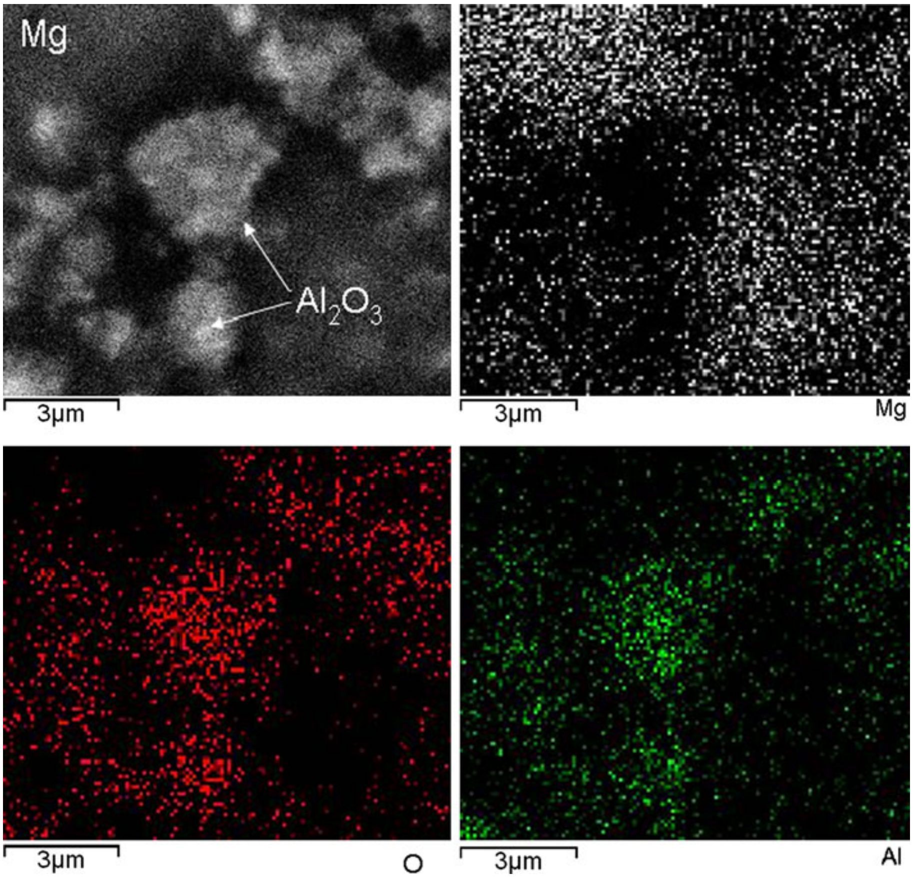

Fig. 5 SEM image and O, Al, and Mg X-ray maps of the master alloy Mg-15 wt%Al_2O_3

nanoparticles of ~30 nm in size introduced into the AZ91E alloy (Fig. 4) were mainly accumulated into ~1 μm agglomerates, which were evenly distributed in the Mg matrix.

The X-ray maps of the Mg + 15%Al_2O_3 master alloy (Fig. 5) show that the agglomerates consist of aluminum and oxygen, whereas the matrix consists of magnesium. TEM micrographs of the magnesium matrix revealed that it mainly consists of nano-scale magnesium grains (in the range of 100–200 nm in size) (Fig. 6a, b); a certain amount of non-agglomerated alumina nanoparticles are embedded in the Mg-matrix (Fig. 6c).

The SiC particles in the AZ91E + 10%SiC master alloys are located at the grain boundaries of Mg (Fig. 7a). Close investigation of these regions shows that some non-agglomerated SiC particles are also scattered throughout the Mg matrix (Fig. 7b). Mg_2Si phase (Fig. 7c) was discernible.

The microstructure of the refined AZ91E alloys

The microstructures of the refined gravity cast AZ91E + 1%Al_2O_3, AZ91E + 1%SiC, and AZ91E + 3%SiC alloys were investigated by optical microscopy and SEM.

The injection of the Mg + 15%Al_2O_3 master alloy into the melt resulted in the addition of about 1% of nano-alumina. This, in turn, resulted in a reduction of the average grain size from 110 ± 10 μm for non-refined reference alloy AZ91E, to 20 ± 1 μm for AZ91E + 1%Al_2O_3 alloy (Fig. 8a, b).

