Inoculant Fading-Resistance of Fe-Bearing Mg–3%Al Alloys Refined by Carbon Combining with Calcium Addition

Chengbo Li, Cheng Wen, Jun Du*, Wenfang Li and Meiyan Zhan

School of Materials Science and Engineering, South China University of Technology, Guangzhou 510640, China

Mg–3%Al alloys containing different trace Fe contents were treated by carbon combining with Ca inoculation. The holding time after being inoculation was adjusted from 5 to 80 min. The effect of holding time on grain refinement and the structures of nucleating particles were systematically investigated. Significant grain refinement is obtained for the Mg–3%Al alloys containing trace Fe refined by carbon combining with Ca inoculation. The grain size keep stable with prolonging the holding time and exhibit significant fading-resistance. The duplex-phase particles of Al–Fe coated with Al–C-rich phase could be easily observed and they should actually act as potent nuclei for Mg grains. The Ca content in the Al–C-rich shell is obviously higher than that in the Mg matrix. The segregation of Ca on the surfaces of different phases contributes to the formation of duplex-phase particles and keeps the duplex phase structure particles stable. Consequently, no inoculant-fading of carbon-inoculation occurred due to the high stability of the duplex phase structure particles. [doi:10.2320/matertrans.M2018208]

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1. Introduction

Magnesium alloys are excellent light metal materials to be utilized in automotive, aerospace, computer, communication and consumer industries due to the low density and high specific strength.¹⁾ However, magnesium alloys are also associated with some limitations, such as poor workability, poor corrosion resistance, low absolute strength and wear. Particularly, it is noticeable that Mg–Al based alloys, which play a dominating role in commercial Mg alloys, have poor mechanical properties. These defects lead Mg–Al based alloys to be incapable of meeting the requirements in many applications.²⁾ In general, grain refinement is a valid method to improve both mechanical properties and workability of Mg castings.^{3–5)} To date, some melt treatment processes of grain refinement for Mg–Al based alloys have been intensively researched, including the superheating treatment,^{6–8)} the Elfin process,⁹⁾ carbon inoculation^{10–12)} and solute addition.¹³⁾

Among these refining routes, carbon-inoculation and solute addition have been widely paid attention during the past two decades.^{14–18)} For these two refining routes, their refining mechanisms are different. The nucleation of Al–C-rich particle which is formed in Mg–Al melt is considered to be the mechanism of the carbon inoculation.^{16,17,19,20)} The grain refinement of solute addition is mainly controlled by constitutional supercooling.²¹⁾ Heterogeneous nucleation is based on the assumption that the nucleant particles should have good orientation relationships with the matrix in order to minimise the interfacial energy between the nuclei and the matrix. Until now, the exact Al–C particle which is formed in the carbon-inoculated Mg–Al melt remain controversial. Researchers have proposed that Al_4C_3 , Al_2OC , Al_2MgC_2 may be the heterogeneous nucleation particles. However, it is difficult to identify the exact phase composition since the Al–C-rich compounds are easily hydrolyzed.^{22,23)}

As for the carbon-inoculated Mg–Al alloy, recent researches demonstrate that grain refining potency of Mg–

Al alloy was easily influenced by the two key factors: impurity elements and holding time.^{9,11,24,25)} The impurity element of Fe is inevitable in the industrial Mg–Al alloys.²⁶⁾ The content of impurity iron in the primary magnesium is usually higher than 100 ppm, which is thought to be one of the main causes of poor corrosion resistance and low plasticity in commercial magnesium alloys. As for the Mg–Al alloys refined by carbon-inoculated, Fe was known as an unfavourable element for grain refinement by transforming Al_4C_3 into Al–C–Fe-rich particles or coating on the surface of Al_4C_3 particles.²⁷⁾ Contrary to the observations reported previously, Pan *et al.*²⁸⁾ indicated that the Al–C–O–Fe–Mn-rich particles could constitute the heterogeneous nucleation particles of primary Mg grains. Fe was a favourable element in the constitution of the nucleating particles rather than inhibiting element. The following research carried out by Du *et al.* reported that whether Fe inhibits the grain refinement of the Mg–Al alloy or not depends on the sequence of Fe addition and carbon inoculation.²⁵⁾ The result shows that Fe has no distinct effect on the grain refinement of Mg–Al alloy by carbon inoculation in the condition of Fe addition before carbon inoculation. In contrast, Fe played an unfavourable role in the grain refinement under the condition that the Mg–Al melt was fully inoculated by carbon before Fe addition. Based on this research, the present authors continued to investigate the influence of 0.1%Fe addition on grain refinement of Mg–3%Al alloy refined by carbon and Ca inoculations.²⁷⁾ Interestingly, the result shows that the existence of Ca could effectively avoid grain coarsening by Fe, regardless of the Fe addition sequence in the carbon-inoculated Mg–Al melt. A new concept of poisoning-free effect was provided in this study. Likewise, the same poisoning-free effect was substantiated in the grain refinement of Mg–3%Al alloy contained 0.1%Fe refined by carbon and Sr addition.¹³⁾

