Postprint: Free Solidification Path Selection in Mg-Zn-Gd Ternary Cast Magnesium Alloys

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Abstract

This study employs both experimental and numerical methods, taking Mg-4.58Zn-2.6Gd as an example, to investigate the selection of free solidification paths in Mg-Zn-Gd ternary cast magnesium alloys. Experiments under different mold conditions demonstrate that at relatively low mold cooling rates, the experimental alloy forms an (Mg) + W(Mg3Zn3Gd2) eutectic structure; as the mold cooling rate increases, the experimental alloy forms an (Mg) + I(Mg3Zn6Gd) eutectic structure. A computational model for the primary phase solidification path in multicomponent alloys was established, comprehensively considering factors of alloy liquid-phase diffusion and cooling rate. By coupling the thermodynamic calculation software Thermo-Calc and its database to obtain the thermodynamic data required for calculating the solidification path of the experimental alloy, it was found that the computational results agree well with the experimental results.

Full Text

Preamble

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Selection of the Solidification Path of Mg-Zn-Gd Ternary Casting Alloy

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Abstract

Mg-Zn-Gd base alloys possess significant advantages, including high strength, light weight, and low cost, making them favorable for applications in various airframe components. Two types of eutectic phases, W(Mg Zn Gd) and I(Mg Zn Gd), are commonly observed in Mg-Zn-Gd alloys under traditional casting conditions. The interface between the W phase and (Mg) is incoherent and thus weak, whereas the I phase has a quasiperiodic lattice that leads to a coherent interface with (Mg). Consequently, compared with the W phase, the I phase is more effective at obstructing dislocation slip and thereby efficiently strengthening the alloy. Therefore, controlling the solidification path—that is, controlling the relative amounts of I phase and W phase—is critical for enhancing the heat resistance of Mg-Zn-Gd magnesium alloys.

In this work, the solidification path of Mg-4.58Zn-2.6Gd ternary casting alloy was investigated through experiments and numerical analysis. Experimental results showed that at lower cooling rates (0.75 K/s), an +W(Mg Zn Gd) eutectic forms first, while at higher cooling rates (7.71 K/s), an (Mg)+I(Mg Zn Gd) eutectic forms first. A numerical model for predicting the solidification path of the primary phase in multi-component alloys was developed, considering the effects of solute diffusion in the liquid phase and cooling rate. The thermodynamic data for the computation model were obtained using the Thermo-Calc database. The numerical results were in favorable agreement with experimental observations. The model established in this work provides a direct and convenient method to predict the solidification path of Mg-Zn-Gd alloys under different casting conditions. The validity of this model was further confirmed using three additional Mg-Zn-Gd alloys: Mg-3.8Zn-2.0Gd, Mg-5.5Zn-2.0Gd, and Mg-5.5Zn-4Gd. It was also found that for Mg-Zn-Gd alloys, higher Zn content and higher cooling rates promote the formation of the I phase, whereas higher Gd content and lower cooling rates favor the formation of the W phase.

KEY WORDS Mg-Zn-Gd ternary magnesium alloy, solidification path, cooling rate, numerical model

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Introduction

Magnesium alloys are important lightweight green engineering structural materials with broad application prospects in automotive, electronics, aerospace, and defense industries [1]. Among them, Mg-Zn-Gd heat-resistant magnesium alloys exhibit good room-temperature mechanical properties, ductility, corrosion resistance, and favorable high-temperature mechanical performance, making them a current research focus both domestically and internationally [2,3]. Studies [4] have found that the interface bonding between the W(Mg Zn Gd) phase and (Mg) matrix in Mg-Zn-Gd alloys is weak, and when the volume fraction of the W phase exceeds a certain threshold, the mechanical properties of the alloy decrease with increasing W phase content. In contrast, the I(Mg Zn Gd) phase exhibits strong interface bonding with the (Mg) matrix and demonstrates good thermal stability [5]. Thus, the I phase provides better strengthening effects than the W phase [6]. Therefore, rationally controlling the relative contents of the W and I phases in Mg-Zn-Gd alloys holds significant scientific value and engineering importance for designing and preparing high-strength, creep-resistant Mg-Zn-Gd magnesium alloys.

