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Effects of Fe addition and addition sequence on carbon inoculation of Mg–3%Al alloy

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ABSTRACT

The Mg–3%Al melt was treated by carbon inoculation and/or Fe addition. The effects of Fe addition and addition sequence on the carbon inoculation of Mg–3%Al alloy were investigated in the present study. The role of Fe in the grain refinement of Mg–3%Al alloy treated by carbon inoculation was closely associated with the operating sequence of carbon inoculation and Fe addition. Fe has no obvious effect on the grain refinement of Mg–3%Al alloy by carbon inoculation under the condition that Fe pre-existed in the Mg–3%Al melt before carbon inoculation. However, Fe played an inhibiting role under the condition that the Mg–3%Al melt had been inoculated by carbon before Fe addition. The Al–C–O particles were observed in the sample treated only by carbon inoculation. In addition to Al–C–O particles, Al–C–O–Fe particles could be observed in the sample treated by Fe addition and then carbon inoculation. These Al–C–O and Al–C–O–Fe particles, actually being Al–C and Al–C–Fe phases, should be the potent nucleating substrates for Mg grains, resulting in the grain refinement. However, the Al–C–O–Fe-rich intermetallic particles were mainly observed in the samples treated by carbon inoculation and then Fe addition. The Al–C–O–Fe particles, actually being Al–C–Fe phases, formed under this condition should not be the potent nucleating substrates for Mg grains, resulting in the grain coarsening.

1. Introduction

During the past two decades, the consumption of magnesium alloys has steadily increased in the industries of electronics and automobile parts since magnesium is the lightest structural metal currently available in the world [1–3]. Among a broad range of magnesium alloys, Mg–Al type alloys take a dominant position in the magnesium products [1–3]. The grain refinement has been proved to be a very effective route to improve the mechanical properties of the Mg–Al type alloys [4–6]. Many grain refining methods have been developed, such as addition of solute elements [4,7,8], superheating [7–10], $FeCl_3$ inoculation [11] and carbon inoculation [5–8,12–19]. Among them, the carbon inoculation offers many practical advantages, like the lower cost, the lower operating temperature and the less fading [7,8]. The refining mechanism of the carbon inoculation firstly proposed by Emley in his book [20] is that the Al_4C_3 particles formed in the Mg–Al melt act as nucleating substrates for Mg grains during solidification. This hypothesis has been widely appreciated to date by many researchers [5–10,12–18].

The element of Fe was proved to be an important factor to determine the refining efficiency for the Mg–Al alloys refined by carbon inoculation [21–24]. Discrepant results that whether Fe inhibits the grain refinement or not were obtained by some researchers [21–24]. Haitani et al. [21] concluded firstly that Fe was an inhibiting element for grain refinement, since it poisoned the potency of the Al_4C_3 nucleating particles by transforming Al_4C_3 into Al–C–Fe-rich intermetallic compounds. From then on, this viewpoint was widely accepted by many researchers [7,8,10,22]. However, Pan et al. [23] insisted that Fe played a positive role in the formation of the nucleating particle rather than an inhibiting element. The same result was also obtained in the authors' previous study [24]. In these studies, the Al–C–Fe-rich intermetallic particles were also observed. However, these Al–C–Fe-rich particles acted as nucleating substrates for Mg grains resulting in the grain refinement [23,24]. It is difficult to understand clearly why contradictory conclusions were made for the same phenomenon. The exact mechanism is not disclosed yet.

It should be noted that the ultra-high purity raw materials, having very low content of Fe (<10 ppm), were used in the studies performed by Haitani and Cao et al. [21,22]. However, the commercial raw materials with relatively high content of Fe (0.05%) were employed by Pan et al. [23]. In the authors' previous study [24], different Fe contents (from 0.05% to 0.5%) were added into the Mg–Al melt before being refined by carbon inoculation. As far as the ultra-high purity Mg–Al alloys are concerned, Cao et al. [22] found

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they have native grain refinement due to the existence of native Al_4C_3 particles. In the Haitani's study [21], therefore, the native Al_4C_3 particles should pre-exist in the melt before Fe addition. On the contrary, the element Fe pre-existed in the Mg–Al melt before being refined by carbon inoculation in the studies performed by Pan and authors [23,24]. Therefore, it seems that whether Fe plays an inhibiting role or not in the grain refinement of Mg–Al alloys by carbon inoculation should be associated closely with the operating sequence of carbon inoculation and Fe addition.

