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Abnormal Grain Refinement Behaviour in High-Pressure Die Casting of Pure Mg with Addition of Zr as Grain Refiner

WENCHAO YANG,1,4 SHOUXUN JI,2 RUIRONG ZHANG,3,5 JUN ZHANG,1 and LIN LIU1

1.—State Key Laboratory of Solidification Processing, Northwestern Polytechnical University, Xi’an 710072, China. 2.—Institute of Materials and Manufacturing, Brunel University London, Uxbridge, Middlesex UB8 3PH, UK. 3.—Ministry of Education Key Laboratory of Micro/Nano Systems for Aerospace, School of Mechanical Engineering, Northwestern Polytechnical University, Xi’an 710­072, China. 4.—e-mail: wenchaoyang@nwpu.edu.cn. 5.—e-mail: ruirongzhang@nwpu.edu.cn

Abnormal grain refinement behavior was found during high-pressure die casting of pure Mg with addition of Zr as grain refiner. The grain size of die-cast pure Mg was only 6.71 lm, whereas it abnormally increased to 18.93 lm after addition of 1 wt.% Zr particles, indicating loss of the grain refinement effect. Further experimental results showed that a melt quenching effect in combination with an increased number of effective nuclei could result in ex­tremely refined grains in die-cast pure Mg, because many MgO particles could be activated simultaneously as nuclei. Therefore, it can be suggested that, before nucleation in high-pressure die-casting conditions, in the absence of effective (Zr) particles with small mis.t, particles (MgO) with larger mis.t and high number density might represent the most effective grain refiner.

INTRODUCTION

Refinement of cast structures is usually desirable for solidification processing of metallic materials, since it not only improves their mechanical perfor­mance but also enhances the casting process by reducing defects and improving its ef.ciency.1 The most widely used approach to achieve such refined structure is addition of particles to promote solidification, which depends on the lattice mis.t between the solid and substrate.2 For effective nucleation, the lattice mis.t between the nucleating substrate and nucleated phase should generally be as small as possible, to enhance the nucleation process by minimizing the interfacial energy and the under-cooling required for nucleation; For example, for Al alloys,3 addition of TiB2 particles is believed to be the most effective approach, offering lattice mis.t of 0.09% and nucleation undercooling usually less than 1 K.4.

Clearly, the crystallographic atomic matching between the particles and metal matrix is very important when estimating the nucleation effect of such particle addition, as the undercooling required for nucleation increases sharply with increasing lattice mismatch; For example, when used as nuclei for Mg alloys, the undercooling required for MgO particles with 5.46% lattice mis.t was found to be larger than that when using Zr particles with 0.61% lattice mis.t.5,6 Effective grain refinement requires many effective substrate particles to achieve hetero­geneous nucleation, as this allows greater under-cooling, so that more particles can participate in nucleation at the solidification front. In other words, if greater undercooling can be provided, more nuclei will be activated simultaneously before recalescence.

It has always been believed that Zr particles represent the most effective grain refiner for Mg­based alloys without Al addition during conven­tional metal mold casting, due to their lowest mis.t value (0.61%).7 However, abnormal grain refine­ment behaviour of Zr particles has been found for commercial pure magnesium (CP-Mg) grains under high-pressure die casting (HPDC) conditions. Therefore, the current research focused on this abnormal grain refinement behavior. A new hetero­geneous nucleation mechanism is proposed, which might help scientists develop more effective grain refiners.

EXPERIMENTAL PROCEDURES

CP-Mg and Mg-1 wt.%Zr alloys were melted separately in a steel crucible with 700 g melt under protection by 0.5% SF6 in dry N2 gas at 7000C for 4 h, followed by casting of /6.35 mm samples using a 4500-kN die-casting machine, used to provide a high cooling rate (about 103 K/s) and greater undercooling in the die cavity.8 The detailed param­eters of this HPDC process can be found in Ref. 8. For comparison, experimental condition TP1 (with cooling rate of about 3.5 K/s9) was adopted for the CP-Mg and Mg-1 wt.%Zr alloys. At the same time, 0.1 wt.% Zr particles were also added into the molten CP-Mg melt for die casting. To inhibit dissolution of the added Zr particles, the die-casting process was conducted within 5 s. The pouring temperature was set at about 6700C, and the Zr particles were added in the form of Mg-33.3 wt.%Zr master alloy (Zirmax, provided by Magnesium Elektron Ltd.). In addition, different superheating temperatures were also used to investigate the effect of melt quenching in the HPDC condition.

