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Semisolid slurry of ZA27 alloy was prepared by Self-inoculation Method (SIM), the effects of isothermal holding parameters on microstructures of rheo-diecasting were researched, and the mechanical properties of ZA27 rheo-diecastings were tested. The results indicate that the dendritic microstructure of ZA27 alloy formed by permanent mold casting can be significantly modified by RDC with SIM, and obtain fine spherical microstructures. After comprehensive consideration, the suitable melt treatment temperature for the ZA27 alloy semisolid processing is 550~560°C. The isothermal holding process of ZA27 alloy slurry has great effect on primary α -Al particles (α_1), while has little effect on the microstructure of secondary solidification in the process of thin-walled rheo-diecasting, and the suitable isothermal holding time of semisolid slurry for rheo-diecasting is 3 min. Compared with HPDC, the RDC process can increase the tensile strength of ZA27 alloy by more than 6.9%, with a maximum increase of about 12.5%. The best performance die casting can be obtained when the slurry holding time is 3-5 min.

Keywords: ZA27 alloy, Primary particle, Secondary particle, Rheo-diecasting, Mechanical property.

1. Introduction

Zn-Al series alloy have wide range of uses in structural materials and wear-resistant sealing materials due to its excellent casting properties, high mechanical properties and wear resistance, good castability, good workability and low raw material costs¹, which is the ideal material to replace expensive copper alloy. As a representative of Zn-Al series alloy, ZA27 alloy is regarded as one of the ideal candidate materials for sliding bearings due to excellent mechanical properties and wear resistance, such as strength at room temperature reaches more than 400MPa and hardness reaches more than 110HB². However, ZA27 alloy is easy to form shrinkage pores and component segregation during the casting process due to its wide crystallization temperature range (108°C), as a result, the composition and microstructure of ZA27 alloy prepared by traditional casting are not uniform, which limits its application³. Therefore, how to optimize the casting process is an important research goal to improve the performance of ZA27 alloy. While the semisolid forming technology can perfectly solve this problem in theory.

Semisolid metal forming technology has attracted wide attention as soon as it is proposed, and is hailed as the most promising modern processing technology in the 21st century. In the semisolid metal forming process, the solid-liquid mixed slurry solidifies in a non-dendritic manner, so that the remaining liquid phase can communicate with each other, which can effectively supplement even eliminate solidification shrinkage and thermal cracking. Therefore, the semisolid forming technology can theoretically obtain products without holes and defects⁴⁻⁸.

High pressure die casting (HPDC) is a processing technology that applies high pressure to molten metal to form metal parts. Compared with conventional casting, HPDC is widely used in the aerospace, automotive and electronics industries due to its advantages of high manufacturing accuracy, high production efficiency and low energy consumption⁹⁻¹¹. However, the liquid metal mainly fills the mold by turbulent flow due to the high speed of filling the cavity during liquid metal die casting, hence it is easy to form hole-like defects inside the casting, which will seriously affect the compactness and mechanical properties of the castings12. In contrast, the apparent viscosity of the semisolid slurry is higher than that of the liquid metal, hence its flow is more stable than the liquid state during the die-casting and filling stage, which can effectively reduce or even eliminate the injection, turbulence and gas phenomenon during liquid metal injection. Therefore, the semisolid rheological die-casting (RDC) technology using semisolid slurry combined with HPDC can further improve the mechanical properties of the casting.

Based on low superheat pouring, liquid-liquid mixed casting, solid-liquid mixed casting, suspension casting and inclined cooling method, professor Li developed a new method for slurry preparation called Self-Inoculation Method (SIM)¹³. In this paper, the semisolid slurry of ZA27 alloy was prepared by SIM (based on the previous work)¹⁴, then the RDC was employed combining SIM with HPDC to produce thin-walled plates. The effects of different parameters of SIM

on microstructures and mechanical properties of ZA27 alloy were studied to provide a theoretic basis for the optimization of process parameters and its application.

2. Experimental Detail

2.1 Preparation of self-inoculants

The ZA27 alloy was used as the raw material (actual composition is shown in Table 1). The molten alloy was degassed at 700°C, then cooled to 580°C and poured into a metal mold to obtain the metal bars with the size of Φ 15 mm×150 mm. Then the bars were machined into small particles as self-inoculants with sizes of about 5 mm×5 mm.