Moreover, holding time after carbon inoculation was also an important factor for grain refining efficiency. It is well known that an important phenomenon of fading effect is an inevitable issue during inoculation. The grain refining efficiency decreases with prolonging the holding time. This

*Corresponding author, E-mail: tandujun@sina.com

decreasing effectiveness is known as inoculant fading, which is closely related to the stability of nuclei and remaining number of effective inoculant particles.^{29–35} In the previous researches performed by Chen *et al.*, the grain sizes increased significantly with the extension of holding time for the AZ91 alloy inoculated by MgCO_3 and SiC, i.e., obvious inoculant fading phenomenon was observed.^{36,37} They believed that the number of effective nucleant substrates was decreased when the holding time was extended. However, no evidence was provided in their studies. In our recent study, no obvious inoculant fading was found when the holding time was prolonged to 120 min in high purity Mg-3%Al alloy.¹¹ However, the existence of 0.1%Fe could accelerate the inoculant-fading and the grain refining efficiency disappeared when the holding time was over than 30 min.³⁸

It is well known that the impurity element Fe is inevitable during the preparation of magnesium alloys.^{9,13,26} Carbon combining with Ca inoculation is an effective way to refine Mg-Al alloys and the poisoning influence of Fe on grain refinement can be inhibited due to the existence of Ca.²⁷ However, few studies were conducted to investigate the inoculant fading-resistance of Mg-3%Al alloy contained trace Fe refined by carbon combining with Ca inoculation. In the present study, the Mg-3%Al melt containing different trace Fe were treated by carbon combining with Ca inoculation. The holding time after carbon inoculation was extended from 5 min to 80 min. The following key issues are clarified: (1) how grain size changes with the holding time; (2) whether Fe accelerates inoculant-fading of carbon combining with Ca inoculation; (3) how the inoculating particles changes in the carbon-inoculated Mg-3%Al alloy containing trace Fe as a result of the Ca existence. Identification of these issues will contribute to deeply disclose the influence mechanism of Ca on grain refinement of carbon-inoculated Mg-Al alloys containing trace Fe.

2. Experimental Procedure

Mg-3%Al alloy was made from high-purity Mg (99.98%) and Al (99.99%). Mg-10%Ca master alloy were utilized in the present research. The graphite, magnesium and aluminum powders with mass ratio of 1:4:5 were mixed and prepared into cylindrical pellets ($\Phi 10 \times 5$ mm). The pellets were prepared by cold isostatic press (CIP) under a pressure of 150 MPa for 2 minutes. The addition contents of carbon and calcium were both 0.2% (mass ratio, the same below) of the melt. Al-15%Fe master alloys was used for Fe source. The different addition contents of Fe were 0.02%, 0.05% and 0.1%. About 350 g Mg-3%Al alloy was melted at 780°C in the high-purity MgO crucible under the protection of flux (SF_6 and N_2) using an electrical resistance furnace. After that, Mg-10%Ca master alloy was plunged into the Mg-3%Al melt. Then the carbon-containing pellets were added into the melt. During the inoculation, the melt was stirred manually with an MgO rod for a few seconds before being poured into a mould. After being held for different time (5, 20, 30, 50 and 80 min), the melt was poured into a tapered iron mould preheated at 500°C. The diameter of the tapered iron mould was $\Phi 20 \times \Phi 22 \times 30$ mm. It should be note that the melt

