Journal of Alloys and Compounds 496 (2010) 218–225

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Grain refinement of AZ91D magnesium alloy by SiC

T.J. Chen*, X.D. Jiang, Y. Ma, Y.D. Li, Y. Hao

Key Laboratory of Gansu Advanced Nonferrous Materials, Lanzhou University of Technology, Lanzhou 730050, China

ARTICLE INFO

Article history:
Received 9 January 2010
Received in revised form 26 February 2010
Accepted 1 March 2010
Available online 4 March 2010

Keywords:
AZ91D alloy
Grain refinement
SiC particle
Refining mechanism
Al_4C_3 particle

ABSTRACT

AZ91D magnesium alloy has been grain-refined by SiC particles. The effects of grain-refining parameters on its grain size have been investigated. Simultaneously, the corresponding refining mechanism has also been discussed. The results indicate that the SiC particle is an effective grain refiner for AZ91D alloy and can decrease the grain size from 311 μm of the not refined alloy to 71 μm under an optimized refining technology. The added SiC particles cannot directly act as the nucleation sites of α-Mg crystals and the Al_4C_3 particles formed from the reaction between the SiC particles and the molten alloy are the actual nucleation sites.

1. Introduction

Mg alloys are very attractive for applications in aerospace and automobile industries owing to their high specific strength. However, AZ91D alloy, one of the most commonly used Mg alloys, suffers from the challenge in meeting the requirements of strength, ductility, fatigue and creep resistance [1]. It is well known that grain refinement can improve mechanical properties of most of alloys. Thus, a fine-grain microstructure is important for overcoming the relatively low mechanical properties of AZ91D alloy. In addition, a fine-grain microstructure is also important for the properties of semi-fabricated products, e.g., ingots for extrusion and semisolid forming [2,3].

In view of grain refinement, Mg alloys can be classified into two broad groups: aluminum free and aluminum bearing. Aluminum free alloys can be well grain-refined by Zr and the corresponding technique has been commercially used. But for aluminum bearing alloys, such as AZ91D, AM50, AM60 and so on, there is no a commercially available grain refiner although several approaches have been developed [4]. These approaches mainly include four kinds, superheating [4–7], the Elfinal process [4,5,7], grain refinement by other additives [4,7–14] and carbon inoculation [4,15–18]. Comparatively, carbon inoculation has the best refining effect and good adaptability to alloys with different compositions and impurity contents [4]. So this method has attracted much attention. The carbon inoculation refers to that a quality of carbon-containing materials is added into Mg melt or bubbling the melt with carbonaceous gases prior to pouring. The key step of this method is the introduction of carbon into molten Mg alloys. Reported methods to introducing carbon include, but are not limited to, graphite, paraffin wax, lampblack, organic compounds such as C_2Cl_6 and C_6Cl_6, carbides (Al_4C_3, SiC, CaC_2), and bubbling the melt with CO, CO_2 and CH_4 gasses [4,15–19]. It can be expected that the absorptivity of carbon for the bubbling method are difficult to be accurately controlled and the reliability is not so well to guarantee similarly good refining effect for reach operation. For the additions of organic compounds of C_2Cl_6, C_6Cl_6, the introduced carbon also results from gasses decomposed from the additives and they have similar shortcomings to the bubbling method. Among the commonly used carbides, SiC has the largest potential in commercial applications because of its good grain-refining effect and relatively low cost [4,15]. In addition, the resulting Mg_2Si phase can improve creep strength of Mg alloys and it does not generate deleterious products [20].

However, there is no reference to detailedly report how the SiC inoculation parameters, such as addition amount, addition temperature, holding time at addition temperature and cooling rate from the addition temperature to pouring temperature affect the grain size and what are the optimal parameters. In addition, from the preparation of SiC particle reinforced Mg matrix composites, it is well known that it is quite difficult to introduce SiC particles into molten Mg alloys. It always needs special technology, i.e., preheating or roasting the SiC particles, mechanical stirring at semisolid state of Mg alloys [21,22]. To promptly introduce SiC particles into Mg melts in a short time prior to pouring, the addition, not similar to the composites, is in form of pure SiC particles, but a mixture with the other dilute powders. Furthermore, the dimensions of casting ingots affect the cooling rate during solidification, and thus the grain size. But the existing references have not involved these

* Corresponding author. Tel.: +86 931 2976573; fax: +86 931 2976578.
E-mail addresses: chentj1971@126.com, chentj@lut.cn (T.J. Chen).

0925-8388/$ – see front matter
doi:10.1016/j.jallcom.2010.03.002

Table 1
The detailed refining parameters used in this work.