2.2 Slurry preparation and rheo-diecasting

Figure 1 shows the schematic diagram of the rheo-diecasting process with the slurry preparation method of SIM. The fluid director was inclined at 45° with a length of 500 mm. The ZA27 alloy was melted and degassed. Then adjusted the melt temperature to 570°C, 560°C, 550°C and 540°C, respectively and added 5% (mass fraction of the melt) inoculants into the melt, followed by hand stirring the melt with a iron bar quickly to make them dissolved. Then the mixed melt was collected through fluid director to the slurry collector

Table 1. Chemical composition of the ZA27 alloy (mass fraction, %).

Al	Cu	Mg	Fe	Zn
26.5	2.25	0.015	≦0.1	Balance

to obtain semisolid slurry. After that, the slurry was poured into water to obtain transient slurry microstructure select optimal slurry preparation parameters (which mainly depends on the solid fraction of the slurry suitable for rheological forming). Finally, prepared slurry with selected optimal slurry preparation parameters, then the slurry was isothermally held for a specific time (0 min, 3 min, 5 min and 10 min, respectively) at 480°C. Subsequently, the prepared slurry was employed to the rheo-diecasting experiment of thin-walled part with DAK-450 die casting machine. The dies were preheated to 200°C by hot circulating oil and shot chamber was preheated to 300°C. The injection rate was 1.2m/sec with pressurization of 160MPa. Real diagram of die-casting is shown in Figure 2 with the diameter of 200mm and the wall thickness of 2mm.

2.3 Microstructure observation, quantitative analysis and mechanical properties testing

The sampling position of the die casting is shown in Figure 2. The Specimens were prepared by the standard technique of grinding with SiC abrasive paper and polishing with an Al₃O₂ suspension solution, followed by etching in nitric acid aqueous solution (4mLHNO₃+96mLH₂O). The Optical Microscopy (OM) was carried out to observe the microstructures of primary particles, and the average particle sizes (D=(4A/ π)^{1/2}, where A is area of the particle) and shape factors (F= P²/(4 π A), where P is the perimeter of particle) of primary particles were measured using image analysis software Image Proplus 6.0¹⁵. The FEG450 scanning electron microscopy (SEM) was carried out, equipped with an energy







Figure 2. The die casting component and the sampling position.

dispersive spectroscopy (EDS) facility and operated at an accelerating voltage of 3-20 kV to observe the morphologies of secondary particles. At last, the mechanical properties of diecastings with different processing parameters were tested by WDW-100D tensile testing machine. Sampling position and size were shown in Figure 2 (sample processing size is based on national standard GBT228.1-2010), tensile speed is 0.5mm/min, and test 5 samples for each parameter, then take the average value as the final test result.



Figure 3. Solidification curve of the ZA27 alloy.

3. Results and Discussion

3.1 Effect of melt treatment temperature on ZA27 alloy semisolid slurry

The theoretical solidification curve of the ZA27 alloy as shown in Figure 3 (which is measured by a thermodynamic software of Pandat). It can be seen from the scheil (non-equilibrium) solidification curve in Figure 3 that the solidification process starts when the temperature is about 490°C, and the eutectic reaction starts when the temperature is about 380°C, meaning that the liquid/solid temperature range of the ZA27 alloy is about 110°C, which is suitable for semisolid processing. Meanwhile, considering the feasibility of the operation and the fluidity of the slurry during the forming process, the solid fraction of the ZA27 alloy can be controlled below 30%, corresponding with the processing temperature range of 460°C~490°C. Moreover, it has been measured via the experiment that the average change of the melt temperature during the slurry preparation of the SIM process is about 80°C, which means that the melt treatment temperature range can be controlled to 540°C~570°C.

Figure 4 shows the ZA27 alloy microstructures fabricated by different processes. It can be seen that the liquid permanent mould casting microstructure is mainly dendrites, while the semisolid permanent mould casting microstructure is dendrite fragments and rose-shaped crystals. In comparison, the



Figure 4. ZA27 alloy microstructures fabricated by different processes (a) liquid permanent mould casting; (b) semisolid permanent mould casting microstructure; (c) HPDC; (d) RDC.

HPDC microstructure consists of dendrites and small chilled crystals, while the RDC microstructure consists of dendrite fragments, small chilled crystals and even some spherical grains. Moreover, chilled crystals in RDC are smaller than those of HPDC. Therefore, compared with liquid permanent mould forming, HPDC can significantly refine dendritic primary grains, while RDC using self-inoculation method can obtain small, round and uniformly distributed primary grains. Hence, it is necessary to study the ZA27 alloy semisolid forming and the relationship between its microstructure and properties.