Grain size was examined by conventional optical microscopy. High-resolution transmission electron microscopy (HRTEM, JEOL 2100F) was used for microstructure investigations. To prepare thin foils for transmission electron microscopy (TEM), slices cut from the middle of die-cast samples were mechanically grounded before cutting into 3-mm round discs. These discs were further ground to 100 lm thickness, and subsequently ion-beam thinned using a Gatan precision ion polishing system at voltage of 5.0 kV and angle of incidence of 40to 60.

RESULTS AND DISCUSSION

Figure 1a and b show the microstructures of the CP-Mg and Mg-1 wt.%Zr alloy, respectively, obtained using the TP1 test condition, with corre­sponding macrographs inset in the top-right corner. It is clear that the microstructure of the CP-Mg sample presented basically coarse columnar grains, while the microstructure of the Mg-1 wt.%Zr alloy displayed .ne equiaxed grains with size of about 250 lm. There is an obvious grain refinement after addition of Zr particles to the CP-Mg melt. The microstructure of the CP-Mg and Mg-1 wt.%Zr alloy under the HPDC condition is shown in Fig. 1c and d, respectively. It is interesting to note that the grain size of the die-cast CP-Mg sample was very .ne, only about 6.71 lm. However, after 1 wt.%Zr particles were added into the CP-Mg melt, the grain size in the resulting die-cast Mg-1 wt.%Zr alloy was abnormally increased to about 18.93 lm (Fig. 1d). Compared with the results using the TP1 condition, the microstructure of the die-cast Mg-1 wt.%Zr alloy presented an obvious abnormal grain refine­ment behaviour.

Mg is easily oxidized at high temperatures, and no other nucleants were added to the CP-Mg melt. Therefore, formation of a large amount of MgO .lm or particles in the molten CP-Mg melt was inevi­table.5 During the HPDC process, when the molten CP-Mg melt passed through the ingate into the die cavity, it was sheared and mixed, so that such MgO .lms could be dispersed to increase the number density of MgO particles in the melt.10 Previous research confirmed that these MgO particles have a certain orientation relationship with the Mg matrix and could act as nucleation sites for Mg grains in AZ91D alloy.10 Therefore, these dispersed MgO particles might be able to act as nucleation sites for CP-Mg grains during die casting.

To verify the role of MgO particles, several factors must be isolated. Two key factors that should be considered for the HPDC solidification condition are: (1) the high shear resulting from the turbulent flow, and (2) melt quenching resulting from the high cooling rate in the die cavity. High shear resulting from the turbulent flow can occur when the CP-Mg melt passes through the ingate during the HPDC process, which could break the MgO films to form a large number of MgO particles. Similar high-shear technology developed by the Brunel Centre for Advanced Solidification Technology was used to con.rm this ingate effect in the HPDC machine, revealing that the number density of MgO particles dispersed from MgO films in the melt was indeed significantly increased.11 Men et al.12 confirmed that the total number of MgO particles in AZ91 alloy was about 2.1 9 105 mm-3, but this number increased sharply to 3.2 9 108 mm -3 after strong shearing. It is clear that the density of potential nucleation sites in the sheared melt is about three orders of magnitude higher than for the non-sheared melt. To con.rm the nucleation effect of MgO particles, a wedge model with different cooling rates was used for CP-Mg solidification. The cooling rate at different positions in the wedge model was calculated based on the equation developed by Burden and Jones,13 which can be written as

**E =T ¼ Zn**

where T is the cooling rate in K/s, the wedge thickness Z is in mm, and E and n are 250 and 1.1, respectively. The resulting curve of cooling rate versus thickness is presented in Fig. 2a, revealing a cooling rate of about 684.97 K/s at the wedge tip within 0.4 mm thickness. With increasing thick­ness, the cooling rate reduced sharply to 105.02 K/s when the thickness was increased to about 2.2 mm. Thereafter, the cooling rate dropped slowly. When the thickness was about 31.5 mm, the cooling rate was only about 5.62 K/s. The corresponding exper­imental results for CP-Mg samples without and with shearing are shown in Fig. 2b and c. Also, the microstructure at the wedge tip (. 0.4 mm thick­ness) is shown in the top-left corner. It is clear that, after the CP-Mg melt without shearing was poured into the wedge model, the columnar width gradually

Fig. 1. Microstructure of TP1 (a, b) and HPDC samples (c, d) of CP-Mg (a, c) and Mg-1 wt.%Zr alloy (b, d). The macrostructure on the TP1 cross-section of CP-Mg and Mg-1 wt.%Zr alloy is shown inset in the top-right corner.

decreased with reducing thickness, until the colum­nar grains basically became equiaxed grains at the wedge tip, where the grain size was about 200 film to 400 film. Although the CP-Mg melt with shearing (Fig. 2c) also presented columnar grains, the colum­nar width was observably reduced compared with the case without shearing (Fig. 2b). Also, the grain size of the sheared CP-Mg sample was only 25 film to 50 film at the wedge tip with basically the same thickness. According to classical nucleation theory finer grains mean that more nuclei were activated during solidification. These results therefore con­.rm that more MgO particles were activated as nucleation sites for Mg grains after the strong shearing of the CP-Mg melt.