Agglomerates of alumina nanoparticles were found in the center of most of the Mg grains (Fig. 9a).

Typical microstructures of AZ91E alloy refined by SiC particles are shown in Fig. 8c, d. Most of the SiC particles are located at the grain boundary regions (Fig. 9b). The grain refinement is evident by comparing the reference alloy and SiC refined ones (Fig. 8). The best refinement was obtained in alloy AZ91E + 3%SiC (1 μm particles).

The grain sizes typical of various regions in the reference and refined gravity cast AZ91E alloys are summarized in Fig. 10. The microstructural refinement using alumina or SiC particles is clearly evident from Fig. 10.

The microstructures of the modified high-pressure die cast (HPDC) AZ91E + 1%Al_2O_3, AZ91E + 1%SiC, and AZ91E + 3%SiC alloys were also investigated by optical microscopy and SEM. The average grain size of all HPDC alloys, including the reference (not modified) AZ91E alloy, was about 20 μm (Fig. 11). The microstructures of the alloys were similar to those obtained by gravity casting.

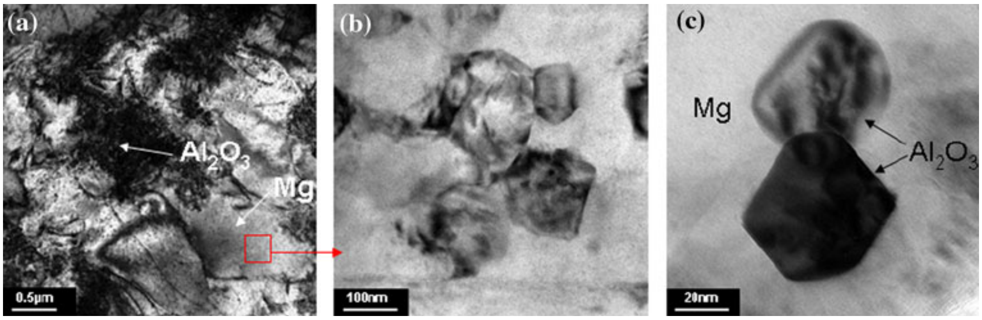

Fig. 6 TEM micrographs of the Mg-15 wt%Al_2O_3 master alloy: **a** ~1 µm alumina agglomerate in Mg matrix; **b** Mg matrix consisting of ~100–200 nm grains; **c** single alumina nanoparticles embedded in the Mg grain