Liu et al. [7] comprehensively analyzed the influence of initial alloy composition on the solidification microstructure of Mg-Zn-Gd alloys, finding that when the Zn/Gd ratio ranges from 1.5 to 40.0, or when the Zn content exceeds 3 at.% with Zn/Gd ratios of 10 or 25, the I phase forms in the microstructure. When the Zn/Gd ratio ranges from 0.25 to 6.0, the W phase forms. However, no studies have been reported on the effects of cooling rate on the free solidification casting microstructure and phase selection behavior of Mg-Zn-Gd alloys.

Determining alloy solidification paths is crucial for accurately predicting casting microstructure and properties, holding both theoretical significance and engineering application value [8,9]. Solidification of complex alloys typically begins with the primary phase. The growth of the primary phase changes the composition of the remaining liquid, creating compositional conditions for the precipitation of other phases and constraining their growth [10]. According to ternary alloy phase diagrams, the degrees of freedom at the solid/liquid interface during primary phase solidification are greater than one, meaning different solidification conditions lead to different solidification paths. When the liquid composition reaches the eutectic valley monovariant line composition, solidification can only proceed along the monovariant line from high to low temperature. Thus, the selection of the primary phase solidification path represents the main uncertain factor affecting the solidification microstructure of multi-component alloys [9] and remains a hot topic in materials research [11].

In the 1970s, Mehrabian and Flemings [12] first predicted the solidification path of Al-4.5Cu-5.6Ni (wt.%) ternary alloy, assuming that solutes Cu and Ni in the alloy matrix followed the Scheil model and deriving a functional expression for the solidification path within the (Al) primary phase region. Subsequently, Clyne and Kurz [13], Ohnaka [14], and Kobayashi [15] established corresponding

analytical models for solidification paths by modifying the diffusion factor term in the Scheil model. Due to the lack of reliable thermodynamic data for multi-component alloy solidification in early models, data from binary alloy systems had to be used as approximations, leading to significant deviations between calculated and experimental results [16].

The emergence and practical application of computational thermodynamics for materials phase transformations solved the problem of lacking thermodynamic data for multi-component alloy solidification systems [9]. Sundman et al. [17] used the Thermo-Calc phase diagram software with the Scheil and lever models to analyze solute microsegregation during solidification of Al-1.5Cu-2.5Mg-6Zn alloy. Zhao et al. [9] built upon Dupont et al.' s [18] research and established a theoretical calculation model for microsegregation of the primary phase in multi-component alloys based on a weighted Scheil model coupled with phase diagram thermodynamics. However, these studies and models were based on the Scheil model, primarily examining the effects of back diffusion in the solid phase on the solidification path while assuming complete solute diffusion in the liquid phase. This assumption differs significantly from actual conditions and leads to deviations between calculated and experimental results [10].

In reality, the solute diffusion coefficient in the liquid phase is approximately three orders of magnitude larger than that in the solid phase during actual solidification. Therefore, solid-state diffusion can often be neglected, while liquid-phase diffusion significantly influences the solidification process. Rappaz and Boettinger [19] assumed only liquid-phase diffusion and, using a single equiaxed dendrite as the research object, proposed a microsegregation equation for multi-component alloys. Using Al-1Mg-1Si ternary aluminum alloy as an example, they successfully predicted the experimental alloy' s solidification behavior.

Based on the modeling approach of Rappaz and Boettinger [19], this work establishes a computational model for the solidification path of the primary phase in multi-component alloys by coupling thermodynamic equilibrium equations with solute conservation, heat conservation, and mass conservation equations. The model comprehensively considers both liquid-phase diffusion and cooling rate effects. Experimental and numerical methods were employed to investigate the free solidification paths of Mg-4.58Zn-2.6Gd ternary magnesium alloy under different mould conditions, providing a reasonable predictive method for calculating the solidification paths of casting magnesium alloys.

Experimental Methods

The experimental alloy was prepared using pure Mg (99.99%), pure Zn (99.99%), and Mg-28Gd master alloy. Melting was conducted in a self-made 12 kg resistance furnace under RJ-4 flux protection, and casting was performed at 750 °C. Chemical composition analysis by inductively coupled plasma atomic emission spectroscopy (ICP-AES) confirmed the alloy composition as Mg-4.58Zn-2.6Gd.