The other factor to consider is the melt quenching effect resulting from the high cooling rate in the die cavity, due to which the melt is quenched from liquid to solid with strong undercooling to form .ne grains. Obviously, the degree of superheating in the melt is a determining factor for the undercooling and thereby the grain refinement. Therefore, differ­ent levels of superheating were selected to deter­mine a suitable temperature such that the alloy melt was quenched just below the alloy liquidus to obtain maximum undercooling and copious nuclei for significantly enhanced heterogeneous nucle­ation. If the nuclei were uniformly distributed throughout the entire melt volume, their growth would ensure a relatively uniform melt temperature in the die cavity, meaning that almost all of the nuclei could be activated simultaneously for grain refinement under a condition of greater undercool­ing. The grain size and associated microstructure of die-cast CP Mg samples obtained with different levels of superheating are presented in Fig. 3. Clearly, the grain size increased with increasing melt superheating, following the well-known S-shaped curve. When the pouring temperature was about 6600C (superheating of 10 K) and 6700C (superheating of 20 K), which lie close to the CP-Mg liquidus (6500C), the Mg grain size was very .ne at only 5 film to 6 film. However, when the super­heating temperature was increased from 20 K to 50 K, the grain size increased sharply from 6.7 film to 29.0 film. When the superheating exceeded 50 K, the grain size remained basically unchanged at about 29.9 film. This result indicates that the melt quenching resulting from superheating had a stronger effect on the grain size of the die-cast CP-Mg samples. When molten CP-Mg passed through the ingate into the die cavity, there would be a rapid decreased with reducing thickness, until the columnar grains basically became equiaxed grains at the wedge tip, where the grain size was about 200 lm to 400 lm. Although the CP-Mg melt with shearing (Fig. 2c) also presented columnar grains, the columnar width was observably reduced compared with the case without shearing (Fig. 2b). Also, the grain size of the sheared CP-Mg sample was only 25 film to 50 film at the wedge tip with basically the same thickness. According to classical nucleation theory, finer grains mean that more nuclei were activated during solidification. These results therefore confirm that more MgO particles were activated as nucleation sites for Mg grains after the strong shearing of the CP-Mg melt.

Fig. 2. Thickness versus cooling rate curve at different positions in the wedge model (a), and corresponding macrostructure in CP-Mg wedge samples cast without (b) and with shearing (c), showing that MgO particles could effectively refine CP-Mg grains and more MgO particles were activated after strong shearing of the CP-Mg melt. The microstructure of the wedge tip( 0.4 mm thickness) is shown inset in the top-left corner in (b) and (c).

Fig. 3. Effect of superheating on the grain size of HPDC CP-Mg samples. Scale bar 200 lm for all images.

Figure 4 shows bright-field TEM and HRTEM images of a cluster of Zr particles in the die-cast Mg-Superheat (K) 1 wt.%Zr alloy.

The melt quenching temperature would gradually rise above liquidus, delaying the onset of the melt quenching effect, e.g., superheating of 50 K or more. Therefore, the grain size was coarsened. Comparing the results in Figs. 1–3, the melt quenching effect in combination with the increased number of effective nuclei could result in extremely refined grains in the CP-Mg samples, because many MgO particles could be activated simultaneously as nuclei.

fluid flow, meaning that the melt would achieve a more uniform temperature. At a temperature close to liquidus with low superheating, the melt quenching effect could result in greater undercooling with a relatively uniform temperature distribution in the melt in the die cavity. As a result, many Mg grains could be simultaneously nucleated by means of diffraction pattern (SADP) obtained from one nucleated Zr particle and a-Mg grain with the electron beam parallel to [011

11]a-Mg direction is shown inset at the top-right corner. It is clear that the diffraction spots from each pattern superimpose on one another, revealing a full parallel axis orientation relationship between the Zr particle and a-Mg grain. Figure 4b shows a HRTEM image of this interface, marked by the rectangle in Fig. 4a, with the corresponding fast Fourier transform (FFT) pattern from

the a-Mg grain and Zr particle shown inset on the right side, revealing the same diffraction patterns. These lattice fringes clearly suggest that this Zr particle had a perfect matching relationship with the a-Mg phase. Using the FFT pattern, the inter-planar spacing of the (11011)a-Mg/Zr plane from the a-Mg phase and Zr particle was measured accurately to be 0.245 nm and 0.246 nm, respectively. The lattice misfit across the interface between the (11011)a-Mg plane is therefore just1011)Zr plane and (10.41%. It is clear that the interface between the a- Mg grain and Zr particle was basically coherent with very low lattice misfit. The Zr particles could therefore act quickly as nucleation sites during the HPDC process with very little undercooling.