Slurry preparation is a prerequisite for semisolid forming. Therefore, the ZA27 alloy semisolid slurry was prepared by the self-inoculation method. Figure 5 shows the water-quenched microstructures of the ZA27 alloy prepared by SIM at different melt treatment temperature. When the melt treatment temperature is 570°C, there is only a small amount of non-dendritic primary particle (as shown in Figure 5a). In contrast, when the melt treatment temperature is 560°C and 550°C, respectively, the primary particles are significantly increasing (as shown in Figure 5b, 5c). When the melt treatment temperature is 540°C, after treated by SIM process, there are large amount of primary solid particles in the water quenched microstructure, even appears some large dendrites (as the black circles show in Figure 5d). Hence it can be concluded that the melt treatment temperature has a great influence on the microstructure of the ZA27 alloy semisolid slurry when the angle of the flow director and the addition amount of self-inoculants are certain. Namely, the solid fraction of ZA27 alloy semisolid slurry gradually increases with the decrease of the melt treatment temperature.

During the semisolid slurry preparation process of the ZA27 alloy by SIM, the temperature of the ZA27 alloy melt will be decreased rapidly after adding the self-inoculants. As a result, there will be a large number of high melting points and "large sized atomic clusters" in the local position of the melt, which will be used as the nucleation substrates. On the other hand, the addition of self-inoculants can be regarded as the addition of heterogeneous nucleation substrates in the melt, making the nucleation rate increased, which is called the process of primary inoculation. When the melt flows through the fluid director, the solidified shell is formed rapidly under the chilling of director surface due to the low temperature of the director. Subsequently, free grains and dendritic fragments are formed and involved in the melt when the subsequent melt scour and shear the solidified shell strongly, and finally evolve into rose-shape and fine dendritic primary particles. During this process, the temperature of the melt decreased and the undercooling of the semisolid slurry increased due to the heat transfer and convection, leading to the dendritic primary particles survived, which is called the process of secondary inoculation. At the end of the director, turbulence



Figure 5. Water-quenched microstructure of the ZA27 alloy at different melt treatment temperature (a) 570°C; (b) 560°C; (c) 550°C and (d) 540°C.

occurs when two streams of the melt are converged, which promotes thermal field and concentration field of the melt to be homogeneous. Finally, when the slurry collected in the accumulator, the microstructure exhibits the fine equiaxed crystals due to the fusing of rose-like crystals^{16,17}.

However, the melt treatment temperature has great effect on solid fraction of the slurry, which will further affect the subsequent forming process. In the present work, when the melt treatment temperature is 570°C, the self-inoculants will be melted rapidly, and the high melting points and "large sized atomic clusters" will be remelted. After flowing through the fluid director, the melt temperature is high enough to remelt the dendritic fragments. Hence almost without non-dendritic primary particle. While if the melt treatment temperature is 540°C, the high melting points and "large sized atomic clusters" will be survived after the self-inoculants add into the melt. Meanwhile, when the melt flows through the fluid director, the solidified shell is much thick due to the poor fluidity, which causes the large dendrites in the final microstructure of the slurry (as shown in Figure 5d). Moreover, the dendritic fragments in the accumulator could not be remelted due to the low temperature of the remaining liquid, which will further increase the solid fraction of the slurry. In comparison, when the melt temperature is appropriate (such as 550~560°C), the dendritic fragments in the accumulated will be partially remelted and passivated by the remaining liquid, causing the primary solid particles fine and spherical. Hence, the suitable melt treatment temperature for the ZA27 alloy semisolid processing by SIM is 550~560°C.

3.2 Effect of isothermal holding time on primary grains of rheo-diecastings

According to section 3.1, 560°C was selected as the melt treatment temperature for SIM slurry preparation, and 480°C was the holding temperature of the slurry (the temperature setting is based on the measured value: the average change of the melt temperature during the slurry preparation of the SIM process is about 80°C. Moreover, according to Figure 3, 480°C is between solidus and liquidus of ZA27 alloy). The microstructures of the ZA27 alloy produced by rheo-diecasting technology with the different isothermal holding time of the semisolid slurry are shown in Figure 6. It can be clearly observed from the microstructure of rheo-diecasting without isothermal holding that the primary particles (α_1) present fine structure with some dendritic fragments (Figure 6a). After the isothermal holding process, the size of α_1 , is gradually increasing (as shown in Figure 6b). With the isothermal holding time further increased, the merging phenomenon occurs, leading to the irregularly growth of the α_1 (Figure 6c and 6d). The average grain sizes and shape factors are measured as shown in Figure 7 (take 200 grains in each group for statistical measurement, and take the



Figure 6. Microstructures of ZA27 alloy rheo-diecasting by SIM under different holding time (a) 0min; (b) 3min; (c) 5min and (d) 10min.