was stirred before being poured for different holding time. All the samples with the different holding time were poured from the same melt. It is well known that the cooling rate has an effect on the grain size.^{39,40} In this study the cooling rate of all samples were the same, therefore the effect of cooling rate on grain size will not be considered. Metallographic specimens were taken from the position of 15 mm from the samples bottom. Each sample was divided into two parts, one part was treated by heat treatment to observe the grain microstructures. The other part was without heat treatment to observe the nucleated particles. The heat-treated specimens (420°C for six hours and then cooled in the air) were polished and subsequently chemically etched. The etchant consists of picric acid (4.2 g), glacial acetic acid (10 ml), ethyl alcohol (70 ml) and distilled water (10 ml). Leica DFC320 optical microscope were utilized to observe the grain microstructures. The grain size was measured by linear intercept method (ASTM Standard E112-88⁴¹). To disclose the nucleation particles and their compositions, the cast samples etched by 2 vol% nitride acid ethanol solution were subsequently observed by electron probe microanalyzer (EPMA-1600) equipped with EDAX Genesis.

3. Results

3.1 Grain refining efficiency

The grain morphologies of the Mg-3%Al alloy containing different trace Fe are displayed in Fig. 1. The grain size of original Mg-3%Al alloy is about $434 \pm 23 \mu\text{m}$, as shown in Fig. 1(a). The grain size of Mg-3%Al alloy is increased to $557 \pm 46 \mu\text{m}$, after 0.02% Fe addition. Whereas, the grain size is decreased to $425 \pm 26 \mu\text{m}$ and $419 \pm 12 \mu\text{m}$ when 0.05% and 0.1% Fe were further added, respectively. No obvious grain refinement phenomenon appeared after Fe addition. The results indicate that Fe could not refine Mg-3%Al alloy and the grain size remain coarse.

Figure 2 shows the grain morphologies of the Mg-3%Al alloy refined by carbon combining with Ca inoculation with different holding time. The contents of C and Ca addition were 0.2%. The grain morphology of the sample with the

Fig. 1 Grain morphologies of the Mg-3%Al alloy with different Fe addition contents ((a) 0%Fe; (b) 0.02%Fe; (c) 0.05%Fe; (d) 0.1%Fe).

Fig. 2 Grain morphologies of the Mg-3%Al alloy refined by 0.2%C combining with 0.2%Ca inoculation with different holding time: (a) 5 min; (b) 20 min; (c) 30 min; (d) 80 min.

holding time of 50 min was not listed to avoid repeating. Obviously, the grain size of the Mg-3%Al alloy was significant refined by carbon combining with Ca inoculation. When the holding time was 5 min, the grain size was sharply reduced from $434 \pm 23 \mu\text{m}$ (shown in Fig. 1(a)) to about $188 \pm 5 \mu\text{m}$ (Fig. 2(a)). With prolonging the holding time, the grain size remained stable and no fading phenomenon occurred, as shown in Figs. 2(b) to (d). Moreover, the finest grain size with about $118 \mu\text{m}$ was achieved when the holding time was prolonged to 80 min. The result shows that the Mg-3%Al alloy refined by carbon combining with Ca inoculation had obvious advantage of fading-resistance.

The effects of Fe addition content and holding time on grain refinement of Mg-3%Al alloy refined by carbon combining with Ca inoculation were mainly investigated in this research. The grain morphologies of the parts of samples are shown in Fig. 3. Figures 3(a-d) present the grain morphologies of the Mg-3%Al alloy containing 0.02% Fe refined by carbon combining with Ca inoculation with the holding time of 5 min, 20 min, 30 min and 80 min. The grain size is sharply decreased from $531 \mu\text{m}$ (shown in Fig. 1(b)) to $232 \mu\text{m}$ and $215 \mu\text{m}$ when the holding time was extended to 20 min and 30 min, respectively. The grain size was further refined to $133 \mu\text{m}$ with prolonging the holding time to 80 min. Figures 3(e-f) and Figs. 3(g-h) show the microstructures of the Mg-3%Al alloy containing 0.05%Fe and 0.1%Fe refined by carbon combining with Ca inoculation with the holding time of 30 min and 80 min, respectively. Likewise, the grain sizes were very small and remarkable grain refining efficiency could be found even though the contents of Fe was increased to 0.05% and 0.1%. Also, no inoculant fading occurred with holding time extending to 80 min.