Fig. 5. Microstructure of die-cast CP-Mg sample with addition of 0.1% Zr particles.

To further demonstrate this abnormal grain refinement behavior in the HPDC condition, a small amount of Zr particles (only 0.1 wt.% content) was added into the molten CP-Mg. To confirm the presence of activated Zr particles in the CP-Mg melt, it was poured into the die-casting machine and a sample taken within 5 s. The result is shown in Fig. 5. Compared with the microstructure of the die-cast CP-Mg sample (Fig. 1c), the average grain size in the die-cast CP-Mg sample with addition of0.1 wt.% Zr was increased to about 31.53 lm, much larger than that (6.71 lm) in the die-cast CP-Mg sample without Zr addition. Note that the grain size in this special CP-Mg sample with 0.1 wt.% Zr addition was not uniform, with the size of some grains exceeding 100 lm while others were smaller than 10 lm. This may be due to the combined effect of MgO nuclei with greater misfit and Zr nuclei with smaller misfit. In the HPDC condition, the Zr particles first act as nucleation sites for Mg grains, inhibiting the nucleation from the MgO particles due to the release of latent heat from the grains initially nucleated by Zr particles because of the smaller misfit. However, once a certain level of undercooling is reached, in a very short time, the MgO particles with high number density could be simultaneously activated to obtain a large number of fine grains, as shown in Fig. 5, which also indicates that the Zr particles may be less effective for grain refinement in die-cast Mg-1 wt.%Zr alloy (Fig. 1d).

For effective grain refinement, the solid particles not only need to have good lattice matching, but also need to be completely wetted, well dispersed, and uniformly distributed in the liquid phase, and have sufficient number density. In this work, the HPDC condition was used to ensure complete wetting, effective dispersion, and a uniform distribution of MgO particles. Because only MgO particles were present in the CP-Mg melt, many dispersed MgO particles may be activated simultaneously as nucleation sites for Mg grains in the HPDC condition, resulting in the extremely fine grain size. However, addition of Zr particles could inhibit such nucleation from MgO particles, due to the release of latent heat from the grains initially nucleated by Zr particles because of the smaller misfit. A schematic diagram for the die-cast samples to further elucidate this abnormal grain refinement behavior is shown in Fig. 6. Although both Zr and MgO particles can act as nucleation sites for Mg grains, the undercooling required for the Zr particles is lower than that required for the MgO particles, because of their different levels of misfit, as shown in Fig. 6. Therefore, after addition of Zr particles to the CP-Mg melt, even at very low content, they could act as nucleation sites first, before activation of the MgO particles. In other words, such addition of Zr particles could inhibit nucleation of Mg grains by MgO particles. It can therefore be concluded that, before nucleation occurs in the absence of more effective Zr particles in the melt, MgO particles with greater misfit and high number density might represent the most effective heterogeneous nucleation sites for grain refinement under certain conditions, e.g., HPDC.

Fig. 6. Schematic of abnormal grain refinement, where many MgO particles can be simultaneously activated as nucleation sites once a required level of undercooling is reached, but addition of a few Zr particles can inhibit this nucleation effect.

CONCLUSION

Abnormal grain refinement behavior was found during high-pressure die casting of Mg-Zr alloy. The size of Mg grains abnormally increased from 6.71 to 18.93 lm after addition of 1 wt.% Zr as grain refiner. Further experimental investigations revealed that a melt quenching effect in combination with the increased number of effective MgO particles is responsible for these extremely refined grains in the die-cast CP-Mg sample, because many MgO particles can be activated simultaneously as nuclei. Finally, a new grain refinement mechanism is proposed. Before nucleation, if there are no more effective (Zr) particles in the melt, (MgO) particles with greater misfit and high number density could represent the most effective heterogeneous nucleation sites for grain refinement in the HPDC condition. Although the experimental results of the present study provide some evidence for the formation of extremely refined primary Mg grains in the HPDC CP-Mg sample, further studies must still be performed to understand the detailed mechanism.

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