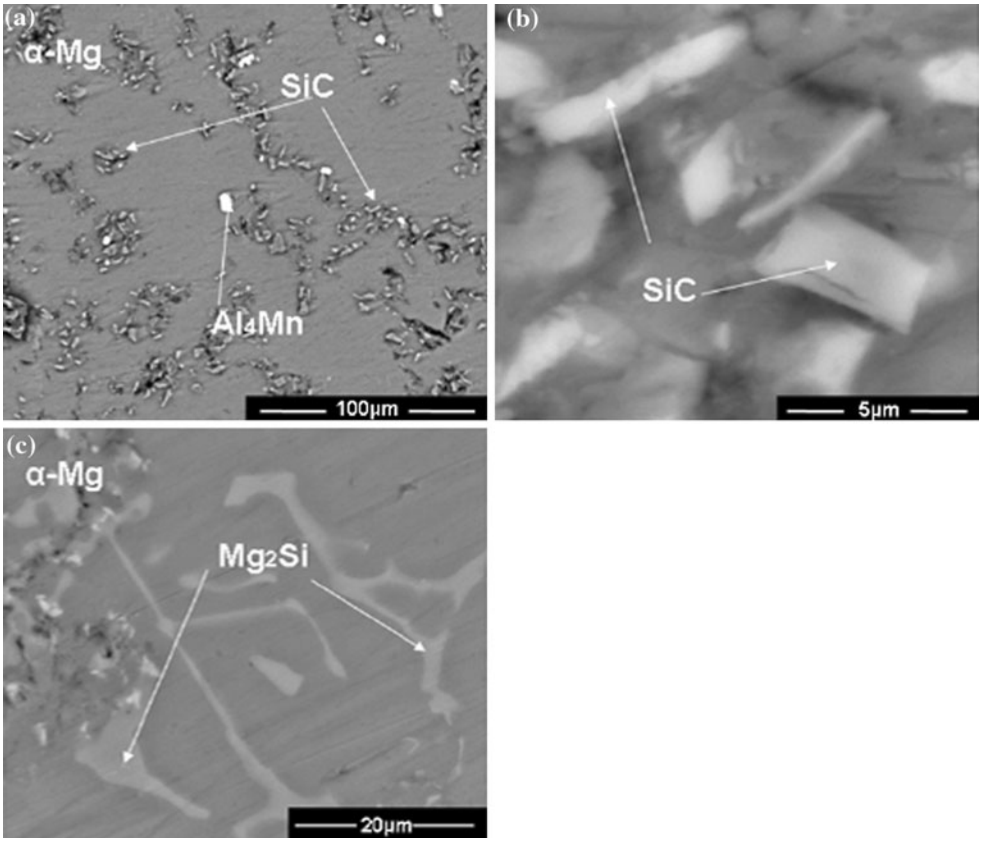

Fig. 7 SEM micrographs of the alloy AZ91E + 10%SiC (3 µm powder): **a** SiC particles arranged along the grain boundaries of Mg; **b** single SiC particles embedded in the Mg matrix; **c** Mg_2Si phase formed during casting

Mechanical properties of the refined alloys

The averaged tensile and yield strengths and maximum elongation of the refined alloys are presented in Tables 1 and 2. The deviation of the measured values for a given specimen from the average values was within 10% of corresponding values. All refined alloys exhibit improved mechanical properties as against the AZ91E reference alloy. The mechanical properties of the HPDC alloys modified by ceramic particles and non-modified reference alloy are better than those of the gravity-cast counterparts, due to the finer and more uniform microstructure. The high-pressure die cast AZ91E + 1%Al_2O_3 alloy exhibits the best combination of strength and ductility (Table 1).

Discussion

The inferior wetting of ceramic particles by liquid Mg can be attributed to the molecular oxygen adsorbed to the

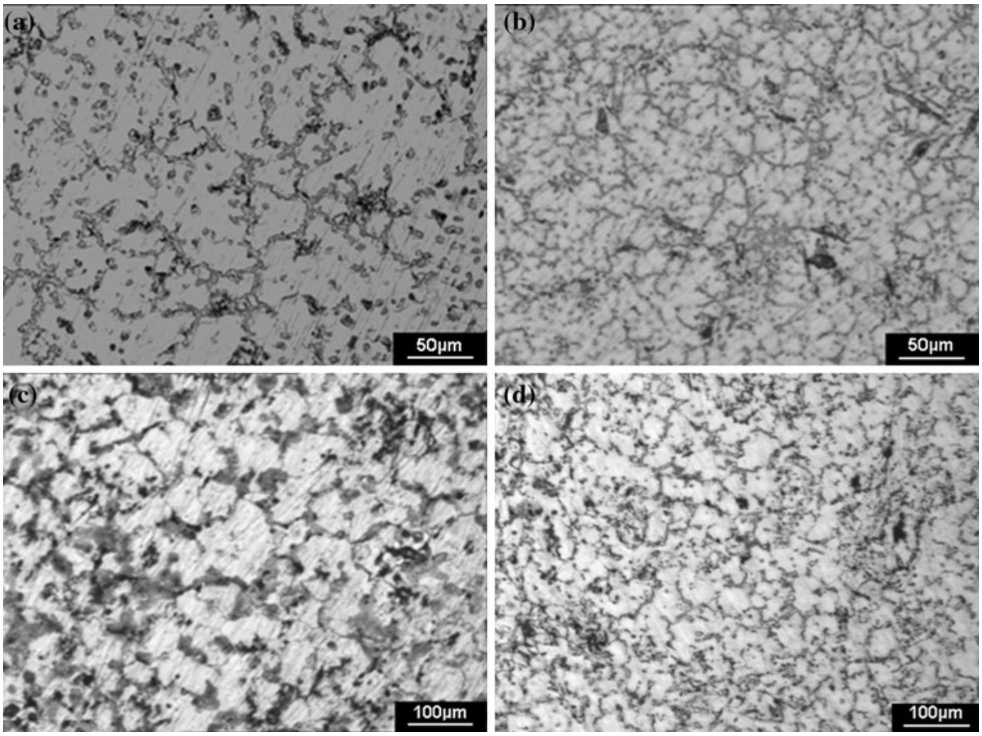

Fig. 8 Optical micrographs of half radius regions of gravity casting samples: **a** reference AZ91E alloy, **b** refined AZ91E + 1% Al_2O_3 alloy, **c** refined AZ91E + 3%SiC (3 μm particles), **d** refined AZ91E + 3%SiC (1 μm particles)