This work aimed to study the effects of Fe addition and addition sequence on carbon inoculation of the Mg–3%Al alloy. Fe is an inevitable impurity element in the commercial Mg–Al alloys. From the viewpoint of commercial industries, such investigation has more practical significance, and also some important data can be provided to develop a suitable grain refiner, *i.e.* reliable and easy to be applied to Mg–Al alloys.

2. Experimental procedure

The raw materials used in the present study included relatively high purity magnesium (99.95%Mg, 0.002%Fe, 0.002%Mn), high purity aluminum (99.99%Al). The alloy used in the present study was Mg–3%Al alloy, which has the basic compositions widely used in industries as wrought magnesium alloy. To inoculate the Mg–Al melt, the pellets containing carbon powder were prepared beforehand. The details on the pellets have been described elsewhere [17,18].

The MgO crucible of relatively high purity was used in the present study to avoid the uptake of other impurity elements. The Mg–3%Al alloy of about 20 g was melted in an electric resistance furnace at 760 °C. To avoid oxidation, the melt was covered by a protective flux (45%$MgCl_2$, 35%KCl, 10%CaF_2, 10%NaCl (mass ratio)). The high purity Al–15%Fe master alloy was used to add Fe into Mg–Al melt. The addition amounts of Fe and carbon were 0.1% and 0.2% (mass ratio) of the melt, respectively. To exactly control the Al content in Mg–Al melt, the amounts of Al in the pellets and Al–15%Fe master alloy were taken into consideration.

Six samples were prepared in the present study. They were the sample of Mg–3%Al alloy without treatment and the two samples treated separately by carbon inoculation and Fe addition, as well as the three samples treated by the combination of carbon inoculation and Fe addition. The preparation details of the six samples, corresponding to the process Nos. 1–6, were described as following.

The pure Mg and pure Al were melted together and the melt was held for 20 min before being poured. This process route corresponded to process No.1 to prepare the sample without treatment. The pellets containing carbon powder were plunged into the Mg–Al melt. After that, the melt was held for 10 min, manually stirred for 1 min with a magnesia rod, and continued to be held for 10 min. This process route corresponded to process No. 2 to prepare the samp1e treated only by carbon inoculation. As for the process No. 3 to prepare the sample treated only by Fe addition, the pure Mg, pure Al and Al–15%Fe master alloy were melted together and the melt was held for 20 min before being poured.

The pure Mg, pure Al and Al–15%Fe master alloy were melted together, and then the melt containing 0.1%Fe was further treated by carbon inoculation, like as the process No. 2. This process route corresponded to the process No. 4. As for the process route No. 5, the Mg–Al melt was firstly treated by carbon inoculation, like as the process No. 2. After that, this Mg–Al melt was further treated by 0.1%Fe addition and was held for 10 min before being poured. The process No. 6 was almost the same as process No. 5. The carbon-inoculated melt further treated by 0.1%Fe addition was held for a longer time of 20 min before being poured.

For the samples prepared through process Nos. 4–6, they were all treated by the combination of carbon inoculation and Fe addition. However, the operating sequences of carbon inoculation and Fe addition were different. For the sample prepared through process No. 4, the Mg–Al melt was firstly treated by 0.1%Fe addition and then inoculated by carbon. The contrary sequence was carried out in process Nos. 5 and 6. The Mg–Al melt was firstly inoculated by carbon and then treated by 0.1%Fe addition.

