Postprint of Free Solidification Path Selection in Mg-Zn-Gd Ternary Cast Magnesium Alloy

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Date: 2023-03-19T00:00:00+00:00

Abstract

Through experimental and numerical approaches, the selection of free solidification paths in Mg-4.58Zn-2.6Gd ternary cast magnesium alloy was investigated. Experimental results indicate that at mold cooling rates $ $0.75 K/s, the primary eutectic formed in the alloy is a(Mg)+W(Mg3Zn3Gd2); whereas at mold cooling rates $ $7.71 K/s, the primary eutectic is a(Mg)+I(Mg3Zn6Gd). A computational model for the primary phase solidification path of multicomponent alloys was established, comprehensively considering factors of liquid-phase diffusion and cooling rate. By coupling with the thermodynamic calculation software Thermo-Calc and its database, the thermodynamic data required for calculating the solidification path of the g-4.58Zn-2.6Gd alloy were obtained, and the calculated results were found to be in good agreement with experimental data.

Full Text

Preamble

Acta Metallurgica Sinica, Vol. 51, No. 5, May 2015, pp. 580-586

Selection of the Solidification Path of Mg-Zn-Gd Ternary Casting Magnesium Alloys

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Supported by: National Natural Science Foundation of China (Nos. 51071129 and 51227001)

Manuscript received: 2014-09-15, in revised form 2015-02-11

Abstract

Mg-Zn-Gd base alloys possess significant advantages, including high strength, light weight, and low cost, making them favorable for application in various airframe components. Under traditional casting conditions, two types of eutectic phases can typically be found in Mg-Zn-Gd alloys: W($Mg_3Zn_3Gd_2$) and I(Mg_3Zn_6Gd). The interface between the W phase and α(Mg) is incoherent and thus weak. However, the I phase has a quasiperiodic lattice that leads to a coherent interface with α(Mg). Therefore, compared with the W phase, the I phase is more effective at obstructing dislocation slip and thus efficiently strengthens the alloy. Consequently, controlling the solidification path—that is, controlling the relative amounts of I phase and W phase—is critical for improving 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 ($ $0.75 K/s), the α+W($Mg_3Zn_3Gd_2$) eutectic forms first, while at higher cooling rates ($ $7.71 K/s), the α(Mg)+I(Mg_3Zn_6Gd) 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 required for the computation model were obtained using the Thermo-Calc database. The numerical results showed 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.

Keywords: Mg-Zn-Gd ternary magnesium alloy, solidification path, cooling rate, numerical model

1. Introduction

Mg-Zn-Gd alloys have attracted considerable attention for aerospace applications due to their excellent specific strength and cost-effectiveness. The mechanical properties of these alloys are strongly influenced by the type and distribution of eutectic phases formed during solidification. Two primary eutectic phases can form: the W phase ($Mg_3Zn_3Gd_2$) and the I phase (Mg_3Zn_6Gd). The W phase forms an incoherent interface with the α-Mg matrix, resulting in weak interfacial bonding, whereas the I phase forms a coherent interface due to its quasiperiodic lattice structure. This coherent interface makes the I phase more effective at impeding dislocation motion and thus provides superior strengthening. Therefore, controlling the solidification path to favor I phase formation is essential for enhancing the high-temperature performance of these alloys. This study combines experimental investigation with numerical modeling to understand and predict the solidification path selection in Mg-Zn-Gd alloys under various cooling conditions.

2. Experimental Methods

Temperature measurements were performed using thermocouples placed at the center of the mold cavity, 40 mm from the top, as shown in [Figure 1: see original paper]. The cooling curves for Mg-4.58Zn-2.6Gd alloy in different molds were recorded, and the cooling rates were determined to be 10.08, 7.71, 0.75, and 0.32 K/s [Figure 2: see original paper]. Metallographic samples were sectioned near the thermocouple positions, ground, polished, and etched using a solution of 4% HNO_3 + 96% C_2H_5OH (volume fraction). Microstructures were examined using an Olympus PM-G3 optical microscope (OM) and a JSM-5800 scanning electron microscope (SEM). Phase identification was conducted using Oxford Inca energy-dispersive spectroscopy (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.