particles' surface. It is assumed that this is the main reason for the poor wettability of SiC and Al_2O_3 particles by molten Mg. Here, the failure of direct introduction of these particles into molten Mg by means of intensive mixing resulted in high-gas porosity and poor mechanical properties. The removal of this oxygen cannot be achieved by direct reaction with nitrogen at the temperatures applied during Mg casting [13]. On the other hand, the adsorbed oxygen can be removed by Mg_3N_2 formed in the reaction of N_2 with the liquid Mg [13]:

$$3\mathrm{Mg(l)} + \mathrm{N_2(g)} \rightarrow \mathrm{Mg_3N_2(s)} \qquad (1)$$

The most probable reaction of magnesium nitride with oxygen is the following:

$$\frac{1}{2}\mathrm{Mg_3N_2} + \mathrm{O_2} \rightarrow \frac{3}{2}\mathrm{MgO} + \frac{1}{2}\mathrm{N_2O} \qquad (2)$$

with the free energy change $\Delta F = -534.749$ kJ/mol [14]. When the nitrogen bubbles through the molten Mg, reaction (1) takes place at the nitrogen bubbles' surface. It increases substantially the amount of magnesium nitride produced compared to the amount produced at the molten Mg bath surface, when reacted with the N_2 atmosphere above it. The Mg_3N_2 clusters are carried by liquid magnesium to the ceramic particles and react with the adsorbed oxygen, according to reaction (2). The removal of the molecular oxygen layer is apparently the reason for the improved wetting of the particles by the molten Mg, which is reflected by the uniform distribution of the ceramic particles in the master alloys.

In the case of alumina particles, the Mg + 15%Al_2O_3 master alloy consisted of alumina agglomerates of about 1 μm in size, evenly distributed in the Mg matrix. The matrix consisted of small Mg grains (~100–200 nm) with some amount of non-agglomerated Al_2O_3 nanoparticles embedded in it. These nanoparticles may serve as nucleation sites in the following casting procedures. The use of this master alloy for grain refinement of AZ91E indeed resulted in substantial grain refinement (Fig. 8a, b) in the case of gravity casting and improvement of the mechanical properties in both gravity and high-pressure die casting (Tables 1, 2). The presence of alumina nanoparticles in the centre of Mg grains indicates that they served as nucleation sites for Mg crystallization.

In the case of SiC particles, the nitrogen-induced wetting of SiC particles by liquid Mg prevents their agglomeration. The SiC particles were located mostly at the grain boundaries of α-Mg matrix (Fig. 6a, b). The presence of Mg_2Si phase (Fig. 6c) indicates that the silicon carbide particles were partially decomposed. The released carbon may form aluminum carbides Al_4C_3, which can serve for nucleation of Mg crystals during the following casting [6]. However, such carbides were not detected in the present investigation. Modification of gravity cast AZ91E by using