Figure 7. Changes of primary particle size and shape factor with holding time.



Figure 8. Linear fitting of primary particle size of ZA27 alloy.

average value as the final result). In the microstructure of rheo-diecasting without isothermal holding, the average grain size of α_1 is $32.38\pm6.5\mu$ m, the corresponding shape factor is about 2.08. When the isothermal holding time are 3 min and 5 min, the average grain sizes of α_1 are $44.47\pm4.8\mu$ m and $56.43\pm4.3\mu$ m, with the corresponding shape factor of about 1.49 and 1.88, respectively. The average grain size of α_1 increased to $72.92\pm5.7\mu$ m with the corresponding shape factor of about 2.04 when the isothermal holding time increased to 10 min.

Figure 8 shows the linear fitting of the growth of primary grains with different isothermal holding time. It is evident combining with Figure 7 that primary grains are gradually growing and spheroidizing in the early stage of isothermal holding process, and the growth rate of the primary grains in the isothermal holding process conforms to the dynamic equation of $D_t^3-D_0^3=Kt^{18}$ (where D_0 is the primary solid particle diameter without isothermal holding for t seconds, and K is the coarsening rate constant). After comprehensive analysis from Figure 6 to Figure 8, 3 min is chosen as the suitable isothermal holding time of semisolid slurry for the rheo-diecasting process of the ZA27 alloy.

Self-inoculation rheo-diecasting is a novel rheo-diecasting process combined slurry preparation process by SIM with HPDC. And the preparation of the fine semisolid slurry is the precondition to ensure the high quality and integrity of the die castings. When the slurry is prepared without isothermal holding, there are amount of dendritic fragments and high melting point particles inside the melt. After collecting in accumulator, the convection will be generated when two streams of the melt are converged, making the tip of dendrite fragments passivated. The degree of supercooling caused by the curvature ΔT_{e} can be expressed as follows¹⁹:

$$\Delta T_r = -\frac{2T_m k\sigma}{\rho_s L_m} \tag{1}$$

Where σ is surface tension, T_m is equilibrium melting point temperature, k is curvature of solid-liquid interface, ρ_s is solid phase density and L_m is latent heat of crystallization.

As can be seen from Equation 1, the greater the curvature, the greater the ΔT_r . In this experiment, the primary particles in the slurry contain a large number of dendrite fragments, and the dendrite fragments are fused due to enrichment of the root solute during isothermal holding process, which lead to the formation of single irregular particles and increase of interfacial energy. The large curvature at the sharp corners of these particles lead to great ΔT_r , hence generate low melting point. Therefore, the sharp corners must be melted and the grains are gradually rounded during isothermal holding process.

On the other hand, primary particles, as the substrates to absorb solute atoms from liquid phase, are rounded and spherical under the influence of the driving force that the interfacial energy can be reduced as far as possible. Consequently, primary particles are increased and spherical with the extension of isothermal holding time. However, different sizes of original dendritic fragments result in different diameter of spherical primary particles after isothermal holding for a short time. The solute concentration of liquid phase around smaller particles is lower than that around larger particles. With the further extension of the holding time, Al, Cu elements will continue to diffuse from large particles to small particles, while the Zn elements have the opposite diffusion path^{14,16}. As the result, large particles become larger and small particles become smaller even melted and disappeared, which is called Oswald ripening²⁰. The "8" shaped and "spindle-like" structures are formed as the intensification of merge phenomenon in the late stage of isothermal holding process. When the two particles with large difference in size are incorporated and grow into a new shape, the new particle will eventually be spherical under the driving force of the interfacial energy reduced. But when the two particles with same sizes are merged into a new particle, it will be very difficult to be spherical, and eventually grow into "8" or "shuttle" shaped clusters. According to the previous experimental study, the suitable isothermal holding time of the slurry for rheological forming of the ZA27 alloy is 3 min. In this condition, the sizes of α_1 particles are not very large and the roundness of particles is the best.