To investigate the effect of cooling rate on solidification microstructure, four types of mould materials were selected: copper, graphite, water glass sand, and aluminum silicate fiber insulation. The mould dimensions are shown in [Figure 1: see original paper]. Temperature data during solidification were collected using a calibrated K-type thermocouple and a DX1012 twelve-channel paperless recorder to determine cooling rates in different moulds. The temperature measurement location was at the center of the mould cavity, 40 mm from the top, as shown in [Figure 1: see original paper]. The measured cooling curves for the alloy in various moulds are presented in [Figure 2: see original paper], yielding calculated cooling rates of 10.08, 7.71, 0.75, and 0.32 K/s for the four mould types.

Metallographic specimens were selected near the thermocouple position in each mould. After grinding and polishing, samples were etched using a 4% HNO + 96% C H OH (volume fraction) solution. Microstructures were observed using an Olympus PM-G3 optical microscope (OM) and a JSM-5800 scanning electron microscope (SEM). Phase identification was performed using an Oxford Inca energy dispersive spectrometer (EDS) and an X' Pert Pro MPD X-ray diffractometer (XRD). The volume fractions of secondary phases were measured using Image-Pro image analysis software.

Results

2.1 Microstructural Characterization

[Figure 3: see original paper] shows the solidification microstructures and SEM images of grain boundary secondary phases in Mg-4.58Zn-2.6Gd alloy under different cooling conditions. As the cooling rate increases from 0.32 K/s to 10.08 K/s, the grain boundary secondary phase morphology transitions from coarse, continuous network eutectic structures to fine, discontinuous island-like eutectics. presents the EDS analysis results of the eutectic secondary phases and matrix in Mg-4.58Zn-2.6Gd alloy. With increasing cooling rate, the solute contents of Zn and Gd in the eutectic phases decrease dramatically. This occurs because at higher cooling rates, solute elements Zn and Gd do not have sufficient time to diffuse to the solid-liquid interface front, resulting in eutectic phases with lower solute concentrations [20]. The EDS analysis reveals that phases A1 and B1 have Zn/Gd ratios of approximately 6:1, identifying them as I(Mg Zn Gd) phase, while phases C1 and D1 have Zn/Gd ratios of approximately 1.5:1, identifying them as W(Mg Gd Zn) phase.

To further confirm phase identification, [Figure 4: see original paper] presents the XRD spectra of Mg-4.58Zn-2.6Gd alloy under different mould conditions. In the insulated and sand moulds with lower cooling rates, the solidified microstructure consists primarily of (Mg), W(Mg Gd Zn) phase, and small amounts of I(Mg Zn Gd) phase. In contrast, in the graphite and copper moulds with higher

cooling rates, the solidified microstructure contains only (Mg) and I(Mg Zn Gd) phases.

Theoretical Model

3.1 Thermodynamic Principles

Under traditional casting conditions, the solid-liquid interface during alloy solidification maintains local thermodynamic equilibrium. According to the second law of thermodynamics, when a multi-component system reaches equilibrium at constant temperature and pressure, the chemical potential ( ) of each component i is equal in the solid (s) and liquid (l) phases [21]:

$$\mu_i^s = \mu_i^l \quad (1)$$

According to the Redlich-Kister-Muggianu model [22], the chemical potential of component i is a function of solute concentration and temperature. When solid-liquid equilibrium is established, if the chemical potentials of solute elements in the solid and liquid phases are known, the equilibrium solute concentrations in the solid and liquid phases ($w_{s,i}^*$ and $w_{l,i}^*$) and the equilibrium temperature $T_L(w_{l,i}^*)$ can be obtained by solving the solid-liquid equilibrium equations.

3.2 Microscopic Solidification Model

During free solidification, industrial alloys typically solidify as equiaxed dendrites. Equiaxed dendrites have complex branching morphologies, and comprehensively evaluating all influencing factors would inevitably introduce additional unknown parameters and increase computational time. Considering industrial applicability, this work adopts a single dendrite arm as the research object, assuming no lateral branching and that solidification occurs in a closed system with no mass exchange with the external environment. Additionally, solute elements experience no back diffusion in the solid phase and only diffuse in the liquid phase [8,19].