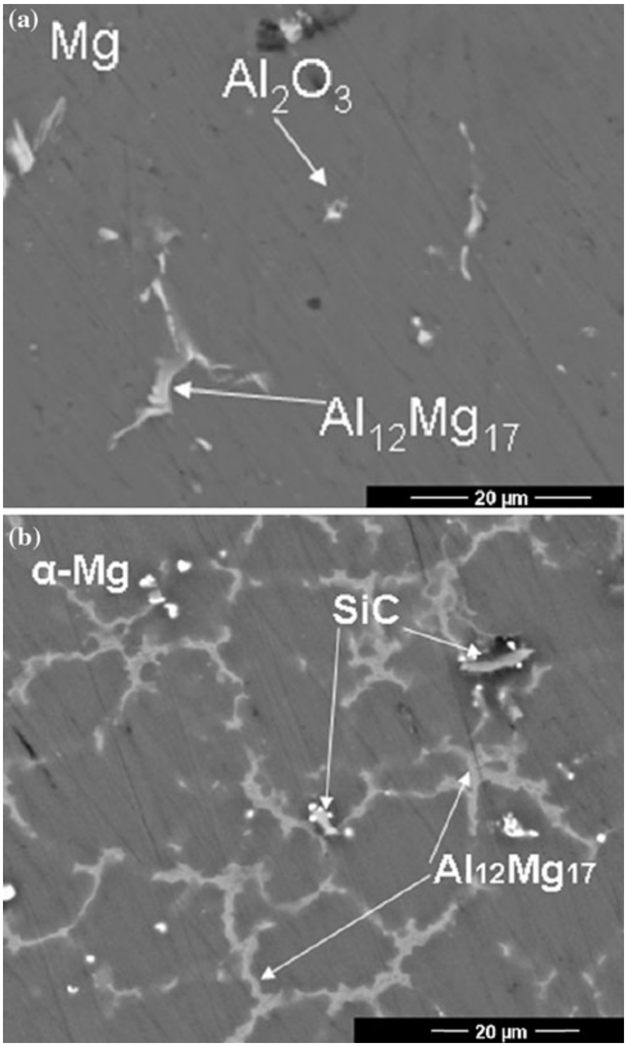

Fig. 9 SEM micrograph of gravity casting samples: **a** refined AZ91E + 1% Al_2O_3 alloy, **b** refined AZ91E + 1%SiC (3 µm powder)

the master alloys AZ91E + 10%SiC resulted in refined microstructures (Fig. 8c, d) and improvement of the mechanical properties (Tables 1, 2). The grain refinement mechanism is apparently restriction growth, since most of the SiC particles were located at the grain boundaries (Fig. 9b). Alternative mechanism of refinement, namely the formation of Al_2MgC_2 nucleation sites [15], could not be revealed.

The results (Tables 1, 2) prove that the introduction of ceramic particles into the Mg matrix improves the mechanical properties of AZ91E alloy. The overall effect is apparently a combination of reinforcement of the matrix by ceramic particles and a grain refinement effect. The improvement of tensile properties of the reference (without the addition of ceramic particles) AZ91E alloy due to grain refinement exclusively by rapid cooling (from ~110 µm for gravity casting, and to ~20 µm in HPDC) was about 16% for tensile strength and about 40% for yield strength, although it was accompanied by reduction in the maximum elongation (Tables 1, 2). In the case of ceramic-particles-added HPDC alloys, an additional improvement of mechanical properties (Table 1) was achieved by a second mechanism, namely restriction of the dislocation movement and grain boundary sliding (GBS) by ceramic particles (composite strengthening). Compared to the reference HPDC AZ91E alloy, the composite strengthening (calculated as the tensile strength increase) can be evaluated as 25–30% for 1 µm-SiC particles (6–12% for 3 µm-SiC particles), and about 60% for the AZ91E + 1 wt% Al_2O_3 particles (Table 1). The yield strength is substantially increased only for the AZ91E + 1 wt% Al_2O_3 alloy (~50%). It should be noted that the maximum elongation is also increased and reaches the value of ~3% for this alloy.

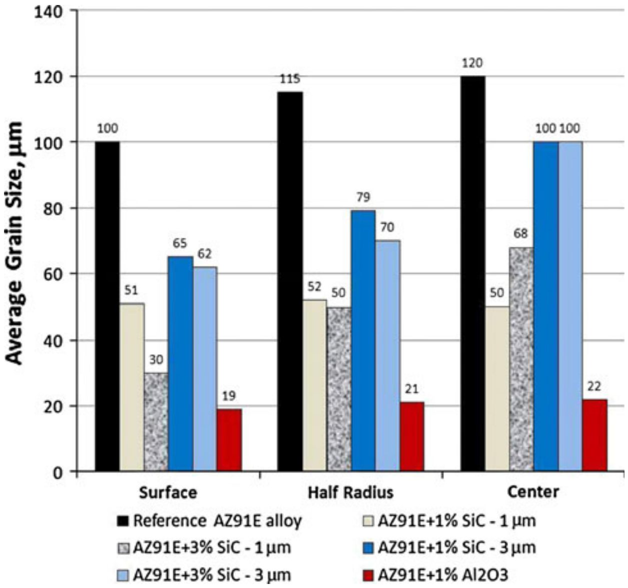

Fig. 10 Average grain sizes of the reference and refined AZ91E + SiC and AZ91E + Al_2O_3 alloys

In the case of gravity casting, the improvement may be mainly the result of grain refinement.