3.3 Secondary solidification behavior of ZA27 alloy in the rheo-diecasting process

Figure 9 shows the morphologies of secondary particles (α_2) in rheo-diecastings with different isothermal holding times. It can be clearly observed that the sizes of secondary particles are smaller than primary particles due to the existence of primary particles (α_1) before secondary solidification process. The α_2 particles, which are connected with each other, are nearly spherical and rose-like shape in the microstructures of different holding times. Meanwhile, there is no obvious difference among four isothermal holding parameters of Figure 9, indicating the low effects of isothermal holding times on secondary solidification microstructures of thin-walled rheo-diecastings. Therefore, the specimens, isothermal holding for 3 min, are used for the subsequent research on secondary solidification behavior of the thin-walled rheo-diecastings.

The elements distribution in the microstructure of the ZA27 alloy is shown in Figure 10. It can be seen from Figure 10a that the Al element mainly distributes in primary particles (α_1) and secondary particles (α_2), while the Zn element distributes throughout the microstructure, and enriches in intergranular eutectic structures. The Cu element mainly distributes in intergranular eutectic structures due to its low content in original alloy. As shown in Figure 10b and Table 2, the content of the Al element in α_1 is higher than α_2 , while the content of the Zn and Cu elements in α_1 are lower than α_2 , indicating the different between α_1 and α_2 . In addition,

it can be seen from Figure 8 and Figure 10a that the colors of the secondary particles in same specimen are different, such as the α_2 as shown in Figure 10a point 5 with light color and point 4 with dark color. The EDS results show that the contents of the Zn and Cu elements in light color particles are higher than dark color particles, and the element ratio in light color particles is similar to the peritectic phase (point 2 in Figure 10a), meaning that the α_2 particles have different growing patterns.

Secondary solidification process starts when the ZA27 semisolid slurry leaves holding furnace. When the semisolid slurry is injected into die cavity, there are two processes in the remaining liquid, nucleation and growth. The thickness of the forming part in present experiment is 2mm. During the filling process, a large supercooling can be provided when the slurry contact with the cold mould under high pressure. The nucleation rate is expressed as follows²¹:

$$N = Kexp\left(\frac{-\Delta G}{kT}\right) \bullet exp(\frac{-Q}{kT})$$
(2)

Table 2. Elements content in different point.

Contents of different points (wt%)						
1	2	3	4	5	6	
44.5	75.8	61.5	57.6	75.6	90.1	
54.4	22.2	36.7	40.6	21.5	5.7	
1.1	2.0	1.8	1.8	2.9	4.2	
	1 44.5 54.4 1.1	Content 1 2 44.5 75.8 54.4 22.2 1.1 2.0	Contents of diffe 1 2 3 44.5 75.8 61.5 54.4 22.2 36.7 1.1 2.0 1.8	Contents of different point 1 2 3 4 44.5 75.8 61.5 57.6 54.4 22.2 36.7 40.6 1.1 2.0 1.8 1.8	Contents of different points (wt%) 1 2 3 4 5 44.5 75.8 61.5 57.6 75.6 54.4 22.2 36.7 40.6 21.5 1.1 2.0 1.8 1.8 2.9	



Figure 9. SEM images of rheo-diecasting by SIM under different holding time (a) 0min; (b) 3min; (c) 5min and (d) 10min.



Figure 10. Elements distribution diagram of the ZA27 alloy by RDC (a) surface; (b) line.

here K is a constant, $\triangle G$ is the nucleation energy, Q is the diffusion activation energy of atoms across the liquid/solid interface, k is the Boltzmann constant, T is thermodynamic temperature. For most alloy melt, the nucleation rate is increased significantly when the value of relative supercooling is between $0.15 \cdot 0.25T_m$ (T_m is the melting temperature of alloy). The melting temperature of the ZA27 alloy used in this experiment is about 490°C, while the dies are preheated to 200°C and the pouring temperature of the slurry is 480°C, which provides a large relative supercooling for nucleation. Therefore, nucleation occurs throughout the whole remaining liquid in the thin-walled positions. Furthermore, the nucleus can be survived due to high cooling rate provided by die cavity.