Figure 4 illustrates the influence of holding time on grain sizes of the Mg-3%Al alloy with different contents of Fe refined by carbon combining with Ca inoculation. The grain sizes of the Mg-3%Al alloy containing different trace Fe contents are coarse (shown in Fig. 1). After being inoculated by carbon combining with Ca, their grain sizes were

Fig. 3 Grain morphologies of the Mg-3%Al alloy containing different Fe addition contents refined by carbon combining with Ca inoculation with the different holding time. (a)-(d) Mg-3%Al-0.02%Fe with the holding time of 5 min, 20 min, 30 min and 80 min; (e)-(f) Mg-3%Al-0.05%Fe with the holding time of 30 min and 80 min; (g)-(h) Mg-3%Al-0.1%Fe with the holding time of 30 min and 80 min.

Fig. 4 Effect of holding time on grain sizes of the Mg-3%Al alloy with different Fe contents refined by carbon combining with Ca inoculation.

Fig. 5 Low magnification EPMA-BSE micrographs of the Mg-3%Al alloy containing different trace Fe contents refined by carbon combining with Ca inoculation with the holding time of 5 min ((a) 0% Fe; (b) 0.02% Fe; (c) 0.05%Fe; (d) 0.1%Fe).

significantly refined even though the holding time is 5 min. With increasing in the holding time, the grain sizes gradually decrease and keep stable when the holding time was over than 50 min. As for the effect of Fe content is concerned, the finest grain size can be fined in the sample containing with 0.05%Fe. The grain size is coarse when the Fe content is 0.02%. Finally, the grain sizes of all samples are almost same when the holding time is over than 50 min. The smallest grain sizes of all samples are obtained at 80 min and their grain sizes are about 115 μm . Obviously, the grain refining efficiency of carbon combining with Ca inoculation did not diminish even though the holding time was extended to 80 min. In our previous study, it was found that 0.1%Fe can accelerate the inoculant-fading for the Mg-3%Al melt refined only by carbon inoculation. When the holding time exceeded 30 min, the grain refinement phenomenon was disappeared.³⁸⁾ Based on the above results, it can be concluded that Fe had no effect on Mg-3%Al alloy refined by carbon combining with Ca inoculation. Moreover, the existence of Ca in the melt could inhibit the inoculant-fading for the Mg-3%Al melt containing trace Fe inoculated by carbon.

3.2 Investigation of nucleating particles

Detailed microscopic observation was conducted for the refined samples by EPMA in the backscattered electron model (BSE). Figure 5 shows the typical low magnification EPMA micrographs of the as-cast Mg-3%Al alloys containing different trace Fe refined by carbon combining with Ca inoculation with the holding time of 5 min. There exist many particles of white particles and tiny gray particles in the sample without Fe addition, as shown in Fig. 5(a). In the samples containing Fe (Figs. 5(b) to (c)), there exist three types of particles, i.e., white particles, tiny gray particles and particular particles with white core surrounded by grey halos. The white and gray particles are decreased sharply with the content of Fe increased. Figure 6 presents the micrographs of three different Fe-bearing Mg-3%Al alloys refined by

Fig. 6 Low magnification EPMA micrographs of Mg-3%Al alloy containing trace different Fe addition refined by carbon combining with Ca inoculation. (a)–(b) Mg-3%Al-0.02%Fe with the holding time of 30 min and 80 min; (c)–(d) Mg-3%Al-0.05%Fe with the holding time of 30 min and 80 min; (e)–(f) Mg-3%Al-0.1%Fe with the holding time of 30 min and 80 min.

Fig. 7 EPMA analysis of Mg-3%Al refined by carbon combining with Ca inoculation for 5 min.

carbon combining with Ca inoculation with the holding time of 30 and 80 min. There exist many particular particles in both refined alloys even the holding time is prolonged to 80 min. The morphology of these particular particles did not change and their number evidently increased.

To disclose the accurate chemical compositions, two typical particles existed in the sample of Fe-free Mg-3%Al alloy refined by carbon combine Ca inoculation were characterized by EPMA-EDS under high magnification, as shown in Fig. 7. The chemical analysis of particle A, B and the Mg matrix were shown in Table 1. The carbon and oxygen elements in the Mg matrix should be the resultant of

Table 1 Chemical compositions of the particle A, B, and Matrix as shown in Fig. 7.