The influence of grain refinement on the mechanical properties of AZ91 alloy was investigated by Suresh et al. [8]. They achieved grain reduction from ~100 to ~35 µm by small additions of boron, accompanied by increase in the tensile strength from 180 to 226 Mpa and in the yield strength from 95 to 113 MPa. Their results can be well-described by Hall-Petch relationship $\sigma = \sigma_0 + k/d^{1/2}$ with $\sigma_0 = 73$ MPa and $k = 0.22$ MPa $m^{-1/2}$. In the case of gravity cast alloys, the present results for yield strength can be also well-described by the Hall-Petch relationship with $\sigma_0 = 79$ MPa and $k = 0.36$ MPa $m^{-1/2}$ (Fig. 12a). Using the same Hall-Petch slope, $k = 0.36$ MPa $m^{-1/2}$, for the tensile strength of gravity cast alloys (Fig. 12b), one can

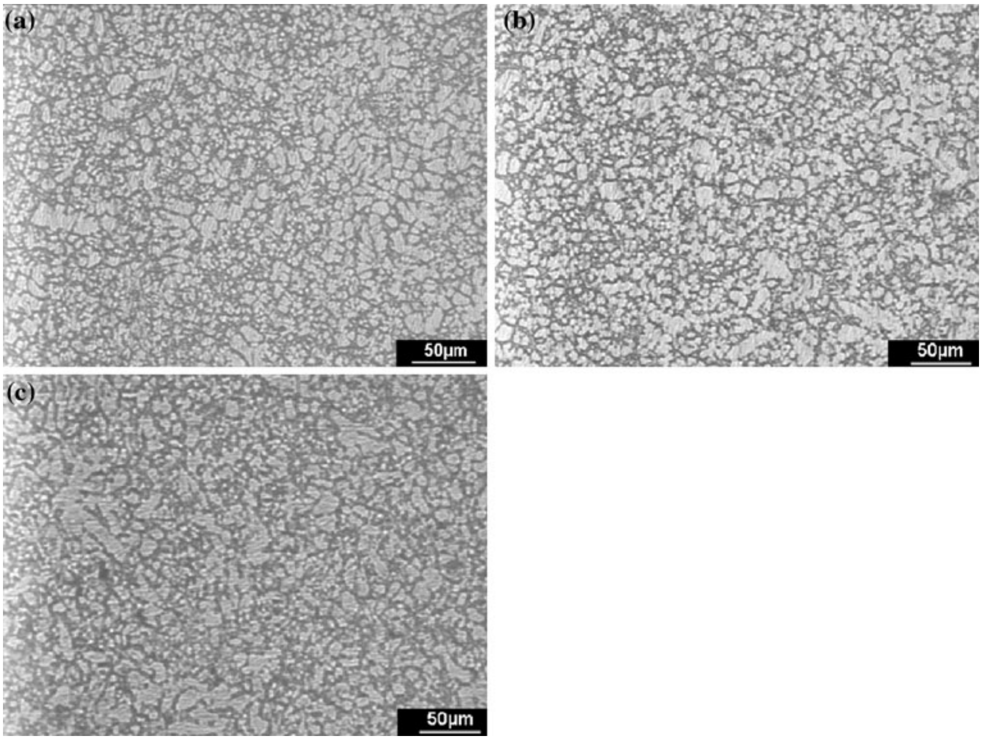

Fig. 11 Optical micrographs of half radius regions of high-pressure die casting samples: **a** reference AZ91E alloy, **b** refined AZ91E + 1% Al_2O_3 alloy, **c** refined AZ91E + 3%SiC (1 μm particles)

Table 1 Tensile test results for high-pressure die-casting samples (standard ASTM E 8 M)

	AZ91E	AZ91E + 1%SiC 1 μm powder size	AZ91E + 1%SiC 3 μm powder size	AZ91E + 3%SiC 1 μm powder size	AZ91E + 3%SiC 3 μm powder size	AZ91E + 1%Al_2O_3 30 nm powder size
Tensile strength (MPa)	183	230	204.8	238	195	300
Yield strength (MPa)	160	168	160	180	155	240
Elongation (%)	1	1.7	1.2	1.5	1.3	3

Table 2 Tensile test results for gravity-casting samples (standard ASTM E 8 M)

