Effect of Al_4C_3 Particle Size Distribution in a Al–2.5C Master Alloy on the Refining Efficiency of the AZ31 Alloy

Yu-Zhen Zhao¹ · Xiao-Teng Liu¹ · Hai Hao¹

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Abstract The Al–2.5C master alloy is prepared to investigate the effect of the Al_4C_3 particle size distribution on the refining efficiency of the AZ31 alloy. The results indicate that the Al_4C_3 particles are potent nucleation substrates for primary α -Mg grains. With 1.0 wt% master alloy addition, the grain size is reduced from 204 to 70 μm . The grain refining efficiency of the Al_4C_3 particles on the AZ31 alloy is calculated to be 0.04%–0.75%. Such low refining efficiency is mainly attributed to the size distribution of the Al_4C_3 particles. The particle sizes are in the range from 0.18 to 7.08 μm , and their distribution is well fitted by a log-normal function. The optimum particle size range for significant grain refinement is proposed to be around 5.0–7.08 μm in the present conditions.

KEY WORDS: Particle size distribution; Grain refining efficiency; Al–2.5C master alloy; Magnesium alloys

1 Introduction

Magnesium alloys are becoming increasingly attractive and promising in automotive and aerospace industries due to their excellent properties, such as low density, high specific strength and good castability [1–3]. However, Mg alloys are also associated with a number of limitations compared to other metallic materials. These limitations include poor ductility and strength, low creep resistance and poor workability [4, 5]. Grain refinement has been considered as one of the most effective approaches to simultaneously increase the strength, ductility and formability [1, 5].

Carbon inoculation, as an effective grain refining method for Mg–Al based alloys, has been widely studied in the past

decades [6–13]. One of the most commonly accepted grain refinement mechanisms of carbon inoculation is the Al_4C_3 nucleus hypothesis, namely the idea that the Al_4C_3 particles act as potent nucleation substrates for primary α -Mg grains [10, 11, 14]. In the past few years, various grain refiners based on the Al_4C_3 nucleus hypothesis have been fabricated and applied to refine magnesium alloys, such as Al–C master alloy [9, 15], Al–Ti–C master alloy [16] and Mg–50% Al_4C_3 master alloy [17]. All of these refiners have shown significant refinement effects on magnesium alloys. However, the emphasis of these researches focused on developing new grain refiners and investigating the influence of the refiner addition level on the refining effect for Mg cast alloys, but ignoring the effect of the nucleants size which also significantly affects the heterogeneous nucleation rate, varying the grain refining efficiency [18, 19]. The free growth model [20] revealed that the critical supercooling ΔT_n of the grains grown freely on the heterogeneous nucleating substrate is inversely proportional to the particle (nucleant) diameter d_p :

$$\Delta T_n = 4\sigma / \Delta S_v d_p, \quad (1)$$

where σ is the solid–liquid interfacial energy and ΔS_v is the entropy of fusion per unit volume. Quested et al. [21] found

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✉ Hai Hao
haohai@dlut.edu.cn

¹ Key Laboratory of Solidification Control and Digital Preparation Technology (Liaoning Province), School of Materials Science and Engineering, Dalian University of Technology, Dalian 116024, China

that the nucleant TiB_2 particles in a commercial Al–5Ti–1B refiner have a log-normal diameter distribution, which can be used to quantitatively predict the grain size in aluminum alloys. Sun *et al.* [22] revealed that the key factor in determining the Mg–Zr master alloy grain refinement efficiency on Mg–Gd–Y alloys is the number density of Zr particles of appropriate size ranging between 1 and 5 μm . Nevertheless, rather limited experimental data are available concerning the size distribution of Al_4C_3 particles and its refining efficiency.

In the present study, the Al–2.5C master alloy was prepared to verify the refinement mechanism of the Al_4C_3 particles as nucleation sites for α -Mg grain. Furthermore, the refining efficiency of the Al_4C_3 particles and the inherent mechanism were systematically investigated. The ultimate purpose is to explain the reason why only a small proportion of added inoculant particles nucleate grains and to provide reference for the development of improved refiners.

2 Experimental

The Al–2.5C master alloys were fabricated by the powder metallurgy method. The mixture of Al powders (98% purity) and graphite powders (99.85% purity) was milled in a planetary ball mill for 10 h. Then, the mixture was cold-pressed into a cylindrical preform with a diameter of 30 mm. Subsequently, the cylindrical preform was sintered at 1000 °C for 1 h in vacuum condition and cooled down to room temperature in the furnace. The microstructures of the samples were characterized by scanning electron microscopy (SEM) after etching with Keller's reagent (solution of 1 mL hydrofluoric acid, 1.5 mL hydrochloric acid, 2.5 mL nitric acid and 95 mL H_2O). The statistical results of the total number and the size distribution of the Al_4C_3 particles were obtained through the combined application of Photoshop and Image Pro Plus software.