The growth process of the secondary solidification of ZA27 alloy contains renucleated nucleus growth and attachment growth (Al atoms crystallized in the remaining liquid will grow attaching α_1 particles²²). The nucleus in the remaining liquid will firstly grow into fine spherical particles. As the solidification process proceeds, α , particles will grow unstable after growing into their critical size of stable growth. Within the limitation of solidification region, the α_{2} particles present the near spherical particles and merged irregular particles (as shown in Figure 8). At the same time, the attachment growth around α_1 particles is also proceeding. As a result, a layer of attachment growth appears around α_1 particles, and its composition is the same as α_2 particles (as point 2 and 5 show in Figure 9a). The composition of α_1 particles and α_2 particles is obviously different due to their different solidification stages. A portion of Al is first precipitated in the liquid alloy to form α_1 particles, hence the Al content in the remaining liquid phase is reduced compared to the original alloy, which leads to less Al content in α_2 particles than it in α_1 particles.

3.4 Peritectic reaction and eutectic reaction of ZA27 alloy

Peritectic phase growth can be divided into three stages: peritectic reaction stage, peritectic transformation stage and direct solidification stage23,24. Peritectic reaction is the process of forming a peritectic phase by reacting the primary phase with the liquid phase $(\alpha + L \rightarrow \beta)$. The peritectic transformation is a process that dissolving the initial phase into a peritectic phase through the atoms diffusion of solid phase $(\alpha \rightarrow \beta)$. Direct solidification is a process in which the liquid phase grows and thickens directly on the existing peritectic phase $(L \rightarrow \beta)$. In present work, α_1 particles (α phase) are formed during the slurry preparation process. After filling in the mold, the liquid phase with high Zn content encapsulates the α_1 particles, and the peritectic reaction begins to occur in the mold when the temperature reaches about 440°C²⁵. Then a peritectic reaction $(\alpha+L\rightarrow\beta)$ occurs at the front of the solid-liquid interface of α_1 particles to form a layer of β phase, which will prevent the further peritectic reaction.

The subsequent growth of the peritectic phase is achieved by the atoms diffusion of α_1 particles. At the same time as the peritectic transformation, α_2 particles in the remaining liquid phase discharges the solute, thereby reducing the Zn concentration gradient in the remaining liquid phase, hindering the Zn diffusion and enriching Zn in the liquid phase at the front of the solid-liquid interface of α_1 particles, which will cause the β phase to grow directly on the peritectic transition layer of α_1 particles (as point 2 shows in Figure 9a). On the other hand, the β phase will directly nucleate and grow in the local supercooling region when reaches its nucleation condition (as point 4 shows in Figure 9a). Then eutectic reaction ($(L \rightarrow \beta + \eta)$ occurs in the small amount of remaining liquid phase (η phase as point 6 shows). And the eutectoid transformation ($\beta \rightarrow \alpha + \eta$) occurs when the temperature reaches about 285°C^{26,27}. Therefore, as shown in Figure 11, there are only α and η phases in the XRD detection results, while no β phase.

ZA27 is a typical peritectic alloy^{28,29}, and there is no eutectic n phase under equilibrium solidification conditions, while the solute elements cannot diffuse sufficiently during non-equilibrium solidification process. In this experiment, peritectic reaction causes a large amount of Zn to be discharged into the remaining liquid phase due to large cooling rate, and then increases the Zn content in the remaining liquid, thereby eutectic reaction occurs. Finally, a eutectic structure is formed between the peritectic β phases. Therefore, it can be seen from Figure 9a and Table. 2 that Zn content in n phase is the highest. Moreover, a part of the Cu element is dissolved in the α and β phases, and the rest is discharged into the eutectic structure that is finally solidified. Mg element is not detected due to its low content. Compared with the eutectic structure of HPDC and RDC (as shown in Figure 12), The eutectic n phase of RDC is small and uniformly distributed, while the n phase of HPDC is coarse and has obvious segregation. The main reasons are as follows: 1. During RDC process, the primary phase is spherical and uniformly distributed; 2. A large number of uniformly distributed small secondary particles are formed in the remaining liquid phase, the eutectic reaction is limited into small area; 3. The solidification time of RDC is shorter than HPDC due to low pouring temperature, hence refine the eutectic structure.

3.5 Mechanical properties

Figure 13 shows the mechanical properties of ZA27 alloy diecastings with different processing parameters. It can be seen that the mechanical properties of RDC are better than HPDC (412.6MPa), and the isothermal holding times of



Figure 11. XRD of ZA27 alloy by RDC.