	AZ91E	AZ91E + 1%SiC 1 μm powder size	AZ91E + 1%SiC 3 μm powder size	AZ91E + 3%SiC 1 μm powder size	AZ91E + 3%SiC 3 μm powder size	AZ91E + 1%Al_2O_3 30 nm powder size
Tensile strength (MPa)	157	190	169	173	167	270
Yield strength (MPa)	112.7	135	140	120	130	170
Elongation (%)	1.4	3.1	3.1	1.2	1.3	2.5

evaluate the contribution of the composite strengthening to the tensile strength. As can be seen, a minor reinforcement was obtained for the alloy with 1% of 1 μm-SiC particles (~10%), but a significant reinforcement was found in the AZ91E + 1 wt% Al_2O_3 alloy (~33%). The smaller reinforcement effect in gravity cast alloys compared to that achieved in HPDC alloys can be attributed to the smaller amount of grain boundaries in gravity casting, as against these in the HPDC counterparts. Therefore, the prevention of GBS by ceramic particles is less significant in gravity cast alloys (excluding AZ91E + 1 wt% Al_2O_3 alloy) due to the minor contribution of GBS to the overall plastic deformation.

Summary

The Mg/ceramic-particles master alloys Mg-15%Al_2O_3 and AZ91E + 10%SiC (1 and 3 μm SiC powders) were prepared using a nitrogen-induced wetting of ceramic

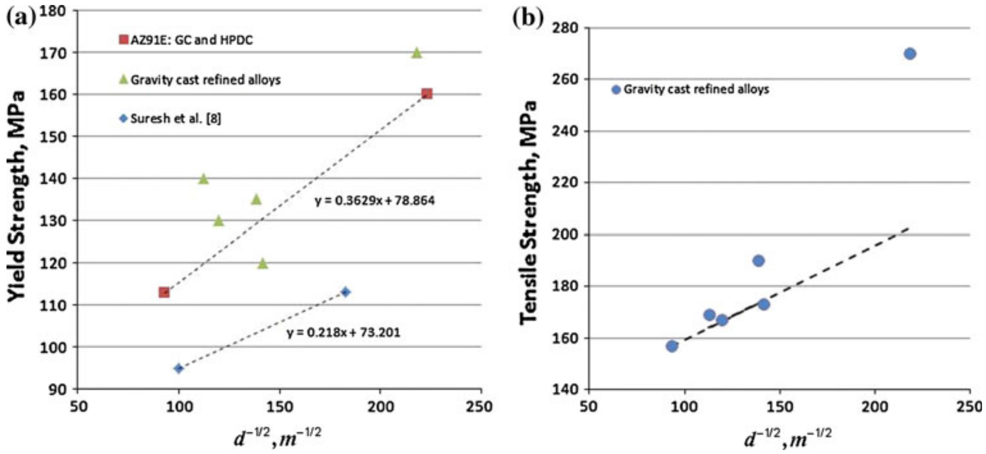

Fig. 12 Yield strength (**a**) and tensile strength (**b**) of the gravity die-cast alloys (Table 2) as a function of average grain size. The *dashed lines* correspond to the Hall-Petch relationships $\sigma = \sigma_0 + k/d^{1/2}$ with $k = 0.36$ MPa $\text{m}^{-1/2}$, $\sigma_0 = 79$ MPa (**a**) and $\sigma_0 = 123$ MPa (**b**)

particles by liquid Mg. Then these master alloys were used to modify the microstructure of AZ91E alloys by introducing low concentrations of ceramic particles into the melt before gravity and high-pressure die casting.

The mechanical properties of HPDC alloys with addition of ceramic particles were substantially improved as against the gravity die cast counterparts. This is a combined effect of grain refinement by a characteristic rapid cooling and reinforcement of the grain boundary regions of the alloys by ceramic particles (referred to as "composite strengthening"). The gravity cast alloys were grain refined by additions of ceramic particles: the alloy AZ91E + 1%Al_2O_3 was grain refined to ~20 μm and the alloys AZ91E + SiC were grain refined to ~50 μm, as against 100 ÷ 120 μm of non-refined reference alloy. The mechanical properties of the gravity cast refined alloys are substantially better than those of the AZ91E reference alloy. This improvement is mainly attributed to the grain refinement effect, whereas the composite strengthening is significant only for the alloy AZ91E + 1%Al_2O_3, which exhibited the best mechanical properties.

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