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Evolutions of grain size and nucleating particles in carbon-inoculated Mg–3% Al alloy

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ABSTRACT

The grain refinement of primary α-Mg phase in the Mg–3% Al alloy was studied by carbon inoculation. The grain size and nucleating particles in the samples cast from the melt held at different times after inoculation were observed. It is found that the primary α-Mg grains in the Mg–3% Al alloy could be effectively refined from the melt immediately inoculated. The grain size maintained relatively stable with increasing holding time from 5 to 120 min. Therefore, no obvious fading effect could be observed in the Mg–3% Al alloy inoculated by carbon. However, the holding time had no obvious effect on the particle densities, particle size distribution and the mean size of Al–C rich particles in the samples held over 5 min after inoculation. The particles varied in a range of 2–4.5 μm with a mean size of 2.85 μm. The number of active nucleating particles with the size larger than 3 μm was stable at prolonged holding time over 5 min, which resulted in the less fading in the inoculated melt.

1. Introduction

So far, magnesium alloys have been widely utilized in the electronic and automobile industries due to their low density and high specific strength [1,2]. However, wider applications are limited by their poor ductility and formability. Improvements in ductility and formability are therefore desirable. Grain refinement is an effective method to improve the microstructural homogeneity, mechanical properties and formability of magnesium alloys [3–8]. In the various magnesium alloys, Mg–Al based alloys are the most common and economic commercial ones for which many grain refining methods have been developed [6–13]. Among these grain refining methods, carbon inoculation has drawn significant interest because of the excellent grain refining efficiency [6–9,14–22]. For example, Du et al. [6] found that the grain size of AZ31 magnesium alloy was refined from 480 to 180 μm by the addition of 0.2 wt.% graphite. Suresha et al. [7] discovered that the addition of 0.5 wt.% charcoal could reduce the grain size of Mg–3Al alloy from 500 to 80 μm. Wang et al. [8] investigated the grain refinement of AZ31 inoculated by 1 wt.% magnesium carbonate ($MgCO_3$). The grain size was refined from 310 to 117 μm.

Grain refining efficiency of carbon inoculation was closely related with process parameters (operating temperature and holding time, etc.) and carbonaceous agents. To date, many carbonaceous agents were utilized as grain refiner for Mg–Al alloys, such as graphite [6], charcoal [7], carbonates ($MgCO_3$ [8,9], $HfCO_3$ [15], $MnCO_3$ [16]), C_2Cl_6 [17], SiC [18,19] and Al_4C_3 particles [20,21]. The refining efficiency was also affected by the interactions between process parameters and types of carbonaceous agents. In the work of Motegi and Yano et al. [10,22], carbon powder was used to refine AZ91E alloy. There was no grain refinement if the operating temperature was less than 750 °C. $MgCO_3$ powder was used to refine AZ91D alloy by Chen et al. [9]. Grain refining efficiency was improved with increasing in the operating temperature from 650 to 790 °C. In another study from the same group [18], optimum operating temperature was about 760 °C for AZ91D alloy refined by SiC powders.

Besides operating temperature, the 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 inoculant effectiveness decreases after a prolonged holding time. This decreasing effectiveness is known as inoculant fading, which is closely related with the stability of nuclei and remained effective inoculant elements [23–27]. As for the carbon inoculation in Mg–Al alloys, the advantage of less fading has been widely appreciated [13,14]. However, contrary result was obtained by Chen et al. recently. The grain sizes were significantly increased with the extension of holding time for the AZ91 alloy inoculated by $MgCO_3$ and SiC, *i.e.*, obvious inoculant fading phenomenon was observed [9,18]. They believed that the number of effective nucleant substrates was

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decreased when holding time was extended. However, no evidence was provided in their studies.

From the viewpoint of processing, less fading is very important. Otherwise, the melt should be poured immediately after the melt is treated by inoculation. Carbon inoculation was regarded as a promising grain refining method for Mg–Al alloys. However, few studies were conducted to investigate the inoculant fading and its mechanism. In the present study, the Mg–3% Al alloy was chosen to avoid the influence of other elements. The Mg–3% Al melt was inoculated by carbon and then was held for different time. The evolutions of grain size and nucleating particles with the holding time were systematically investigated.

2. Experimental procedure

Highly pure magnesium (99.95%) and aluminum (99.99%) were used to avoid unfavorable effect of impurities on grain refinement. The pellets containing carbon (Mg–40% Al–10% C) were prepared from Mg–Al and graphite powders by cold isostatic press (CIP). The designed Mg–3% Al alloy was used in this study. The addition amount of carbon was 0.2 wt.% (mass ratio) of the experimental material. To exactly control the Al content in the Mg–Al melt, the amount of Al in the pellet was taken into consideration. The total weight of pure Mg and pure Al was about 20 g. The Mg–Al alloy was melted in a high-purity MgO crucible using an electric resistance furnace at 760 °C. The MgO crucible was put in a heat resistant steel pipe. Two thermocouples were used to control the holding temperature exactly. One was fixed between electrical resistance heater and steel pipe. The other was put into the crucible to directly measure the melt temperature. The melt was covered by a protective flux to avoid oxidation.