A series of grain refinement experiments were carried out to investigate the refining effect of the prepared Al–2.5C master alloys on the AZ31 alloy. The AZ31 alloy was smelted using an Mg ingot, an Al ingot, a Zn ingot and a Mg–4.5Mn alloy of commercial purity. The master alloy was inoculated into the AZ31 melt at 760 °C with additive amounts of 0.3, 0.6, 1.0, 1.5, 2.0 and 3.4 wt%, respectively. The melt was stirred for 60 s using a mild steel rod after holding isothermally for 25 min and then cast into a steel mold with a diameter of 25 mm and a height of 45 mm at 730 °C. The amount of Al in the master alloy was carefully checked in order to exactly control the Al content in the AZ31 alloy. In order to reveal the grain boundaries, the samples were held at 415 °C for 8 h in a heat treatment furnace and then water-cooled. The chemical compositions of the refined alloys were analyzed on an X-ray

fluorescence spectrometer (XRF-1800). The samples thus produced were sectioned horizontally 20 mm from the bottom and then prepared with a standard metallographic procedure. A solution of picric and acetic acid (solution of 5 mL acetic acid, 5 mL H_2O , 2.1 g picric acid and 35 mL ethanol) was used to highlight the grain boundaries. The micrographs presented in this paper were all taken from the central region of the etched samples. The mean grain size was measured by the linear intercept method. Standard stereological and weighing methods were applied to perform the mathematical calculations [23].

3 Results and Discussion

3.1 Grain Refining Mechanism

There is a general consensus that the Al_4C_3 particles are effective nucleants for Mg–Al alloys. This is supported by the observation that addition of Al_4C_3 results in a significant grain refinement of the Mg–3%Al alloy [11]. It has also been revealed that Al_4C_3 , with a planar disregistry of 4.05%, is a very potent nucleating substrate for primary Mg grains. The first-principles calculations were applied to analyze the sequence of Mg atoms onto the surface of Al_4C_3 (0 0 0 1) [24]. The calculated interfacial energy of the Mg/ Al_4C_3 interface is much smaller than that between α -Mg and magnesium melts, proving the excellent nucleation potency of the Al_4C_3 particles for α -Mg grains from interfacial atomic structure and atomic bonding energy considerations. In the present study, the Al_4C_3 nucleus hypothesis was confirmed by refining experiments of AZ31 alloy inoculated with a Al–2.5C master alloy. Figure 1 shows the optical micrograph of the as-cast AZ31 alloy with the addition of 1.0 wt% master alloy. The α -Mg grains show a typical dendritic structure. In the center of the dendritic structure, the nucleation particle can be clearly

Fig. 1 Optical micrograph of as-cast AZ31 alloy with addition of 1.0 wt% master alloy

observed. Figure 2 presents the SEM image and EDS analysis of a solution-treated AZ31 alloy with the addition of 1.0 wt% master alloy. In the center of the α -Mg grain, there is a particle marked by yellow tag containing the elements Al, C, O and Mg. Considering the thermodynamic improbability of the formation of Al–C–O compounds in view of the extremely low oxygen potential prevailing in the Mg–Al melt, the presence of oxygen is ascribed to the reaction between Al_4C_3 and water during the sample preparation according to the reaction: $\text{Al}_4\text{C}_3(\text{s}) + 12\text{H}_2\text{O}(\text{l}) \rightarrow 4\text{Al}(\text{OH})_3(\text{s}) + 3\text{CH}_4(\text{g})$ [25, 17]. Mg in the particle comes from the matrix. Hence, it is believed that the particle was originally an Al_4C_3 particle which acted as the nucleating substrate of α -Mg grains.

3.2 Size Distribution of the Al_4C_3 Particles

Based on the research of Kennedy *et al.* [26], the thermodynamic conditions of the reaction $4\text{Al}(\text{l}) + 3\text{C}(\text{s}) \rightarrow \text{Al}_4\text{C}_3(\text{s})$ can be satisfied when the sintering temperature is 1000 °C. Figure 3 presents the XRD patterns, SEM micrograph and EDS results of the Al–2.5C master alloy. As shown in Fig. 3a, the master alloy is composed of the phases Al_4C_3 and Al, without residual graphite. Numerous polygon particles are located at the boundaries of the aluminum particles, showing a net-like distribution, as illustrated in Fig. 3b. Han *et al.* [9] also fabricated the Al–2.5C master alloy by the powder metallurgy method. The XRD pattern of the Al–2.5C master alloy also showed no graphite peaks. However, the microstructure of the reaction products was different from that in the present study due to the different experimental conditions. The majority of the dark particles in Fig. 3b are of Al_4C_3 (Fig. 3c), while only a few gray particles are of Al_2O_3 (Fig. 3d). The oxygen present in the Al_4C_3 particles was introduced from the contamination during the sample preparation, as mentioned above. The Al_2O_3 particles were produced by a mild oxidation of Al during the sintering process.

