Materials Research Express

PAPER

Grain refinement and the microstructure evolution of Mg–9Al–5Ca alloy solidified under permanent magnetic stirring

Huanming Ji

Department of Physics and Information Engineering, Jining University, Qufu 273155, People’s Republic of China

E-mail: jihuanming@126.com

Keywords: permanent magnetic stirring, grain refinement, microstructure evolution

Abstract

To achieve the grain refinement of the as-cast Mg–9Al–5Ca alloy and understand the microstructure evolution during the grain refinement process, the permanent magnetic stirring (PMS) was applied to the solidification process of the alloy and the water-quenched experiment was carried out. The experimental results show that, the as-cast microstructure of Mg–9Al–5Ca alloy can be refined by PMS, and the better effect of grain refinement could be obtained with the increase of stirring rate. After applied PMS, the cooling of the melt is improved and the whole solidification time of the alloy is reduced. During the solidification process with PMS, there are more dendrite fragments produced in the melt and more initial dendrite grains at mold wall detached due to the forced convection, and then the grains would gradually grow into the fine and rose-like grains, which lead to the grain refinement of the as-cast alloy.

1. Introduction

As the lightest structural metal, magnesium alloys have been used in the fields of automotive, aerospace and telecommunication industries [1–8]. However, due to the limited mechanical properties, low ductility and poor corrosion resistance [9–13], the further application of magnesium alloys are restricted. As grain refinement of as-cast magnesium alloys is an effective way to improve strength and ductility at the same time [13], it has attracted much attention and becomes one of the most important techniques to extend the application of magnesium alloys.

Among the methods of grain refinement, permanent magnetic stirring (PMS), which is based on the rotating permanent magnets to produce stirring in the melt, has the advantages of no external additives, contactless with the molten metals, low power consumption and simple structure [14–18]. In 1992, Vives was the first to use the PMS in preparing semisolid slurries and obtained the satisfactory performances of solidified slurries [19]. Then, Fang [20] analysed the force field during the PMS process and considered the electromagnetic vibration influences matrix microstructure, subsequently affects corrosion property of the matrix. By thermal analyzing, Ordóñez [21] found the temperatures associated with the solidification of aluminum dendrites and the Al–Si eutectic are reduced and the microstructure is refined when the PMS is imposed. Otsubo [18] found that the growth of crystals for Sn–Cu–Sb alloy and the Al–Cu alloy is inhibited, and the region of equiaxed crystals is extended due to the PMS, which increases the hardness of the alloys. In addition, Zeng [22] found that with increasing the stirring rate and the center magnetic flux density, there is significant improvement in the flow intensity of the liquid as well as the grain refinement. By investigating the influence of PMS on the solidification of Al–4Cu and 2024Al alloys, Wei [17] found that PMS can effectively refine the grain structures of these alloys and lead to a slightly more uniform eutectic phase distribution in 2024Al alloy without changing eutectic phase types. Then, Zhang [15] found the dendritic structure of the Au–Cu alloys can be refined remarkably by a rotating permanent magnetic field, but with a too high rotation speed, the degree of grain refinement is reduced. Recently, El-Daly [23] found the flow driven by the permanent magnetic field has induced columnar-to-equiaxed transition of dendrite and reduced the crystallite size of Sn–Bi solders, which improves the mechanical properties of the solders.

© 2020 The Author(s). Published by IOP Publishing Ltd
It can be seen that the PMS can effectively refine the as-cast microstructure and improve the mechanical properties for many kinds of alloys. However, the investigation of PMS on the grain refinement of as-cast alloys is not enough, the experimental research about the microstructure evolution during the process has not been reported and the mechanism of the microstructure evolution for the PMS process is unclear until now. In the present study, the experimental research about the effect of PMS on the as-cast microstructure of Mg–9Al–5Ca alloy and the microstructure evolution during the PMS process were carried out and investigated.

