Grain refinement and mechanism of CAl$_{0.5}$W$_{0.5}$ compound in Mg-Al alloys

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Abstract

The effect of CAl$_{0.5}$W$_{0.5}$ (CAW) compound on the grain refinement of Mg-Al based alloys was investigated. The results show that CAW compound is an effective and active grain refiner. The grain size of binary Mg-Al alloys is more than 500 µm, and it is changed to about 110 µm with a 1 wt.% CAW addition. The hardness increased with the decrease of grain size monotonously. The mechanical properties are improved by the addition. The fine grain size is mainly ascribed to the dispersed Al$_2$CO particles, which are very potent nucleating substrates for Mg-Al alloys. The nucleation cores formed by chemical reaction directly are well-distributed in the matrix.

Keywords: magnesium alloys; grain refinement; refiner; mechanism; mechanical properties

1. Introduction

In general, the grain size of Mg alloys is one of the most important factors to remarkably affect the quality of products because it is mainly associated with the mechanical properties. Therefore, lots of investigations on Mg alloys have been performed to achieve the small grain size of samples, such as controlling the cooling rate [1], adding other affective alloying elements [2], adding a grain refiner directly before or during the casting process [3-4] and especial extrusion process [5]. However, an effective grain refinement in Mg-Al system alloys is vital to industry application to some extent.

To date, several grain refinement methods have been developed to Mg-Al alloys, such as superheating [6], Elfinal process [7-8], and carbon additions [9]. Superheating treatment should include the existence of a specific high-temperature range for periods of about 30 min, after which the melt is quickly cooled to the normal casting temperature and poured. However, the refinement effect fades greatly when the melt is subsequently held at a low temperature [10]. The Elfinal process is relatively limited by adding anhydrous ferric chloride (FeCl$_3$) to form nucleation of Fe-Mn-Al compounds because the corrosion resistance of the alloy deases obviously with the presence of as little as 0.005 wt.% Fe [9].

Compared to the superheating and Elfinal process, the carbon addition is more attractive to the major industrial grain refinement because of low operating temperature, large melt volumes, and less fading with long holding time [10]. The variety of carbon addition is mainly associated with inorganic materials and organic materials. However, the emission of organic toxic gases and relative high-temperature brings environmental problems [11]. Therefore, a lot of work concentrates on the development of different high effective inorganic carbon-based grain refiners. The addition of various solid carbon containing materials, such as granulated graphite and granulated aluminum carbide, produces Al$_4$C$_3$ nucleation particles. However, the powder carbon is not active, and the reaction temperature is relatively high [5-6]. On the other hand, the Al$_4$C$_3$ powder is used directly [12]. Unfortunately, the effect of introducing Al$_4$C$_3$ is limited, which should be ascribed to the fact that the added grain refiner is prone to flock together during the solidification. Thus, the design of an effective grain refiner for Mg-Al based alloys, such as the zirconium grain refiner for Mg alloys, has been a very important subject.

Combined with the advantages of a traditional grain refiner, a series of ternary grain refiners are prepared in our laboratory. Their effects of grain refinement are investigated in detail. In present work, the novel grain refiner of CAl$_{0.5}$W$_{0.5}$ (CAW) is reported. The results proved that it is an effective grain refiner for Mg-Al alloys. The cores are well-distributed in the matrix instead of aggregation during the solidification. The compound of containing tungsten (W) element is selected by the following reasons. Firstly, the
crystal lattice of CAW is the same as the Mg matrix and thus, it provides the possible condition of a refiner. On the other hand, the chemical properties of W element are very stable and could hardly affect the other properties of alloys. Third, compared with other refiners, the redundant CAW addition could separate rapidly from the alloys because of the difference of density. The refinement mechanism is that the effective nucleation cores could be formed by chemical reaction directly.

2. Experimental

The temperature of the CAW acting as a grain refiner was investigated. High purity Mg ingots (99.98 wt.%) and high purity Al ingots (99.99 wt.%) were used to prepare a high purity Mg-4 wt.% Al (Mg-4Al) alloy. The alloy was melted in an electrical resistance furnace with aluminum oxide crucibles under anti-oxide flux (SF₆ + Ar). The CAW compound powder was prepared by mechanical alloying of C, Al, and W. The detailed experimental method was reported by the other researchers in our laboratory [13]. The Mg-4Al alloy was melted and 1 wt.% CAW was added at 700, 710, 720, and 740 °C for 10 min, and then, the melts were poured into iron mold at 700 °C.

The effect of CAW amount on the grain size of Mg-4Al based alloys was detected. The nominal compositions of experimental alloys were Mg-4Al, Mg-4Al-0.5CAW, Mg-4Al-1CAW, and Mg-4Al-2CAW. The CAW was added into melting alloys at 720 °C and then stirred for 10 min. The ingots were homogenized at 720 °C for 15 min before being poured.

In order to observe the microstructures of the investigated alloys clearly, all samples were subjected to solid solution heat treatment (420 °C for 1 h) to reveal the grain boundaries. Microstructures of the alloys were observed by optical metallography after being polished in alcohol and etched with an acetic-picric solution. The average grain size (AGS) of each sample was measured by the linear intercept method, and the average grain diameter was determined. The remarkable grain refine sample was examined using a scanning electron microscopy (SEM) equipped with an energy-dispersive X-ray spectrometer (EDX). The mean values are shown in the figure. The hardness of the alloy was measured by Brinell hardness (HB) test with a load of 294 N applied for a period of 15 s. The HB value was measured at least 20 points to reduce the error. The phases of the alloy in the bottom are confirmed by X-ray diffraction (XRD).

3. Results and discussion

3.1. Effect of adding temperature on grain sizes

Fig. 1 shows the microstructures of the alloys adding the grain refiner at different temperatures. The alloys are mostly composed of fine grain boundaries and the matrix. In the meantime, some dispersed black spots of Mg₁₇Al₁₂ precipitates are observed after solution heat treatment. It demonstrates that the grain size decreases with the monotonous increase of adding temperature.

![Fig. 1. Optical micrographs of Mg-4Al alloy with 1 wt.% CAW grain refiner at different temperatures after solutionizing at 420°C for 1 h.](image)

The results exhibit that the morphologies of samples formed during the solidification are obviously different. The CAW addition mainly concentrates along the grain boundaries at 700 °C, and the AGS is more than 150 µm. Remarkable grain refinement is observed at 720 °C, and the grain size is well-distributed in the matrix. It is believed that the reaction rate of forming nucleation sites increases greatly at relatively elevated temperatures. The refinement mechanism is similar to that of the previously reported carbon-containing refiner [11]. With the increasing of the number of particles containing carbon, the content of grain nuclei increases correspondingly during the following solidification.

3.2. Grain refinement

Fig. 2 shows the representative grain structures of Mg-4Al-xCAW alloys. Continuous network grain boundaries and some β-Mg₁₇Al₁₂ precipitates are observed in the investigated alloys. The AGS of Mg-4Al alloy is more than 500 µm, and it decreases greatly after 0.5 wt.% of CAW addition at 720°C. The remarkable fine grain size is obtained when adding 1 wt.% CAW compound. The value of AGS further changes slightly with the amount of CAW increasing. The AGS values of the alloys containing different contents of CAW are shown in Fig. 3. It is can be confirmed that the CAW addition can effectively refine the grain size of