Eight samples were prepared in the present study, *i.e.*, the sample of Mg–3% Al alloy without treatment and those treated by carbon inoculation. The carbon-inoculating temperature was also set as 760 °C, which has been proved as the optimum temperature to achieve the high grain refining efficiency [6,10,22]. The pure Mg and pure Al were melted together and held for 20 min, and then this melt was poured to prepare the sample without treatment. The pellets containing carbon powder were plunged into the Mg–Al melt and promptly stirred for 1 min with a magnesia rod. The carbon-inoculated melt was held for different predetermined time (2, 5, 10, 20, 30, 60 and 120 min), respectively. One sample was made for each holding time. The melt was manually stirred before being poured for all samples. For the samples with holding time over 20 min, the melt was periodically stirred during being held. The melt was poured into a cylindric iron-mould (preheated at 500 °C) as quick as possible after being taken out from the furnace. The size of the sample was ∅20 mm × 25 mm. The compositions of the all samples were measured by direct-reading spectrometer (Foundry Master, Germany). Only Al content was given and listed in Table 1. The balance was Mg content. The difference of Al content for all samples was small and the effect of Al content could be negligible on the grain refinement.

Metallographic specimens were cut in the horizontal direction at the position of 10 mm from the samples bottom. To reveal the grain boundaries clearly, the samples were held at 420 °C for 6 h followed by air cooling. Such heat-treatment was widely applied in the researches on the Mg–Al alloys refined by carbon-inoculation [6,9,15,18]. The grain sizes were not altered obviously by this heat-treatment. These heat-treated samples were prepared by a standard procedure and then were etched to reveal the grain morphology. The etchant consists of picric acid (4.2 g), glacial acetic acid (10 ml), ethyl alcohol (70 ml) and distilled water (10 ml). Grain microstructures were observed using Leica DFC320 type optical microscope. Five pictures for every sample were taken from the central area of the metallographic sample. The grain size was evaluated using linear intercept method described in ASTM standard E112-88.

EPMA-1600 electron probe microanalyzer (EPMA) was utilized for the microstructural characterization and quantitative analysis of nucleating particles in the as-cast samples, which was etched with 2 vol.% nitric acid ethanol solution. A field emission transmission electron microscope (FE-TEM, Tecnai G^2 F20 S-TWIN) under high-angle annular dark-field (HAADF) imaging conditions was used to observe the tiny particles in the carbon-inoculated samples to study the formation process of the carbon-inoculating particles in the initial stage. The foils for TEM observation were prepared employing a FISCHIONE twin-jet electropolishing device, using a solution composed of lithium chloride, magnesium perchlorate, 2-butoxyethanol and methyl alcohol.

3. Results

3.1. Evolution of grain size

Fig. 1 shows the grain morphologies of the Mg–3% Al alloy with/without carbon-inoculation treatment. These pictures were taken under relatively high magnification (100×). The pictures used to evaluate the grain sizes were taken under low magnification (50×) since more grains could be observed in the pictures. The effect of holding time on grain size of the carbon-inoculated Mg–3% Al alloy is shown in Fig. 2. For the sample without treatment, the grain was coarse with a size of 610 ± 85 μm (Fig. 1a). The grain size was remarkably refined to 278 ± 57 μm after being inoculated by carbon though the holding time was only 2 min. The grain size was further refined to 223 ± 48 μm with increasing holding time to 5 min. For the samples with the holding time in the range of 10 to 60 min, the grain sizes were relatively stable and maintained in the range between 190 and 210 μm. The grain sizes were 205 ± 32, 193 ± 25, 198 ± 25 and 210 ± 40 μm for the samples with the holding time of 10, 20, 30 and 60 min, respectively. The grain size was slightly increased to 234 ± 31 μm with prolonging holding time to 120 min. Obviously, the grains were significantly refined for all the samples with after carbon inoculation. The holding time had no obvious effect on the grain refinement of the Mg–3% Al alloy which was inoculated by carbon.

3.2. Evolution of nucleating particles

Fig. 3 shows the EPMA back-scattered electron (BSE) images and EPMA line and point analyses of C, O, Mg and Al elements for the sample treated by carbon inoculation with the holding time of 5 min. There are many particles observed in this sample (shown in Fig. 3a). Magnified image was taken for the detailed structural features, as shown in Fig. 3b. These particles assumed mainly two kinds of morphologies. One was shown as the two particles in the area denoted by A in which there was an obvious hopper-like hole in the central area of the particle. The other was shown as the two particles denoted by B and C. There existed notches at the rim of the particles.

Fig. 3c shows the EPMA line analysis results measured from the two particles in the area A. The particles in the area A were further magnified to detect their composition by EPMA point analyses, as shown in Fig. 3d. The results were shown in Fig. 3e and f. Compared with the composition of matrix (shown in Fig. 3f), the contents of Al, C and O elements of the particles were significantly higher. These particles should be the Al–C–O particles. The existence of C and O existing in Mg matrix (Fig. 3f) should be the result of contamination during sample preparation, since the solubility of C and O in the solid Mg is almost zero [27].

As for other samples treated by carbon inoculation with different holding time, the particles containing carbon could be easily observed. Fig. 5 shows the EPMA-BSE images of the particles in the sample treated by carbon inoculation with the holding time of 20 and 60 min. The particles with notches, like the particles B and C in Fig. 3b, also existed in these samples. However, the particles with a hole in their central area were hardly observed. The particle densities for these three samples were almost the same. There were 15–20 particles existing in the pictures shown in Figs. 3a and

Table 1
Al content in the sample without treatment and the carbon-inoculated samples with different holding time (wt.%).

Content	Without treatment	Carbon-inoculated with different holding times (min)						
		2	5	10	20	30	60	120
Al	2.91	2.85	2.86	2.92	2.98	2.96	3.05	3.02