2. Experiment process

In the research, Mg-9(wt%)Al–5(wt%)Ca alloy was prepared with purity magnesium (>99.8 wt%), purity aluminum (>99.9 wt%) and Mg-30(wt%)Ca master alloy (>99.9 wt%) in an experimental electrical resistance furnace, which shows in figure 1(a). Then the alloy was remelt at 700 °C, and stirred with a steel rod for 3 min. After cooled to 650 °C in the furnace and held for 10 min, the melt with steel crucible was took out and solidified with and without PMS under natural cooling, as shown in figure 1(b).

The PMS device used in the research is mainly composed of a pair of arc NbFeB permanent magnets, which service temperature can reach 180 °C, and a variable frequency electric motor, as is illustrated in figure 1(b). During the solidification process with PMS, the melt was magnetically stirred for 5 min with the rotation speeds of 0, 100, 200, 300, 400, 500 and 600 rpm, respectively. Then the alloy was natural cooled to room temperature. To investigate the microstructure evolution during the solidification process with and without PMS, the samples at the solidification temperatures of 585 °C, 575 °C and 565 °C, were quickly quenched into the ice water (0 °C) with crucible till completely cooled to obtain the water-quenched microstructure at different stages of solidification, which named water-quenched experiment. After standard metallographic grounding and polishing, the solidified samples were etched with picric acid solution. Then the as-cast microstructure of the samples solidified with different stirring rate and the microstructure of the water quenched samples were observed by stereomicroscope and metallographic microscope at the cross section of 2 cm from the bottom. At the same time, to understand the mechanism of the microstructure evolution, the longitudinal section of water quenched samples were also observed. To avoid oxidation and combustion of melt, all the experiment processes were carried out under an atmosphere of protective gas (0.5 vol%SF6 + CO2).

In the research, the the phase constitution of the as-cast Mg–9Al–5Ca alloy was detected by x-ray diffraction analysis (XRD), and the distribution of magnetic flux density between permanent magnets is measured with a CH-1600 digital gauss meter. The temperature change of melt during the solidification process was measured and recorded by a K-type armoured thermocouple inserted in the center of melt and linked with temperature recorder and computer. Based on the linear intercept method according to ASTM E112 standard, the average grain size of as-cast samples was measured. To evaluate the evolution of microstructure, the shape of primary α-Mg grains in the water quenched samples was characterized by the shape factor, which was calculated by

\[ SF = \frac{4\pi A}{P^2} \]

where A and P are the area and the perimeter of primary α-Mg grains, respectively (SF = 1:sphere; SF → 0: needle).

In the paper, the average grain size of as-cast samples and the shape factor for microstructure evolution were measured by an open source software of Image J. And the calculation formula of the standard deviation used is shown as follows:
where \( s \) is the standard deviation, \( n \) is the number of measurements, \( x \) represents an individual value and \( \bar{x} \) is the mean value.

### 3. Principle of PMS

Figures 2(a) and (b) show the distribution of magnetic flux density between permanent magnetics and the detail principle for PMS, respectively. As figure 2(a) shows, the whole distribution of magnetic flux density between permanent magnetics is symmetrical and uneven. The magnetic flux density decreases gradually from the inner surface of the permanent magnetics to the center of mold, but the weakest magnetic flux density is at the center of the top and bottom of mold. By rotating the permanent magnets, a rotating magnetic field is generated and an induced current is produced in the melt due to the electromagnetic induction. Under the interaction of the induced current and the rotation magnetic field, an electromagnetic force is generated, which leads to a forced convection in the melt. The electromagnetic force generated in the melt can be divided into the tangential force and the radial force, as figure 2(b) shows. And the calculation of the tangential force and the radial force can be described as follows [16, 18, 24]:

\[
F_t = \frac{1}{2} \sigma \omega r B^2 \\
F_r = \frac{1}{8} \sigma \omega \Gamma \mu_v B^2
\]

where \( F_t \) is the tangential force, \( F_r \) is the radial force, \( \sigma \) is the electrical conductivity of alloy, \( \omega \) is the rotating velocity of the magnet, \( r \) is the distance away from the center of mold, \( \mu_v \) is the kinematic viscosity of alloy and \( B \) is the magnetic flux density. The tangential force promotes the melt flowing in the direction of rotation magnetic field and the radial force can force the melt flowing in the vertical direction. As the electromagnetic force is proportional to the rotating velocity of the magnets, with the increase of stirring rate of PMS, the forced convection in the melt that caused by the electromagnetic force would get more intense.