The melts prepared through different process routes were poured into a cylindric iron-mould with the size of Ø20 mm × 25 mm, which was preheated at 500 °C. Metallographic samples were cut in the horizontal direction at the position of 10 mm from the bottom of the samples. To reveal the grain boundaries clearly, the samples were held at 420 °C for 6 h, and then were air-cooled. These heat-treated samples for grain morphology observation were prepared using a standard procedure. The grain microstructures were observed using the 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. The five data of grain sizes measured from five pictures were averaged. The average value and standard deviation were used to evaluate the grain size of every sample.

To observe the microstructural characteristics of nucleating particles in the samples, the as-cast samples etched with 2 vol.% nitride acid ethanol solution were further studied by Quanta 200 scanning electron microscope (SEM) equipped with IE350MT energy-dispersive X-ray (EDX) spectrometer.

3. Results

3.1. Grain refining efficiency

Fig. 1 shows the grain morphologies of the Mg–3%Al alloy treated through different process routes. 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 existed in the pictures. The grain sizes of the six samples are listed in Fig. 2. For the sample without treatment, the grain was coarse with a size of 610 ± 135 μm (Fig. 1a). The grain was significantly refined for the sample treated by carbon inoculation. Its grain size was decreased to 183 ± 25 μm (Fig. 1b). For the sample treated by 0.1%Fe addition, its grain size was about 525 ± 95 μm (Fig. 1c). For the sample treated through process No. 4, its grain size of 188 ± 31 μm was almost the same as the sample treated by only carbon inoculation. Compared to the samples treated through process Nos. 3 and 4, the grains became very coarse for the samples treated through process Nos. 5 and 6 (Fig. 1e and f). Their grain sizes were 582 ± 140 and 708 ± 165 μm, respectively.

Obviously, Fe had no effect on the grain refinement of the Mg–3%Al alloy by carbon inoculation under the condition that Fe pre-existed in the Mg–Al melt. On the contrary, Fe played an inhibiting role in the grain refinement of the Mg–3%Al alloy if the Mg–Al melt had already been treated by carbon inoculation before Fe was added. Consequently, a conclusion could be drawn that the effect of Fe on grain refinement of Mg–Al alloys by carbon inoculation was closely associated with the operating sequence of carbon inoculation and Fe addition.

3.2. SEM observations

By SEM observation, the Al–C–O particles were easily captured in the sample treated by carbon inoculation. The sizes of these particles distributed in the range between about 0.4 and 3 μm. Fig. 3 shows the typical images of the Al–C–O particles. The particles denoted by A to C were all Al–C–O particles, and their typical EDS spectra measured from the particles denoted by A and B are also illustrated in Fig. 3.

Judged by EDS spectra, two kinds of particles could be observed in the sample treated through process No. 4. They were Al–C–O and Al–C–O–Fe particles. Fig. 4 shows the typical images of the particles existing in this sample. The particle denoted by A was Al–C–O–Fe particle and the other particles denoted by B to D were all Al–C–O particles. The sizes of these particles distributed in the range between about 1.5 and 3 μm. The particles with a size of less than 1 μm were hardly observed.

As for the two samples treated through process Nos. 5 and 6, many intermetallic particles could be also easily observed. These particles were mainly Al–C–O–Fe particles, while the Al–C–O particles were hardly found. The images of the Al–C–O–Fe particles and their typical EDS spectra are shown in Figs. 5 and 6. The sizes of the particles existing in these two samples were obviously larger than those in the samples treated through process Nos. 2 and 3. The size distributions of the particles existing in these two samples were both in the range between about 2 and 10 μm. Compared to the sample treated through process No. 5, more particles with a larger size could be found in the sample treated through process No. 6. Judged by EDS spectra, the Al–C–O–Fe particles in these two samples could be classified into two types. One type was that the particles contained low content of Fe, such as the particles denoted by A in both Figs. 5 and 6. The other type was that the particles contained high content of Fe, such as the particles denoted by B in both Figs. 5 and 6.