The image analysis of Al–2.5C master alloy was used to obtain the size distribution of the Al_4C_3 particles. The total number of particles measured was of the order of eight hundred. The Al_4C_3 particles in the refiner are hexagonal plates with (0 0 0 1) faces on which nucleation occurs. In the present work, these particles are considered by approximation as disks of diameter d . A similar assumption has been used for the statistics of the TiB_2 particles in the Al–5Ti–1B refiner by Greer *et al.* [20]. Hence, the longest particle dimension for Al_4C_3 was measured. Table 1 presents the statistical data of the particles measured. The size distribution of the Al_4C_3 particles is shown in Fig. 4. The particle size ranges from 0.18 to 7.08 μm , with most of the particles having sizes between 0.5 and 2.5 μm .

According to the research by Quested *et al.* [27], the log-normal shape provided a good fit to the measured diameter distribution of the TiB_2 particles in Al–Ti–B master alloy. The log-normal distribution has the form:

$$N(d) = \frac{N_0}{\sigma d \sqrt{2\pi}} \exp - \left(\frac{[\ln(d) - \ln(d_0)]^2}{2\sigma^2} \right), \quad (2)$$

where d is the particle diameter, $N(d)$ is the number of particles of diameter between d and $d + d$, N_0 is the total number of particles, d_0 is the geometric mean diameter, and σ is the geometric standard deviation. This model is also available for any application of inoculation to alloy melts [21, 28]. As shown in Fig. 4, there is a good fit between the measured size distribution of the Al_4C_3 particles and the log-normal function by setting $d_0 = 1.11 \mu\text{m}$ and $\sigma = 0.54$. The mean particle diameter d_0 would be used to calculate the number density of total particles added to AZ31.

3.3 Grain Refining Performance

The analyzed chemical compositions of the refined alloys are listed in Table 2. The contents of the alloying elements are close to the nominal chemical compositions of the

Fig. 2 **a** SEM micrograph of solution-treated AZ31 alloy with addition of 1.0 wt% master alloy, **b** corresponding EDS result of the particle marked in Fig. 2a

Fig. 3 **a** XRD patterns, **b** SEM micrograph of Al-2.5C master alloy, **c**, **d** corresponding EDS results of the particles in Fig. 3b

Table 1 Statistical data of Al₄C₃ particles measured

Range of particle size (μm)	Number of particles	Percent (%)
0.18–0.5	55	6.67
0.5–1.0	270	32.77
1.0–1.5	225	27.31
1.5–2.0	108	13.11
2.0–2.5	75	9.10
2.5–3.0	29	3.52
3.0–3.5	26	3.16
3.5–4.0	16	1.94
4.0–4.5	10	1.21
4.5–5.0	3	0.36
5.0–5.5	1	0.12
5.5–6.0	3	0.36
6.0–6.5	1	0.12
6.5–7.0	1	0.12
7.0–7.08	1	0.12

Fig. 4 Measured size distribution (shaded bars) of Al₄C₃ particles in Al-2.5C master alloy with a log-normal fitting curve (solid curve). The inset shows one of the SEM micrographs used for the statistic of the particle size distribution

AZ31 alloy. The metallographic photographs of the solution-treated samples with different addition of grain refiners illustrated in Fig. 5 show that the Al₄C₃ particles have a significant refining effect on the AZ31 alloy, through comparing the samples with and without master alloy. The change in the grain size with increasing addition of the master alloy is shown in Fig. 6. The grain size sharply decreases by increasing content of master alloy. However,

when the amount exceeds 1.0 wt%, the grain size significantly increases and tends to become relatively stable. The original grain size of AZ31 without refinement is 204 μm. With the addition of 1.0 wt% of master alloy, the grain size is reduced to a minimum value of 70 μm with a decrease of 34.3%. A similar change in the grain size also has been found by Chen *et al.* [29] and Wang *et al.* [30]. Chen *et al.* [29] suggested that there is a saturation level for the melt to

Table 2 Analyzed chemical compositions of the AZ31 alloys inoculated with different additions of master alloy