3. Results and Discussion

3.1 Experimental Results

[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 transforms from coarse, continuous networks to fine, discontinuous island-like eutectics. presents the EDS analysis results of the secondary eutectic phases and matrix. With increasing cooling rate, the solute concentrations of Zn and Gd in the eutectic phases decrease significantly. This occurs because at higher cooling rates, solute elements have insufficient time to diffuse to the solid-liquid interface, resulting in eutectic phases with lower solute content [20]. The EDS analysis indicates that phases A1 and B1 have a Zn/Gd ratio of approximately 6:1, identifying them as the I(Mg_3Zn_6Gd) phase, while phases C1 and D1 have a Zn/Gd ratio of about 1.5:1, corresponding to the W($Mg_3Zn_3Gd_2$) phase.

[Figure 4: see original paper] shows the XRD spectra of Mg-4.58Zn-2.6Gd alloy solidified under different conditions. In the insulated and sand molds with lower cooling rates, the microstructure consists primarily of α(Mg), W($Mg_3Gd_2Zn_3$), and a small amount of I(Mg_3Zn_6Gd). In contrast, in the graphite and copper molds with higher cooling rates, the microstructure comprises only α(Mg) and I(Mg_3Zn_6Gd) phases.

3.2 Thermodynamic Principles

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

_i^s = _i^l

From the Redlich-Kister-Muggianu model [22], the chemical potential _i is a function of solute concentration and temperature. When solid-liquid equilibrium is established, 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 if the chemical potentials are known.

3.3 Microscopic Solidification Model

During free solidification, industrial alloys typically form equiaxed dendrites. Given the complex branching and varied morphologies of equiaxed dendrites, a comprehensive evaluation would inevitably introduce unknown parameters and increase computational time. For industrial applicability, this work considers a single dendrite arm of an equiaxed grain with no side branching. Solidification is assumed to occur in a closed system with no mass exchange with the surroundings, no back diffusion of solute elements in the solid phase, and solute transport occurring only by diffusion 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]:

0 = d (T = dT/dt)

where T is the cooling rate, T and t are the solidification temperature and time, respectively, H and c__p represent the latent heat of fusion and specific heat per unit mole, and f__s is the solid volume fraction.

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

w__l,i/ t = D__i ^{2}w__l,i

with boundary conditions: w__l,i/ x|__{x=x(l)} = 0

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

(w__l,i* - w__s,i*) x__s/ t = D__i w__l,i/ x|__{x=x__s} 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 on the solid and liquid sides of the interface, and x(l) and x_s are the dendrite length and solidified length, respectively.

Local thermodynamic equilibrium is maintained at the interface:

T_{interface} = T_{liquid}(w_l,i*)

where T_{liquid}(w_l,i*) is the liquidus temperature at the interface composition.

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, interface concentration and temperature information are obtained through coupling with thermodynamic calculations, while 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, such as solute concentrations at the solid-liquid interface and liquidus temperatures, were obtained by coupling with Thermo-Calc software and 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.

3.4 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 the solidification path varies with cooling rate. In insulated and sand molds with lower cooling rates, the solidification path is L → L+α(Mg) → L+α(Mg)+W($Mg_3Gd_2Zn_3$), whereas in graphite and copper molds with higher cooling rates, the path is L → L+α(Mg) → L+α(Mg)+I(Mg_3Zn_6Gd).

Qi et al. [23] found that if the α(Mg)+W($Mg_3Zn_3Gd_2$) eutectic forms first in Mg-Zn-Gd alloys, the W($Mg_3Zn_3Gd_2$) phase will undergo a peritectic reaction with the remaining liquid at 532.97 °C: $L+\alpha+W \rightarrow \alpha+I$, generating the I phase. For sand and insulated molds with lower cooling rates, the α(Mg)+W($Mg_3Zn_3Gd_2$) eutectic forms initially. When the temperature decreases to 532.97 °C, residual liquid remains in the Mg-4.58Zn-2.6Gd alloy, which transforms to the I phase through the peritectic reaction until the liquid is consumed. Consequently, a certain amount of I(Mg_3Zn_6Gd) phase is observed in sand and insulated mold samples. In contrast, for graphite and copper molds with higher cooling rates, the α(Mg)+I(Mg_3Zn_6Gd) eutectic forms directly and persists until solidification is complete, resulting in microstructures containing only α(Mg) and I(Mg_3Zn_6Gd) phases.