### 4. Results and discussion

#### 4.1. Grain refinement under PMS

Figure 3 shows the as-cast microstructure of Mg–9Al–5Ca alloy solidified with and without PMS and figure 4 shows the average grain size of the as-cast samples with different stirring rate. As figure 3 shows, without PMS, the grains of the as-cast sample are coarse and the grain distribution is non-uniform, which the grains at the center region of the sample are obviously larger than those at the edge region. After applied PMS, the grains of the as-cast samples are refined and the grain distribution is more uniform than that without PMS, while the shrinkage and inclusions in the as-cast samples are not obviously reduced. With the increase of the stirring rate, the average grain size of the as-cast samples is gradually reduced and the better effect of grain refinement is obtained, which is also showed in figure 4. In addition, it is found from figure 4 that the improvement of grain refinement is fast firstly and then gets slow, and the change of the average grain size of the as-cast samples with the stirring rate fits a simple exponential relationship, which can be written as follows:
Figure 3. The as-cast microstructure of samples solidified with different stirring rate: (a) 0 rpm; (b) 100 rpm; (c) 200 rpm; (d) 300 rpm; (e) 400 rpm; (f) 500 rpm; (g) 600 rpm.

Figure 4. The average grain size of samples solidified with different stirring rate.
where x is rotation rate (less or equal to 600 rpm) and y is the average grain size of the as-cast sample (mm).

### 4.2. Solidification cooling curve

Figure 5 shows the as-cast phase constitution and the solidification cooling curves of Mg–9Al–5Ca alloy. It can be seen that, the as-cast alloy is composed by the phases of α-Mg and Al2Ca. When the melt is cooled to 586 °C, the α-Mg primary phase is firstly generated, followed by the precipitation of the Al2Ca phases below 507 °C, and the alloy is solidified at 426 °C. After applied PMS, the cooling rate of melt is obviously higher than that without PMS, although the characteristic temperatures in the cooling curves are not be significantly affected by PMS. At the same time, the time used for the precipitation of α-Mg phase with PMS is shortened by 11 s compared with that without PMS, and the time for the whole solidification process with PMS is shortened by 19 s. The reason for the high cooling rate and the shortened solidification time with PMS is that the heat dissipation of melt is obviously improved for the forced convection induced by PMS.

### 4.3. Microstructure evolution with PMS

Figure 6 shows the microstructure evolution of Mg–9Al–5Ca alloy with and without PMS. It is shown that a small amount of coarse dendrite grains appears in the melt when the solidification is at 585 °C without PMS. With the further cooling, there are more dendrite grains appear in the melt that are larger than that of dendrite grains solidified at 585 °C. In addition, a few fragments of dendrite grains can be seen in the melt at this stage of solidification, which would be developed into new dendrite grains. With the process of solidification, the melt is almost be occupied by more coarse dendrite grains when solidification is at 565 °C. After applied PMS, the melt develops fine grains when the solidification is at 585 °C. On decreasing the melt temperature, a large number of rose-like dendrite grains generate in the melt, while no highly developed dendrite grains can be seen. Besides, quite a few of dendrite fragments, which would be further grow into new rose-like dendrite grains, and the initial rose-like dendrite grains appear in the rest melt. At this solidification stage, the amount of dendrite fragments in the melt with PMS is more than that without PMS, and the grains are on the rose-like dendrite grains other than the developed dendrite grains due to PMS. When the alloy is at the solidification stage of 565 °C, there are a large amount of fine rose-like dendrite grains appeared in the alloy, which promotes the grain refinement of as-cast alloy. Figure 7 shows the difference of shape factor for primary α-Mg grains with and without PMS during solidification. It can be seen that, after applied PMS, the shape factor of primary α-Mg grains is obviously higher than that without PMS, which means the roundness of primary α-Mg is improved and is agree with the change of morphology for primary α-Mg grains from the coarse developed dendrite grains to the rose-like grains after applied PMS.

