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Full Length Article

A novel approach to melt purification of magnesium alloys

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Abstract

A novel low-cost method for melt purification of magnesium alloys, the melt self-purifying technology (MSPT), has been developed successfully based on a low temperature melt treatment (LTMT) without adding any fluxes. The iron solubility in the molten liquid of magnesium and its alloys, and the settlement velocity of iron particles were calculated. It is shown that the low temperature melt treatment is an effective method to decrease the impurity Fe content in magnesium and its alloys. Without any additions, the Fe content in the AZ31 alloy was reduced to 15 ppm from the initial 65 ppm, and the Fe content in the AZ61 melt was decreased to 20 ppm from the initial 150 ppm after the low temperature melt treatment. The results also showed that the Fe content in AM60 and AM50 dropped to 15 and 18 ppm, respectively, from the initial 150 ppm after the low temperature melt treatment. For ZK 60, the Fe content in the melt down to less than 5 ppm was achieved. After the low temperature melt treatment, the Si content in the above alloys was also decreased obviously.

Keywords: Magnesium alloys; Purification; Impurity; Melt; Iron; Silicon

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1. Introduction

The demand for applications of magnesium alloys in transport and structural fields is continuously increasing due to their low density and high strength-to-weight ratio [1–4]. However, their poor corrosion resistance and low plastic formability limit the viability of the increasing magnesium usage. The corrosion rate of commercial magnesium alloys is usually high in inorganic acidic and neutral solutions [5–10], which results from its high intrinsic dissolution tendency. It was reported that the presence of impurities (Fe, Si, Cu and Ni) with high standard electrode potential and second phases acting as local cathodes caused local galvanic acceleration of corrosion [5–7]. Among these impurities, Fe element, even with a small amount, can severely deteriorate the corrosion resistance of magnesium alloys [2]. Liu et al. [11,12], and Inoue et al. [13] reported that the corrosion rate of the alloy is substantially high due to its contamination with Fe, Ni, or Cu above the tolerance limit. Liu et al. [11,12] theoretically explained the corrosion tolerance limit for Fe through the Mg–Fe phase diagram. It is reported that the corrosion resistance of magnesium alloys is possibly not lower than that of aluminum alloys if the content of iron in magnesium alloys is less than 20 ppm [14]. Additionally, it has been reported that impurity Fe has a harmful effect on grain refinement, mechanical properties and rolling formability in AZ and ZK alloys [15–17]. Therefore, Fe content must be controlled to an extremely low level [2,18] in order to further improve the properties of magnesium alloys, especially corrosion resistance and formability.

At present, the purity of commercial primary magnesium used in industrial production of magnesium alloys is very high. 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. So far, several methods have been used to purify the magnesium alloy melt. The most conventional way of melt purification is adding fluxes to the melt during melting, which contains chloride salts [19,20] or fluoride salts [21]. It is true that some commercial fluxes can effectively

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remove nonmetallic inclusions from the melt of magnesium alloys, but the effects of these flux additions on decreasing the impurity elements of magnesium melt are not very satisfactory [22]. What is more, using fluxes may result in loss of alloying elements from the melt and secondary pollution through bringing in some nonmetallic impurity elements like F and Cl. For example. It is reported that $MgCl_2$ in the flux may cause the loss of Gd and Y from the melt [19–21,23,24]. The Mn addition with reasonable ratio of Fe/Mn has been employed to remove Fe [22,25], but it is difficult to control the ratio of Fe/Mn [26–28], and the content of iron in the melt is still unsatisfactory by using normal melting and casting process. In addition, Haitani et al. and Tamura et al. found that manganese disturbed grain refinement of magnesium alloys [29,30]. Zr, Ti, B or their compounds have also been used to remove Fe, and Atrens's group [5,11,18] has done excellent work on purification of magnesium alloy with Zr addition in lab in the past five years. However, the content of iron in commercial magnesium alloys is usually still higher than 20 ppm after using these additions when traditional melting and casting process is conducted [18,25,27,31–40]. In fact, little work has been carried out about the effects of low temperature melt treatment on the efficacy of removing Fe from the melt.