<i>Element</i>	Particle A		Particle B		Matrix	
	<i>Wt%</i>	<i>At%</i>	<i>Wt%</i>	<i>At%</i>	<i>Wt%</i>	<i>At%</i>
<i>C</i>	8.27	14.71	4.50	10.01	5.36	10.20
<i>O</i>	5.77	8.03	1.70	2.83	2.81	4.02
<i>Mg</i>	69.26	63.47	23.17	25.47	88.91	83.38
<i>Al</i>	16.70	13.79	45.24	44.82	2.70	2.29
<i>Ca</i>	0	0	25.39	16.87	0.22	0.12

contamination during sample polishing and etching. It can be found that the particle A consists of Al, C and O elements since their contents are obviously larger than those in the Mg matrix. As for the particle B, its contents of C and O are low and almost same with the Mg matrix. However, the contents of Al and Ca elements are remarkably higher than those of the particle A and Mg matrix. Its Al and Ca contents are 45.24% and 25.39%, which were far exceeded the addition contents of 0.2%Ca and 3%Al. Therefore, the particles A and B should be Al–C–O-rich and Al–Ca-rich compounds, respectively.

Many particular particles and tiny white particles were easily detected in the Mg–3%Al alloys containing 0.02% Fe, as shown in Fig. 8(a). The two particles existed in the central area were analysed under high magnification to disclose the precise characteristics, as shown in Fig. 8(b). Obvious single phase structure could be observed for the particle A. However, the particle B assumed a typical duplex phase structure with a white core coated with a black shell. The compositions of A and B were characterized by EPMA line scanning and point analyses. The line scanning result is displayed in Fig. 8(c). Through EPMA line analysis, it can be seen that the elements of Al, O and Ca have high peaks at the position of particle A. The composition details obtained

Table 2 Chemical compositions of the particle A as shown in Fig. 8(b).

<i>Element</i>	<i>Wt%</i>	<i>At%</i>
<i>C</i>	4.99	9.74
<i>O</i>	4.41	6.47
<i>Mg</i>	69.70	67.26
<i>Al</i>	15.40	13.39
<i>Ca</i>	4.97	2.91

by point analysis are given in Table 2. The contents of Al, Ca and C were 15.40%, 4.97% and 4.99%, respectively. It can be seen that the contents of Al and Ca were higher than Mg matrix and content of C was almost the same with Mg matrix. Consequently, particle A should be Al–Ca-rich compound. Unlike the particle A, there exist two obvious peaks of O element in the position of bright core edge, as shown in the center of particle B. However, Al and Fe elements had only one peak in the center of bright core. It can be reasonably inferred that there existed a shell coated on the surface of Al–Fe compound. The compositions of the shell and core areas are listed in Table 3. In the particle B, the compositions of Al and Fe in the center core are higher than those in the shell while the content of C, O are lower. Obviously, Particle B is a duplex phase structure that Al–C–O-rich phase coated on the Al–Fe-rich phase.

Figure 9 shows EPMA-EDS line analysis results of a typical duplex-phase particle in the sample with 0.05%Fe. The chemical compositions of the core and shell are given in the Table 4. Obviously, the contents of Al and Fe in the core are higher than those in the shell of the particle. In the edge of the core, there also existed two obvious peaks of O and C element. It is found out that the content of Ca both in core and shell is higher than that in Mg matrix. Known from the Fig. 6, the particles with duplex-phase structure remain stable in the sample with prolonging the holding time to 80 min.

Fig. 8 EPMA analysis of Mg–3%Al–0.02%Fe refined by carbon combining with Ca inoculation with the holding time of 5 min. (a)–(d) Low and high magnification EPMA micrographs; Table 2 and 3: EPMA line and point analyses of the particles.

Table 3 Chemical compositions of the particle B (core and shell) as shown in Fig. 8(b).

Element	Core		Shell	
	Wt%	At%	Wt%	At%
C	5.31	10.25	8.09	14.61
O	6.07	8.80	11.38	15.43
Mg	72.97	69.61	70.71	63.10
Al	10.45	8.99	7.01	5.63
Ca	1.15	0.67	0.89	0.48
Fe	4.05	1.68	0.18	0.07

Table 4 Chemical compositions of the core and shell as shown in Fig. 9.