During the solidification process without PMS, the detachment and the fragmentation of the formed dendrite grains in the solidifying melt is little. Due to the natural convection, the formed nuclei that flow into the inner of melt would be likely remelted for the high temperature, only a small amount of the nuclei can survive as the effective nucleation sites, which leads to the coarse as-cast microstructure.

After applied PMS, as figure 2(b) shows, an electromagnetic force is generated in the melt, which can be divided into the tangential force and the radial force. The tangential force can promotes the melt flowing in the direction of rotation magnetic field, and the radial force can force the melt flowing in the vertical direction, forming a circulation flow. Because of the non-uniform distribution of the magnetic field in the melt, the whole
distribution of electromagnetic force is uneven, which leads to the melt flow as that shown in figure 8(a). Due to the forced convection, the detachment of the dendrite grains from the mold wall and the number of the dendrite fragments would be obviously increased, and the disperse of inclusions in the melt that providing nucleation substrates would be more uniform, which are shown in figures 6(e) and 8(b), respectively.

Then, under the action of the forced convection, as figure 8(a) shows, the detached dendrite grains and the dendrite fragments would be transported and continuous settled from the mold wall to the inner region of melt. In addition, due to the forced convection, the superheat of the melt, especially at the center zone, would be rapidly dissipated, which is confirmed in figure 5(b), and the temperature of the bulk melt would get more
homogenized. Thus, the remelting of the dendrite fragments and the detached dendrite grains would be significantly reduced, and the effective nucleation agents are greatly increased.

During the solidification process with PMS, with the precipitation of $\alpha$-Mg primary phase, induced current firstly pass the formed solid dendrite grains for the better electric conductivity than that of the liquid phase, and much Joule heat is generated, which leads to the partly remelting of the dendrite grains. At the same time, under the action of surface energy, the morphology of grains would gradually transformed from the coarse developed dendrite grains into the rose like grains. With the increase of stirring rate of PMS, both of the induced current in the precipitated $\alpha$-Mg phase and the forced convection in the melt would be increased, which promotes the heterogeneous nucleation and inhibits the growth of grains, achieving the grain refinement of as-cast alloy.

5. Conclusion

In the research, the effect of PMS on the as-cast microstructure of Mg–9Al–5Ca alloy and the microstructure evolution during the solidification process with PMS were investigated. The main conclusions are as follows:

(1) After applied PMS, the grains of as-cast samples are refined and the grain distribution is more uniform. With the increase of the stirring rate, the average grain size of the as-cast samples is gradually reduced and the change of the average grain size of the as-cast samples with the stirring rate fits a simple exponential relationship.

(2) The cooling of melt is obviously improved and the whole solidification time is reduced with PMS, but the characteristic temperatures in the cooling curves are not be significantly affected.

(3) During the solidification process without PMS, the grains would gradually grow into the coarse and developed dendrite grains. After applied PMS, there are more dendrite fragments produced in the melt and more initial dendrite grains at mold wall detached due to the forced convection, and then the grains gradually grow into the fine and rose-like grains, which lead to the grain refinement of the as-cast alloy.

Acknowledgments

This work was supported by the PhD research startup foundation of Jining University under Grant [number 2017BSZX02].