Figure 12. SEM microstructure of HPDC (a) and RDC (b).



Figure 13. Mechanical properties of ZA27 alloy diecastings with different processing parameters (a) HPDC; (b) RDC-0min; (c) RDC-3min; (d) RDC-5min; (e) RDC-10min.

the slurry have obvious effect on mechanical properties of RDC. When the isothermal holding time is 0 min (without isothermal holding), the ultimate tensile strength is 441MPa. While there is not much difference between the tensile strength of 3 min and 5 min, with the values of 464.3MPa and 463.5MPa, respectively. And a significant drop occurs in the tensile strength of 10 min, with the values of 452MPa. Meanwhile, the change trend of elongation is similar to that of tensile strength. This difference is closely related to the microstructure of different parameters.

Compared with HPDC, RDC process has fewer defects than HPDC due to the presence of non-dendritic primary solid particles, hence make the filling more stable. In addition, HPDC formed a coarser microstructure than RDC. As a result, the mechanical properties of HPDC are lower than that of RDC. As for RDC with different holding time of the slurry, the solid fraction, pouring temperature and morphology of secondary particles are the same. Therefore, the mechanical properties mainly depend on primary particles. As Figure 6 shows, there are much dendrite fragments in the microstructure of 0 min. Moreover, the particle size in the microstructure of 0 min is the finest in RDC, hence, the solid phase particles have the least obstructive effect on the filling process, which will lead to the formation of pores during the filling process, thereby reducing the mechanical properties of the casting. On the contrary, when the isothermal holding time is 10 min, the size of primary particles is the largest. Large primary particles are hindered by the inner gate during the filling process (which was described by author's research³⁰), which in turn reduces the compactness of the structure. As a result, the casting's property of this parameter is not much different from 0 min. There is not much difference between the microstructure of 3 min and 5 min, and the primary particles are round and the size is not very large. Hence, when filling the cavity, it not only has a certain viscosity, which reduces the pores in the castings, but also has good fluidity to make the structure compactness. Therefore, the casting of these two parameters have best properties. In summary, the semisolid forming can significantly improve the mechanical properties of castings.

4. Conclusions

- 1. The dendritic microstructure of ZA27 alloy formed by permanent mold casting can be significantly modified by RDC with SIM, and obtain fine spherical microstructures.
- The melt treatment temperature has a great influence on the microstructure of the ZA27 alloy semisolid slurry, and the suitable melt treatment temperature for the ZA27 alloy semisolid processing by SIM is 550~560°C.
- The isothermal holding process of ZA27 alloy slurry has great effect on primary α-Al particles (α₁), while has little effect on the microstructure of secondary solidification in the process of thinwalled rheo-diecasting.
- 4. Compared with HPDC, the RDC process can increase the tensile strength of ZA27 alloy by more than 6.9%, with a maximum increase of about 12.5%. The best performance die casting can be obtained when the slurry holding time is 3-5 min.

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6. References

- Chen TJ, Hao Y, Sun J, Di JJ. Microstructure of casting ZA27 alloy. Zhongguo Youse Jinshu Xuebao. 2002;12(2):294-9.
- Zhao HL, Wu RR, Lu Y, Wang RF, Li ZY, Xie B, et al. Effect of melt mixing treatment on the microstructures and mechanical properties of ZA27 alloy. Foundry. 2013;62(10):1018-23.
- Geng HR, Wang SR, Wang Y. Casting alloy of copper and zinc. Beijing: Chemical Industry Press; 2006. 21 p.
- Flemings MC. Behavior of metal alloys in the semi-solid state. Metall Trans. 1991;22A(5):957-81.
- Luo SJ, Jiang YZ, Li YF, Shan WW. Recognition of semi-solid metal forming technologies. Special Casting and Nonferrous Alloy. 2012;32(7):603-7.
- Eskin DG. Suyitno, Katgerman L. Mechanical properties in the semi-solid state and hot tearing of aluminum alloys. Prog Mater Sci. 2004;49(5):629-711.
- Xu J, Zhang ZF. Research progress of semisolid processing technology. J Harbin Univ Sci Technol. 2013;18(2):1-6.
- Zhao JW, Wu SS. Microstructure and mechanical properties of rheo-diecasted A390 alloy. Trans Nonferrous Met Soc China. 2010;20(S3):s754-7.
- Zheng Z, Ji Y, Mao W, Yue R, Liu Z. Influence of rheo-diecasting processing parameters on microstructure and echanical properties of hypereutectic Al-30%Si alloy. Trans Nonferrous Met Soc China. 2017;27(6):1264-72.
- Lumley RN, O'Donnell RG, Gunasegaram DR, Givord M. Heat treatment of high-pressure die castings. Metall Mater Trans, A Phys Metall Mater Sci. 2007;38(10):2564-74.
- Dong XX, Yang HL, Zhu XZ, Ji SX. High strength and ductility aluminium alloy processed by high pressure die casting. J Alloys Compd. 2019;773:86-96.
- Dong XX, Zhu XZ, Ji SX. Effect of super vacuum assisted high pressure die casting on the repeatability of mechanical properties of Al-Si-Mg-Mn die-cast alloys. J Mater Process Technol. 2019;266:105-13.
- Li YD, Yang J, Ma Y, Qu JF, Zhang P. Effect of inoculant parameters on AM60 Mg alloy semisolid slurry prepared by self-inoculation method (II). Trans Nonferrous Met Soc China. 2010;20(11):2178-86.
- Li M, Li YD, Yang WL, Zhang Y, Wang ZG. Effects of forming processes on microstructures and mechanical properties of A356 aluminum alloy prepared by self-inoculation method. Mater Res. 2019;22(3):1-11.
- Li YD, Liu XH, Li YL, Suo JL, Zhou HW, Zhang XL. Microstructure evolutions of semisolid slurry of 2024 wrought