Element	Core		Shell	
	Wt%	At%	Wt%	At%
C	2.52	6.50	17.41	27.23
O	4.81	9.30	25.33	29.74
Mg	33.56	42.69	50.48	39.01
Al	14.61	16.75	4.14	2.88
Ca	0.58	0.45	1.93	0.90
Fe	43.91	24.32	0.72	0.24

Fig. 9 EPMA analysis of Mg–3%Al–0.05%Fe refined by carbon combining with Ca inoculation with the holding time of 5 min. a: High magnification EPMA micrographs and the chemical compositions of the core and shell; Table 4: EPMA line analysis of the duplex-phase particle.

To clearly disclose the element distributions for the duplex-phase particles, the EPMA-WDS map analysis results are illustrated in Fig. 10 for the sample containing 0.05%Fe with the holding time of 80 min. Three typical duplex phase structure particles were chosen for observation in the Fig. 10(a). The concentration of Fe was found to be high (red and blue points) in the center of three typical duplex phase structure particles, as shown in Fig. 10(b). In Figs. 10(c) and (d), it is notable that the C and O element concentrations are also high in the three duplex structure position and constitute a complete circle. In the center of the circle, there were little C and O element. Moreover, the distributions of C and O element always overlap. This observation provides obvious evidence that Al–Fe-rich phase was coated by Al–C–O-rich phase and it is corresponded with the result of the line and point analysis. Obviously, Ca element was distributed around the duplex structure position, as shown in Fig. 10(e). Different from the C and O element, the distribution of Ca element did not form a complete circle. This phenomenon indicates that Ca element was segregated towards to duplex phase particles during the solidification. It should be noted that there exist many little tiny particles of Ca and distributed in the Mg grain randomly. It should be noted that in the position of Fe element, the concentration of Al was found to be high, as shown in Fig. 10(f). These particles were actually Al–Ca-rich particles which were formed by Al and Ca reaction during solidification process.

4. Discussion

Concerning about the refining mechanism of carbon inoculation of Mg–Al alloys, two kinds of Al–C-rich compounds Al_4C_3 and Al_2MgC_2 were considered to be the potent nuclei for Mg grains due to the low disregistry with α -Mg phase.²²⁾ It is worth noting that Al–C–O particles were invariably observed in the carbon-inoculated Mg–Al based alloys,⁴²⁾ as the particle A shown in Fig. 7. These Al–C–O particles were supposed to be the hydrolyzate of Al_4C_3 or Al_2MgC_2 particles via the chemical reaction during sample polishing and etching: $\text{Al}_4\text{C}_3(\text{s}) + 12\text{H}_2\text{O}(\text{l}) \rightarrow 4\text{Al}(\text{OH})_3(\text{s}) + \text{CH}_4(\text{g})\uparrow$ and $2\text{Al}_2\text{MgC}_2 + 8\text{H}_2\text{O} = 2\text{MgAl}_2\text{O}_4 + 4\text{CH}_4\uparrow$.⁴³⁾ The Al–C–O phase was named as Al–C-rich compounds (Al_4C_3 or Al_2MgC_2) to avoid confusion in the following statement. In addition, effective grain refinement could be obtained for due to Ca addition. The refining mechanism was attributed to an intensive constitutional undercooling region in front of the advancing solid/liquid interface due to strong segregation ability of Ca during solidification.^{4,44,45)} In our previous studies,^{25,27)} it has been validated that a higher grain refining efficiency was able to be acquired by carbon combining with Ca inoculation. Known from Figs. 5 and 7, there exist two types of particles (Al–C–O and Al–Ca-rich particles) in the refined Mg–3%Al alloy by carbon combining with Ca inoculation. Addition of Mg–10Ca master alloy into the Mg–3%Al melt would cause the reaction of Al and Ca. Significant grain refinement was

Fig. 10 EPMA-WDS map analysis of Mg-3%Al-0.05%Fe refined by carbon combining with Ca inoculation with the holding time of 80 min. (a) The region of EPMA-WDS map analysis; (b)–(f) The distribution of Fe, C, O, Ca and Al element, respectively.

obtained and no inoculant fading occurred even though the holding time was prolonged to 80 min. The results indicate that the nucleating particles are stable in the Mg-3%Al melt refined by carbon combining with Ca inoculation.