In order to overcome the disadvantages of flux additions and to decrease the content of iron in the melt to a much lower level, a novel approach for melt purification without adding fluxes, i.e. the melt self-purifying technologies (MSPT), has been developed by using low temperature melt treatment (LTMT), which is obviously different from traditional high temperature treatment methods [26,27,34–39]. The effects of different melt treatment temperature and the combination with Mn/Zr additions on the Fe content in the melt of magnesium and its alloys were investigated in the present work, and the super high-purity alloys with less than 5 ppm Fe were prepared.

2. Experimental procedures

2.1. Melt purification processes

The commercial purity magnesium, commercial purity AZ31, AZ61, AZ91, AM50, AM60 and ZK60 magnesium alloys were used in the present work. The used materials were melted in a stainless steel crucible in an electric-resistant furnace under an inert atmosphere with a CO_2 and SF_6 mixture. For commercial magnesium, when the temperature reached 730 °C, the magnesium melt was stirred for 5 min and subsequently held at 710 °C for 45 min, then cooled to different relative low temperatures of 650–690 °C for 30–90 min. For AZ31, AZ61, AZ91, AM50 and AM60 magnesium alloys, when the temperature reached 750 °C, the magnesium melt was stirred for 5 min and then cooled to different relative low temperatures of 610–670 °C for 30–90 min. For ZK60 alloy, when the temperature reached 760 °C, the magnesium melt was stirred for 5 min and subsequently held at 630–750 °C for 30–90 min. The samples for chemical composition analysis were taken from the upper melt in the crucible.

2.2. Melt purification with addition of Zr/Mn

The aim was to investigate the efficiency of Fe removal from magnesium melt using a fixed amount of Zr and Mn at different temperature for different holding time. The experimental procedure was similar to that of melt purification in commercial magnesium. Mg-30 wt.%Zr and Mg-4.27 wt.%Mn master alloys were added to the Mg melt at 740 °C. The melts were held at 730 °C for 45 min after being stirred for 5 min, then held at relatively low temperature for 30–120 min.

2.3. Analysis of chemical composition and second phases

The chemical composition of samples was analyzed using inductively coupled plasma-emission spectrometry (ICP, Optima 8300). Samples for scanning electron microscopy (SEM) were mechanically polished using 1 μm diamond paste, and etched for the same period of 1 min in 4% HNO_3 in C_2H_5OH dried in cool air stream. A TESCAN VEGA 3 LMH SEM, equipped with energy dispersive X-ray spectroscopy (EDX), was employed to characterize the microstructure and impurity particles containing iron in Mg alloys. X-ray diffraction analyses were carried out using Rigaku D/MAX-2500PC with Cu K radiation.

3. Results

3.1. Iron solubility, solid phases and their settlement velocity in the melts

The novel approach for purification is based on the solubility decrease of impurities in the magnesium melt by lowering the melt temperature, and iron particles or compounds containing iron are expected to form and settle out in magnesium melt. Early Mg–Fe and Mg–Fe–X phase diagrams show that Fe solubility in magnesium melt decreases with the lowering melt temperature [11,18]; however, there is the lack of detailed data in the very low iron content corner for most of commercial magnesium alloys. The change of iron solubility in the molten liquid of magnesium and its alloys has been calculated in the present work by using the Pandat Software Package (Database PanMg-2013), and the calculated results are shown in Fig. 1. It is shown from Fig. 1a that iron solubility in the magnesium melt is very high, and the calculated value is about 350 ppm at temperature of 710 °C. When the magnesium melt temperature drops to 650 °C, the iron solubility decreases to 180 ppm. From Fig. 1b, it can been seen that the additions of alloying elements can decrease obviously the iron solubility in the melt. With the decrease of the melt temperature, the iron solubility drops to less than 5 ppm for commercial magnesium alloys, AZ31, AZ91, AM60 and ZK60, which means that it is possible to prepare super-purity magnesium alloys by using suitable low temperature treatment as an additional step of melting and casting processes.

The experimental results by SEM and X-ray analysis showed that the remaining iron existed in the melt as single iron phase or compounds containing iron for commercial primary magnesium due to existence of other minor elements (Fig. 2a). For commercial magnesium alloys, no single iron phase is found and the remaining iron existed in the melt as compounds