Based on these assumptions, the dendrite can be treated as an isothermal system. The heat balance equation for the solidification system is [19]:

$$\dot{T} = \frac{dT}{dt} = \frac{H}{c_p}\frac{df_s}{dt} \quad (2)$$

where $\dot{T}$ is the cooling rate during solidification, T and t are the solidification temperature and time, H and c_p represent the latent heat of fusion and specific heat capacity per mole, and f_s is the solid volume fraction.

Solute diffusion in the liquid phase follows Fick' s second law [10]:

$$\frac{\partial w_{l,i}}{\partial t} = D_i \frac{\partial^2 w_{l,i}}{\partial x^2} \quad (3)$$

with boundary conditions:

$$\left.\frac{\partial w_{l,i}}{\partial x}\right|_{x=x(l)} = 0 \quad (4)$$

The solute balance equation at the solid-liquid interface is:

$$w_{l,i}^*(1-k_i)\frac{dx_s}{dt} = -D_i \left.\frac{\partial w_{l,i}}{\partial x}\right|_{x=x_s} \quad (5)$$

where $w_{l,i}$ and D_i are the mass fraction and diffusion coefficient of solute i in the liquid phase, $w_{s,i}^*$ and $w_{l,i}^*$ are the mass fractions of solute i at the solid-liquid interface on the solid and liquid sides, $x(l)$ and x_s are the dendrite length and solidified solid length, respectively, and k_i is the equilibrium partition coefficient.

Local thermodynamic equilibrium is maintained at the solid-liquid interface:

$$T_{liquid}(w_{l,i}^*) = T \quad (6)$$

where $T_{liquid}(w_{l,i}^*)$ is the liquidus temperature at the solid-liquid interface.

By simultaneously solving the thermodynamic equilibrium equation (1), heat balance equation (2), solute conservation equation (3), and mass conservation equation (5), the solute concentrations at the solid-liquid interface during solidification of multi-component alloys can be determined, thereby obtaining the alloy solidification path. During iterative calculations, information such as interface concentration and temperature is obtained through coupling with phase diagram thermodynamics, while comprehensively considering liquid-phase diffusion and cooling rate effects, making the model more representative of actual industrial casting conditions.

The solidification parameters for the Mg-Zn-Gd ternary alloy system used in calculations, such as solute concentrations at the solid-liquid interface and liquidus temperatures, were obtained by coupling Thermo-Calc software with the latest magnesium alloy thermodynamic database [23]. Other physical parameters used in the calculations are listed in [23,24], with cooling rates taken from experimental measurements.

3.3 Numerical Calculation Results

[Figure 5: see original paper] shows the calculated primary phase solidification paths for Mg-4.58Zn-2.6Gd alloy under different cooling conditions. The results demonstrate that different cooling rates lead to different solidification paths. In the insulated and sand moulds with lower cooling rates, the solidification path is L → L+ (Mg) → L+ (Mg)+W(Mg Gd Zn), while in the graphite and copper moulds with higher cooling rates, the path is L → L+ (Mg) → L+ (Mg)+I(Mg Zn Gd).

Qi et al. [23] found that if the second phase initially formed in Mg-Zn-Gd alloys is the (Mg)+W(Mg Zn Gd) eutectic, the W(Mg Zn Gd) phase will undergo a peritectic reaction L+ +W → +I with the remaining liquid at 532.97 °C as the solidification temperature decreases, generating the I phase. For the sand and insulated moulds with lower cooling rates, the alloy first forms the (Mg)+W(Mg Zn Gd) eutectic. When the solidification temperature drops to 532.97 °C, residual liquid remains in the Mg-4.58Zn-2.6Gd alloy, which generates the I phase through the peritectic reaction L+ +W → +I until the liquid is consumed. Therefore, a certain amount of I(Mg Zn Gd) phase can be observed in the sand and insulated mould alloys. In contrast, in the graphite and copper moulds with higher cooling rates, the alloy first forms the (Mg)+I(Mg Zn Gd) eutectic until solidification is complete, resulting in only (Mg) and I(Mg Zn Gd) phases being observed.

[Figure 6: see original paper] compares the experimentally measured and calculated volume fractions of the primary (Mg) phase and eutectic phases in Mg-4.58Zn-2.6Gd alloy under different cooling conditions. The experimental results show that the volume fraction of primary (Mg) phase increases with increasing cooling rate, while the eutectic phase content decreases. The comparison reveals good agreement between the experimentally measured volume fractions of primary (Mg) and eutectic phases and the calculated values across different cooling conditions, validating the correctness and applicability of the present model.