As an inevitable impurity element, the debate about the influence of Fe on grain refinement of Mg-Al based alloys has lasted for decades. Early works suggested that Fe had superior grain refining ability on Mg alloys.^{9,28,46} Cao *et al.* reported that Elfinol process (anhydrous FeCl_3 addition) could refine the high purity Mg-3%Al and Mg-9%Al alloys.⁹ In other studies, it was found that Fe disturb the refining effect for some grain refinement processes, such as pure Mg refined by Zr⁴⁷ and Mg-Al alloy inoculated by carbon.²⁵ Fe had ever been regarded as a poisoning element by transforming from Al-C-rich nuclei into Al-C-Fe-rich compound.^{24,48} This ternary compound is not easy to be detected due to its low number density in the alloys and its accurate structure has not been revealed in details. Many researchers had proved that Al-C-Fe phase could not be heterogeneous nucleus of α -Mg in Mg-Al based alloys.^{7,49–51} However, Pan *et al.* considered that the Al-C-O-Fe(Mn)-rich particles could act as nucleating site of α -Mg grain.²⁸ In the present study, the addition of different level of Fe could not refine high purity Mg-3%Al alloy, as displayed in Fig. 1. Moreover, Fe had little influence on grain refinement of Mg-3%Al alloy refined by carbon combining with Ca inoculation, as shown in Figs. 3 and 4.

In the present study, Ca and Fe were added in Mg-3%Al melt by Mg-10%Ca and Al-15%Fe master alloys. Mg-10%Ca alloys would be decomposed and Ca was dissolved

Fig. 11 Schematic diagram of the formation processes of duplex-phase structure particle.

into the melt as a solute since the solubility of Ca in Mg melt is about 0.8% at 760°C.⁵² Al-Ca-rich particles were the resultant of Al and Ca reaction in the Mg-3%Al melt during the cooling process. In our previous research, grain refining effect could not be obtained by Fe and Ca addition.²⁷ These Al-Ca-rich particles were not possible to be the potent nucleant particles for α -Mg grains. As for the Al-15%Fe alloy, there existed AlFe_3 and AlFe phases.²⁵ Some Al-Fe-rich particles would remain in the melt due to the high melting point and low solubility of Fe in Mg melt. The Ca solute would segregate in the surface of Al-Fe-rich particles since it is a surface active element.

After being carbon-inoculated, the Al-C-rich particles had already formed in the Mg-3%Al melt. These Al-C-rich particles are very small with the size of less than 100 nm during the initial stage of carbon-inoculation.¹¹ These tiny Al-C-particles could spontaneously gather and grow to large particles. The inoculation and solidification processes for the Mg-3%Al melt containing Fe refined by carbon combining with Ca inoculation are possibly constituted as the following paths. Firstly, the Al-Fe-rich particles would pre-exist in the Mg-3%Al melt due to the addition of Al-15%Fe master alloy. The solute of Ca were segregated around the Al-Fe-rich particles. Secondly, the Al-C-rich particles were formed by a reaction between Al and C after the carbon-containing pellets were plunged into the melt. Some tiny Al-C-rich particles were adsorbed on the surfaces of Al-Fe-rich particles due to its high surface energy. Finally, the duplex phase structure particles were formed by Al-C-rich particles coated on the Al-Fe-rich particles. In addition, a large number of Ca atoms were precipitated from the melt during the solidification. These enrichment of Ca atoms would be further reaction with Al and these reaction would generate a stable Al-Ca-rich particle. The formation processes of duplex-phase structure particle are simply depicted in Fig. 11. In the present study, many typically duplex phase structure particles were discovered in the Mg grains. However, no obvious duplex phase structure particles were

found in the sample of Mg–3%Al–0.1%Fe melt was fully inoculated by 0.2%C without Ca addition.⁵¹⁾ Therefore, the formation of duplex-phase particles was attributed to Ca addition. Ca, C and O elements always overlap in the duplex-phase particles, as shown in Figs. 10(c) to (e). The Ca content in the shell area is about five to ten times as high as that in Mg matrix, as the result shown in Figs. 8 and 9. With the prolonging holding time, more and more solute of Ca was segregated to the duplex phase structure particles. As a consequence, the number of Al–Ca-rich particles were decreased as shown in the Fig. 6. The grain size is also determined by the number and distribution of effective nucleated particles in the constitutional undercooling region. In practice, it is found that the nucleated particles which play the role of heterogeneous nucleation are often less than 1% of the total nucleation particles.⁴²⁾ According to the free growth model:

$$\Delta T_n = \frac{4\sigma_{SL}}{\Delta s_v d_p} \quad (1)$$

where ΔT_n is nucleation undercooling, σ_{SL} is the solid-liquid interface energy, Δs_v is the entropy of fusion per unit volume and d_p is the diameter of the nucleation particle. Many small size nucleation particles can not be used as an effective heterogeneous nucleation particle due to the large nucleation undercooling (ΔT_n) required. Ca is tendency to segregate on the interfaces between different phases and attributes to the formation of duplex-phase particles. These duplex-phase structure will increase the size of nucleation particles (d_p). Therefore, more nucleation particles meet the required nucleation undercooling due to the decrease of the nucleation undercooling (ΔT_n). Consequently, the number of nucleated particles increases with the addition of Ca. The relationship between constitutional undercooling ΔT_{cs} and solid phase mass fraction f_s can be obtained:⁵³⁾

$$\Delta T_{cs} = m_l c_0 \left(1 - \frac{1}{(1 - f_s)^P} \right) \quad (2)$$

Where m_l is the slope of the liquids, c_0 is the alloy composition, $P = 1 - k$, k is the equilibrium distribution coefficient. At the beginning of solidification, the undercooling of initial nucleation is provided or triggered by the constitutional undercooling produced by the solute segregation. The nucleation events occur on the criterion matches $\Delta T_{cs} = \Delta T_n$. The increase rate of constitutional undercooling m can be calculated by eq. (2):

$$m = \frac{d\Delta T_{cs}}{d\Delta f_s} \quad (3)$$

At the beginning of solidification $f_s \rightarrow 0$, the increase rate of constitutional undercooling is about 0.49 and 0.13 with and without Ca addition, calculated by eq. (3). This shows that Ca addition can quickly establish the constitutional undercooling zone at the front of the solid-liquid interface at the beginning of solidification. Ca is tendency to segregate on the interfaces of the solid-liquid, which can increase the rate of constitutional undercooling and promote the occurrence of heterogeneous nucleation.

It is well known that the chemical and structural stabilities of inoculant particles are the key factors to determine the

grain refinement. There existed many duplex-phase particles with Al–C-rich phase coated on Al–Fe phase. Actually, the real potent nucleation particles were the shell of duplex-phase particles which was constituted by Al–C-rich phase. In our previous research, inoculation fading phenomenon was occurred in the Mg–3%Al alloy containing 0.1% Fe refined by carbon inoculation due to the poisoning effect of Fe by transforming the Al–C-rich phase to Al–C–Fe-rich phase.³⁸⁾ In this study, grain sizes of Mg–3%Al alloy containing different trace Fe contents kept stable even though the holding time was prolonged to 80 min. These results may attribute to the stable of the duplex-phase structure particles as shown in Fig. 6. Ca solute segregates on the surface of some phases or the interfaces between different phases and keep the duplex-phase structure particles stable. The enrichment of Ca atoms around the interfaces of Al–Fe-rich phase and Al–C-rich phase could inhibit the reaction of different phases. Consequently, Fe could not accelerate inoculant fading of carbon-inoculation due to the high stability of the duplex phase structure particles.

5. Conclusions

- (1) Significant grain refining efficiency is acquired for the Mg–3%Al alloy containing different trace Fe contents refined by carbon combining with Ca inoculation. The grain size keep stable with prolonging the holding time and no inoculant fading occurred.
- (2) The duplex-phase particles of Al–C-rich phase coated on Al–Fe phase is easily observed in the Mg–3%Al alloy containing Fe refined by carbon combining with Ca inoculation. These particles should be the potent nuclei for Mg grains.
- (3) Ca is tendency to segregate on the interfaces between different phases and attributes to the formation of duplex-phase particles. The Ca content in the Al–C-rich shell is distinctly higher than that in the Mg matrix.
- (4) The enrichment of Ca atoms through adsorption on the surfaces can effectively inhibit the reaction among different phases and keep the duplex-phase structure particles stable. Consequently, Fe could not accelerate inoculant fading of carbon-inoculation due to the high stability of the duplex phase structure particles.

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