Addition amount (wt%)	Element (wt%)			
	Al	Mn	Zn	Mg
0	2.3471	0.2989	0.8372	Balance
0.3	2.4279	0.3019	0.9535	Balance
0.6	2.3883	0.2934	0.7944	Balance
1.0	2.3564	0.2629	0.9069	Balance
1.5	2.2959	0.2694	0.9484	Balance
2.0	2.3816	0.3387	0.8585	Balance
3.4	2.5284	0.1738	1.066	Balance

contain the formed effective substrates. When their concentration exceeds this level, the frequency of mutual collisions, agglomeration and coalescence may sharply increase with massive particles, which will result in the decrease in the effective substrate concentration. In the present work, the agglomeration of the Al_4C_3 particles is one of the reasons that are responsible for the decline of the refining effect, as shown in Fig. 7. Wang *et al.* [30] investigated the grain refinement limit of the 6063 alloy inoculated by Al–Ti–C(B) master alloys and revealed that when two nuclei are close enough, the ability of one nucleus to nucleate a new solid grain will be suppressed by the solute diffusion caused by another nucleus which

Fig. 6 Grain size of AZ31 alloys with different additions of master alloy

nucleated firstly. When the addition of refiner exceeds the optimum amount, this suppression comes into effect, which results in the decrease in the refining effect. Besides, the massive release of solidification heat caused by the recoalescence process upon heterogeneous nucleation has a vital influence on the nucleating process in the tiny adjacent area [30]. Based on these standpoints, such change tendency of grain size can be easily understood.

Fig. 5 Metallographic photographs of solution-treated AZ31 alloy with different additions of master alloy

Fig. 7 SEM micrographs of Al_4C_3 particle cluster in AZ31 alloy

3.4 Nucleation Efficiency of the Al_4C_3 Particles

It has already been mentioned that the refining effect of Al–C master alloys on magnesium alloys is mainly attributed to the presence of Al_4C_3 particles which are considered as heterogeneous nucleation sites for α -Mg. However, not all particles in the melt can promote the heterogeneous nucleation. At typical levels of addition of inoculants to aluminum, the grain refinement is very inefficient, with at best 1% of the added particles acting as growth centers for grains [20, 27]. Supposing the number density of the effective nucleation sites is N_e , and the number density of

the total nucleation sites is N_0 , the nucleation efficiency of Al_4C_3 particles η can be expressed as follows:

$$\eta = N_e/N_0. \quad (3)$$

The number density of the effective nucleation sites was approximately equal to the number density of grains, considering that each nucleation site would eventually form a grain [28]. Based on the particle size distribution function and the amount of refiner added, the number density of the total nucleation sites can be obtained through mathematical calculations. Standard stereological and weighing methods were applied to complete the calculations. All the relevant parameters, the corresponding values and formulas used in this calculation are listed in Table 3. The detailed process of calculations is illustrated in Fig. 8. The calculation results for the addition of different amounts of refiner are listed in Table 4. Figure 9 presents the variation tendency of number density of total and effective particles with increasing amount of the master alloy. There is no doubt that the number density of total particles increases linearly with the addition of master alloy, as shown in Fig. 9. The variation of the effective particles number density, however, is opposite to that of the grain size, and the highest value is 1662 mm^{-3} achieved at 1.0 wt% refiner addition. Table 4 shows that the utilization rate of the Al_4C_3 particles in the refiner is very small, under the present conditions, with a top nucleation efficiency of

Table 3 Parameters and formulas used in the calculations

Quantity	Symbol	Units	Value
Number of particles per unit volume in master alloy	N_V	mm^{-3}	1.18×10^8
Number of particles per unit area in master alloy	N_A	mm^{-2}	1.31×10^5
Mean diameter of particles in master alloy*	d_0	mm	1.11×10^{-3}
Total number of particles measured in master alloy*	N	–	824
Total area measured in master alloy*	A_T	mm^2	6.30×10^{-3}
Mass of master alloy*	M_1	g	100
Volume of master alloy*	V_1	mm^3	1.20×10^4
Density of master alloy	ρ_1	g mm^{-3}	8.33×10^{-3}
Mass of AZ31 alloy ingot*	M_0	g	110
Volume of AZ31 alloy ingot	V_0	mm^3	6.36×10^4
Density of AZ31 alloy ingot*	ρ_0	g mm^{-3}	1.73×10^{-3}
Grain size*	D	μm	–
Number density of total particles added to AZ31	N_0	mm^{-3}	–
Number density of effective particles added to AZ31	N_e	mm^{-3}	–
Addition amount of master alloy*	m	g	–
Nucleation efficiency	η	–	–
Formula	$N_A = \frac{N}{A_T} \quad N_V = \frac{N_A}{d_0} \quad N_e = \frac{0.57^{[28]}}{D^3} \quad N_0 = \frac{N_V \cdot m}{\rho_1 \cdot V_0} \quad \rho = \frac{M}{V}$		

Note: The quantities marked with symbols “*” were obtained by experimental measurement

Fig. 8 Detailed process of calculations (the quantities marked with the symbol “*” were obtained by experimental measurement)

0.75%. This value is close to the efficiency of 0.1%–1% at best proposed for the Al–TiB₂ system [20], but far less than that of Zr particles on Mg–Zr alloys which was estimated as about 48.78% [28].