3.4 Prediction and Experimental Validation of Solidification Paths for Mg-Zn-Gd Alloys with Different Compositions

The solidification path of industrial casting alloys is influenced not only by mould cooling rate but also by the original design composition [8,25]. After validating the computational model, three typical alloy compositions in the Mg-rich corner of the Mg-Zn-Gd system were selected for further study: A (Mg-3.8Zn-2.0Gd), B (Mg-5.5Zn-2.0Gd), and C (Mg-5.5Zn-4Gd). The solidification paths of these alloys were investigated under metal mould (cooling rate 7.10 K/s) and sand mould (cooling rate 0.75 K/s) conditions.

[Figure 7: see original paper] presents the calculated solidification paths for alloys A, B, and C under cooling rates of 7.10 K/s (steel mould) and 0.75 K/s (sand mould). [Figure 8: see original paper] shows the XRD spectra of the three

alloys solidified under metal mould and sand mould conditions. At a cooling rate of 7.10 K/s, alloys A and B contain only (Mg) and I(Mg Zn Gd) phases, while alloy C contains (Mg), W(Mg Gd Zn), and small amounts of I(Mg Zn Gd) phases. At a cooling rate of 0.75 K/s, all three alloys (A, B, and C) produce (Mg), W(Mg Gd Zn), and I(Mg Zn Gd) phases.

Based on the analysis of Mg-4.58Zn-2.6Gd alloy solidification microstructures, when Mg-Zn-Gd alloys first form the (Mg)+W(Mg Zn Gd) second phase, the W(Mg Zn Gd) phase undergoes a peritectic reaction L+ +W → +I with residual liquid at 532.97 °C to generate the I phase. Therefore, for alloy C in the steel mould and alloys A, B, and C in the sand mould, the alloys first form the (Mg)+W(Mg Gd Zn) second phase. In contrast, alloys A and B in the steel mould directly form the (Mg)+I(Mg Zn Gd) eutectic. These experimental results are consistent with the primary phase solidification path predictions shown in [Figure 7: see original paper].

Further analysis of [Figure 7: see original paper] reveals that under the same cooling rate, higher Zn content in the alloy drives the solidification path within the (Mg) region closer to the Mg-Zn boundary of the phase diagram, favoring the formation of the Zn-rich I(Mg Zn Gd) phase. Conversely, higher Gd content drives the solidification path closer to the Mg-Gd boundary, favoring the formation of the Gd-rich W(Mg Gd Zn) phase.

For alloys of the same composition, the higher cooling rate in steel moulds drives the solidification path within the (Mg) region closer to the Mg-Zn boundary, favoring the formation of the Zn-rich I(Mg Zn Gd) phase. The lower cooling rate in sand moulds drives the path closer to the Mg-Gd boundary, favoring the formation of the Gd-rich W(Mg Gd Zn) phase.

Thus, for Mg-Zn-Gd magnesium alloys, higher Zn content and higher cooling rates promote the formation of the thermally stable I(Mg Zn Gd) phase, while higher Gd content and lower cooling rates facilitate the formation of the W(Mg Gd Zn) phase.

Conclusions

1. Experimental results for Mg-4.58Zn-2.6Gd ternary casting magnesium alloy under different cooling conditions demonstrate that when the cooling rate is 0.75 K/s, the alloy first forms an (Mg)+W(Mg Zn Gd) eutectic; when the cooling rate is 7.71 K/s, the alloy first forms an (Mg)+I(Mg Zn Gd) eutectic.
2. By organically coupling solute conservation, heat conservation, and mass conservation equations with thermodynamic calculations, a computational model for the primary phase solidification path in multi-component alloys was established, comprehensively considering liquid-phase diffusion and

cooling rate effects. The calculated results show good agreement with experimental data.

3. Numerical calculations and experimental results indicate that for Mg-Zn-Gd industrial casting magnesium alloys, higher Zn content and higher cooling rates promote the formation of the thermally stable I(Mg Zn Gd) phase, while higher Gd content and lower cooling rates facilitate the formation of the W(Mg Gd Zn) phase.

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Note: Figure translations are in progress. See original paper for figures.