aluminum alloy during continuous cooling and isothermal holding. Trans Nonferrous Met Soc China. 2013;35(1):44-8.

- Xing B, Li YD, Ma Y, Chen TJ, Hao Y. Preparation of nondendritic microstructure of AM60 alloy for rheoforming using self-inoculation method. Int J Cast Met Res. 2012;25(4):232-8.
- Guan RG, Cao FR, Chen LQ, Li JP, Wang C. Dynamical solidification behaviors and microstructural evolution during vibrating wavelike sloping plate process. J Mater Process Technol. 2009;209(5):2592-601.
- Manson-Whitton ED, Stone IC, Jones JR, Grant PS, Cantor B. Isothermal grain coarsening of spray formed alloys in the semi-solid state. Acta Mater. 2002;50(10):2517-35.
- Hu HQ. Metal solidification. Beijing: Metallurgical Industry Press; 1985. 245 p.
- Hardy SC, Voorhees PW. Ostwald ripening in a system with a high volume fraction of coarsening phase. Metall Trans, A, Phys Metall Mater Sci. 1988;19(11):2713-21.
- Hu GX, Cai X, Rong YH. Fundamentals of materials science. Shanghai: Shanghai Jiao Tong University Press; 2015. 5 p.
- Li YD, Chen TJ, Ma Y, Yan FY, Hao Y. Microstructural characteristic and secondary solidification behavior of AZ91D alloy prepared by thixoforming. Trans Nonferrous Met Soc China. 2008;18(1):18-23.
- Kerr HW, Kurz W. Solidification of peritectic alloys. Int Mater Rev. 1996;41(4):129-64.
- Li SM, Lu HY, Li XL, Liu L, Fu HZ. Directional solidification and growth of peritectic alloys. Rare Met Mater Eng. 2005;34(2):235-9.
- Aashuri H. Globular structure of ZA27 alloy by thermo mechanical and semi-solid treatment. Mater Sci Eng A. 2005;391(1-2):77-85.
- Liu Y, Li HY, Jiang HF, Lu XC. Effects of heat treatment on microstructure and mechanical properties of ZA27 alloy. Trans Nonferrous Met Soc China. 2013;23(3):642-9.
- Zhu YH. General rule of phase decomposition in Zn-Al based alloys (II): on effects of external stresses on phase transformation. Mater Trans. 2004;45(11):3083-97.
- Zhu YH, Man HC, Lee WB. Exothermic reaction in eutectic Zn-Al alloys. Mater Sci Eng A. 1999;268(1-2):147-53.
- Jovanovic' MT, Bobié I, Djurié B, Grahovac N, Ilié N. Microstructural and sliding wear behaviour of a heat-treated zinc-based alloy. Tribol Lett. 2006;25(3):173-84.
- Li M, Li YD, Huang XF, Ma Y, Guan RG. Secondary solidification behavior of A356 aluminum alloy prepared by the self-inoculation method. Metals. 2017;7(7):233-51.