Refining parameters	Refiner composition (in wt.)	Addition amount (wt.%)	Addition temperature (°C)	Cooling rate (°C s^{-1})	Holding time (min)	Rod diameter (mm)
Refiner composition	Al/SiC = 3:1, (Mg + JDMJ)/SiC = 3:1, Mg/SiC = 3:1	0.2	770	4.33	10	16
Addition amount	Mg/SiC = 3:1	0, 0.05, 0.1, 0.15, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4	770	4.33	10	16
Addition temperature	Mg/SiC = 3:1	0.2	710, 740, 770, 800	4.33	10	16
Cooling rate	Mg/SiC = 3:1	0.2	770	4.33, 1.57, 0.56, 0.2	10	16
Holding time	Mg/SiC = 3:1	0.2	770	0.2	10, 20, 30, 40	16
Rod diameter	Mg/SiC = 3:1	0.2	770	4.33	10	16, 45, 70

two aspects [4,15–20]. Finally, most of the existing references have focused on the refining mechanism and suggested that SiC particles, Al_4C_3 or Al_2CO particles formed from the reaction between SiC and Mg melt can act as nucleation sites of α-Mg crystals [4,15,16]. But there is dispute which kind of particle on earth acts [18].

Therefore, in this paper, the effects of the refining parameters by SiC particles mentioned above on the microstructure of AZ91D alloy have been investigated and the corresponding mechanism has also been discussed.

2. Experimental process

The alloy used in the work is commercial AZ91D alloy and it contains 9.04% Al, 0.6% Zn, 0.31% Mn and some trace elements or impurities (<0.002% Cu, <0.001% Fe, <0.001% Ni and <0.001% Be) (the percentage in this paper all refers to weight percentage). A quantity of AZ91D alloy was first remelted at 710 °C and degassed by 1.5% C_2Cl_6 (containing <0.002% ignition residue and 0.02% chloride). The melt then was adjusted to a given temperature and a quantity of SiC particle refiner was added and mechanically stirred for 30 s every 10 min (stirred for two times). Following, the melt was held for a given duration, and then cooled to pouring temperature of 705 °C in a given rate, and finally poured into a permanent mould with a given cavity diameter. The detailed parameters are presented in Table 1. Repeating the above experiment procedure according to the parameters shown in Table 1, the cast AZ91D alloy rods prepared by different parameters can be obtained.

Table 1 shows that six parameters, such as refiner composition, addition amount of SiC, addition temperature, cooling rate from addition temperature to pouring temperature, holding time at addition temperature and ingot diameter were considered. The refiner composition refers to the weight rate of the metal powders (Al or Mg) or reagent (JDMJ reagent) to SiC particles. Three kinds of compositions were employed, such as Al/SiC = 3:1, (Mg + JDMJ)/SiC = 3:1 and Mg/SiC = 3:1, which were named Al matrix refiner, hybrid matrix refiner and Mg matrix refiner respectively. In the hybrid matrix refiner, the weight rate of Mg + JDMJ is 1:1. The aim of these tests is to verify which composition can farthest increase the absorptivity of carbon. The size of the used SiC particles is 1–2 μm. The JDMJ is a commercial degassing reagent for Mg alloys and it contains 43–45% $MgCl_2$, 20–30% KCl, 20–30% NaCl, 3–5% $CaCl_2$, 3–4.5% $BaCl_2$ and 1% foaming agent. The powder mixtures with the compositions shown in Table 1 were milled for 2 h in a ball mill and then pressed into small blocks. During experiment, a quantity of the prepared refiner blocks was enwrapped by aluminum foil and then added into the melt. The addition amount in Table 1 refers to the net amount of SiC particles and does not include the other constituents of the refiner.

Some small specimens were cut from the obtained cast rods, and finished and polished by standard metallographic technique. Then they were etched by aqueous solution containing glycerol, nitric acid, hydrochloric acid and acetic acid and observed on an optical microscope (OM). In order to delineate grain boundaries and quantitatively examine the grain size, these specimens were first solution treated for 8 h at 420 °C, and then again processed according to the above procedures for preparing metallographic specimen and observed on the OM. The obtained images were analyzed by Image-Pro Plus 5.0 software. The diameter of a round with equivalent area to a grain is taken as the size of this grain. On each specimen, three images with magnification of 100 times were examined. The average value of all of the rounds' diameters is taken as the grain size of this specimen.

To clarify the grain-refining mechanism of SiC inoculation, the specimen with addition of 0.2% SiC particles were analyzed by energy dispersive spectroscopy (EDS) equipped in a scanning electron microscope (SEM). In addition, in order to obviously show the products formed from the reaction between the SiC particles and Mg melt, and thus deduce the detailed reaction and the refining mechanism, a specific experiment with addition of 5% SiC was carried out. The resulting alloy was observed on SEM and analyzed by X-ray diffractometer (XRD) and electron microprobe analyzer (EPMA).

3. Results and discussion

3.1. Effects of grain-refining parameters on the microstructure

3.1.1. Effect of refiner composition

Fig. 1 presents the microstructures of the AZ91D alloys not refined (i.e., refined by 0% SiC) and refined by the refiners with different compositions. It shows that the primary grains of the not refined alloy are developed dendrites with long secondary dendrite arms (Fig. 1(a)). After being refined by the Al matrix refiner, the third dendrite arms are likely refined, but the secondary dendrite arms, similar to those of the not refined alloy, are still quite developed (Fig. 2(b)). This indicates that the added SiC that has dissolved in the melt is little and the resulting refining role is very limited.