ORCID iDs

Huanming Ji @ https://orcid.org/0000-0002-3878-7705
References

[1] Wang S C et al 2014 Microstructure of Al–4.99Zr–1.1B master alloy and its grain refinement effect on AZ31 magnesium alloy Rare Met. Mater. Eng. 43 2567–71
[2] Wu L Q et al 2018 Microstructure, mechanical properties and wear performance of AZ31 matrix composites reinforced by graphene nanoplatelets (GNPs) J. Alloys Compd. 750 530–6
[3] Wang X J et al 2018 What is going on in magnesium alloys? J. Mater. Process. Tech. 34 243–7
[4] Qiu W et al 2019 Utilization of VN particles for grain refinement and mechanical properties of AZ31 magnesium alloy J. Alloys Compd. 781 1150–8
[5] Mordike B L and Ebert T 2001 Magnesium: properties—applications—potential Mater. Sci. Eng. A 302 37–45
[6] Luo A A 2004 Recent magnesium alloy development for elevated temperature applications Int. Mater. Rev. 49 13–30
[7] Luo A A 2013 Magnesium casting technology for structural applications J. Magn. Alloy 1 2–22
[8] Du J et al 2017 Discussion on grain refining mechanism of AM30 alloy inoculated by MgCO3 J. Magn. Alloy 3 181–8
[9] Tahreen N et al 2015 Influence of aluminum content on twinning and texture development of cast Mg–Al–Zn alloy during compression J. Alloys Compd. 623 15–23
[10] Nie K B et al 2015 Microstructures and mechanical properties of SiCp/ AZ91 magnesium matrix nanocomposites processed by multidirectional forging J. Alloys Compd. 622 1018–26
[11] Mao Y et al 2015 Preparation, characterization and wear behavior of carbon coated magnesium alloy with electroless plating nickel interlayer Appl. Surf. Sci. 327 100–6
[12] Yeganeh M and Saremi M 2015 Corrosion inhibition of magnesium using biocompatible Alkyd coatings incorporated by mesoporous silica nanocontainers Prog. Org. Coat. 79 25–30
[13] Karakulak E 2019 A review: past, present and future of grain refining of magnesium castings J. Magn. Alloy 7 355–69
[14] Aliferov A I, Morev A E and Pronzelev V A 2019 A study of the influence of rotating magnetic field of permanent magnets on the cylindrical melt bath Mater. Sci. Eng. 560 12–30
[15] Zhang J K and Li Y 2017 Effects of different rotation speeds on microstructure, hardness and corrosion resistance of the Au–Cu alloy Gold Bull. 50 137–45
[16] Zeng J et al 2017 A review of permanent magnet stirring during metal solidification Metall. Mater. Trans. B 48 3083–100
[17] Wei H G et al 2017 Effect of permanent magnetic stirring on the solidification microstructure and ingot quality of Al–Cu alloys J. Mater. Process. Tech. 240 344–53
[18] Otsubo F, Nishida S and Era H 2014 Solidification structure of Al–Cu and Sn–Cu–Sb Alloys obtained by casting through induction stirring using permanent magnet Mater. Trans. 55 806–12
[19] Vives C 1992 Elaboration of semisolid alloys by means of new electromagnetic rheocasting processes Metall. Trans. B 23 189–206
[20] Fang C F et al 2007 Research on AZ61 magnesium alloy by electromagnetic stirring and force field analysis Rare Met. Mater. Eng. 36 170–3 http://en.cnki.com.cn/Article_en/CJFDTotal-COSE200701041.htm
[21] Ordoñez S, Bustos O and Colas R 2009 Thermal and microstructural analysis of an A356 aluminium alloy solidified under the effect of magnetic stirring Int. J. Metalcast. 3 37–41
[22] Zeng J et al 2016 Effect of permanent magnet stirring on solidification of Sn–Pb alloy Mater. Desig 108 364–73
[23] El-Daly A A and Ibrahim M A 2018 Influence of rotating magnetic field on solidification microstructure and tensile properties of Sn–Bi lead-free solders Microelectron. Relia. 81 352–61
[24] Chen Z, Wen X L and Chen C L 2010 Fluid flow and microstructure formation in a rotating magnetic field during the directional solidification process J. Alloys Compd. 491 393–401