3.5 Mechanism Analysis of Nucleation Efficiency

Based on the above experimental results, it is found that only a small proportion of Al₄C₃ particles nucleate grains, no matter how much refiner is added. Greer et al.’s free growth model [20] is a major recent effort toward understanding the potency of particles, which involves the size distribution of particles and the particle number density. It is proposed that grain initiation on a potent flat substrate is determined by the linear dimension of the flat substrate, rather than by the nucleation event itself [31]. The critical condition for the Al₄C₃ particles to act as heterogeneous nucleation substrates is $d \geq 2r^*$, where d is the diameter of the particle and r^* is the critical radius of a nucleus, otherwise the nucleation cannot occur [20]. The size of a flat substrate thus has a decisive role in determining the formation of a grain on the substrate. According to Eq. (1), the larger the particle size, the smaller the critical supercooling ΔT_n . Hence, large particles have higher potency to act as heterogeneous nucleation sites, leading to finer

Table 4 Calculation results corresponding to different additions of refiner

Addition amount of master alloy (g)	Grain size (μm)	Number density of total particles (mm ⁻³)	Number density of effective particles (mm ⁻³)	Nucleation efficiency (%)
0.3	114	6.67×10^4	385	0.58
0.6	84	1.33×10^5	962	0.72
1.0	70	2.22×10^5	1662	0.75
1.5	117	3.34×10^5	356	0.11
2.0	111	4.45×10^5	417	0.09
3.4	124	7.56×10^5	299	0.04

Fig. 9 Number density of total particles and effective nucleation particles at different master alloy addition levels

grains. That is, the grain refinement performance is relatively dominated by the larger particles within a certain range.

In general, there is an optimum particle size range, which leads to the optimal refinement effect. This is 1–5 μm for Zr particles in Mg–Zr alloy [32], 6–6.5 μm for Al_2Y particles in Mg–10wt%Y alloy [33], 1–1.7 μm for TiC particles and 3–4.7 μm for TiB_2 particles in aluminum alloy [19, 20]. In the present work, the refining efficiencies of the Al_4C_3 particles are calculated to be 0.04%–0.75%. The optimum particle size range could not be obtained through experimental observation, because it is difficult to find a large number of nucleant particles on polished sections. It is proposed that the optimal size of the Al_4C_3 particles for magnesium alloys refining is about 5.0–7.08 μm in the present case. This conclusion is based on the following two reasons: (1) The larger is the particle size, the easier is the nucleation substrate. The grain formation occurs gradually from large particles to small ones; (2) according to the size distribution of the Al_4C_3 particles, those between 5.0 and 7.08 μm in size account for 0.84% of the total number of particles (see Table 1). This value is appropriate to account for the low efficiency of the inoculant.

To sum up, the particle size control has a great significance for the improvement of the refining efficiency of the Al–C master alloy. This conclusion suggests us to develop further research to prepare a refiner with appropriate particle size in the future.

4 Conclusions

1. The Al_4C_3 particles in Al–2.5C master alloy were confirmed to be the nucleation substrates for α -Mg grains in a refining experiment concerning the AZ31 alloy.
2. The Al_4C_3 particles have a significant refining effect on the AZ31 alloy. With addition of 1.0 wt% master alloy, the grain size was reduced from 204 to 70 μm with a large decrease by 34.3%. However, when the addition exceeds 1.0 wt%, the refining effect declines due to the Al_4C_3 particles agglomeration and the suppression effect of the solute diffusion.
3. The grain refining efficiency of the Al_4C_3 particles on the AZ31 alloy is calculated to be 0.04%–0.75%, with different additions of master alloy. Such low refining efficiency is mainly attributed to the size distribution of the Al_4C_3 particles. The particle sizes are in the range from 0.18 to 7.08 μm , and their distribution is well fitted by a log-normal function. The optimum particle size range for significant grain refinement is proposed to be around 5.0–7.08 μm , which accounts

for only 0.84% of the total number of particles in the present case.

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