[Figure 6: see original paper] compares the experimentally measured and calculated volume fractions of primary α(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 α(Mg) phase increases with increasing cooling rate, while the eutectic phase content decreases. The calculated volume fractions of both primary α(Mg) phase and eutectic phases show good agreement with experimental measurements across all cooling conditions, validating the accuracy and applicability of the model.

3.5 Prediction and Experimental Validation of Solidification Paths for Different Mg-Zn-Gd Alloy Compositions

The solidification path of industrial casting alloys depends not only on mold cooling rate but also on the original alloy composition design [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: Alloy A (Mg-3.8Zn-2.0Gd), Alloy B (Mg-5.5Zn-2.0Gd), and Alloy C (Mg-5.5Zn-4Gd). The solidification paths of these alloys were investigated under metal mold cooling (7.10 K/s) and sand mold cooling (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 (metal mold) and 0.75 K/s (sand mold). [Figure 8: see original paper] shows the corresponding XRD spectra. At a cooling rate of 7.10 K/s, alloys A and B contain only α(Mg) and I(Mg_3Zn_6Gd) phases, while alloy C contains α(Mg), W($Mg_3Gd_2Zn_3$), and a small amount of I(Mg_3Zn_6Gd). At 0.75 K/s, all three alloys (A, B, and C) contain α(Mg), W($Mg_3Gd_2Zn_3$), and I(Mg_3Zn_6Gd) phases.

Based on the analysis of Mg-4.58Zn-2.6Gd alloy, when the α(Mg)+W($Mg_3Zn_3Gd_2$) eutectic forms first, the W($Mg_3Zn_3Gd_2$) phase undergoes a peritectic reaction with residual liquid at 532.97 °C to form the I phase. Therefore, for alloy C in the metal mold and all three alloys in the sand mold, the α(Mg)+W($Mg_3Gd_2Zn_3$) eutectic forms initially. In contrast, for alloys A and B in the metal mold, the α(Mg)+I(Mg_3Zn_6Gd) eutectic forms directly. These experimental results are consistent with the primary phase solidification paths predicted by the model in [Figure 7: see original paper].

Further analysis of [Figure 7: see original paper] reveals that under the same cooling rate, higher Zn content shifts the solidification path in the α(Mg) region closer to the Mg-Zn binary edge of the phase diagram, favoring formation of the Zn-rich I(Mg_3Zn_6Gd) phase. Conversely, higher Gd content shifts the path closer to the Mg-Gd edge, promoting formation of the Gd-rich W($Mg_3Gd_2Zn_3$) phase.

For a given alloy composition, higher cooling rates (metal mold) shift the solidification path toward the Mg-Zn edge, favoring I(Mg_3Zn_6Gd) formation, while lower cooling rates (sand mold) shift it toward the Mg-Gd edge, favoring W($Mg_3Gd_2Zn_3$) formation.

Thus, for Mg-Zn-Gd alloy systems, higher Zn content and higher cooling rates promote formation of the thermally stable I(Mg_3Zn_6Gd) phase, whereas higher Gd content and lower cooling rates favor W($Mg_3Gd_2Zn_3$) formation.

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4. Conclusions

1. Experimental results for Mg-4.58Zn-2.6Gd ternary casting alloy under different cooling conditions demonstrate that when the cooling rate is $ $0.75 K/s, the α(Mg)+W($Mg_3Zn_3Gd_2$) eutectic forms first; when the cooling rate is $ $7.71 K/s, the α(Mg)+I(Mg_3Zn_6Gd) eutectic forms first.
2. By coupling solute conservation, heat conservation, and mass conservation equations with thermodynamic calculations, a numerical model for predicting the primary phase solidification path in multi-component alloys was established, comprehensively considering liquid-phase diffusion and cooling rate effects. The calculated results show good agreement with experimental data.
3. Numerical calculations and experimental results demonstrate that for industrial Mg-Zn-Gd casting alloys, higher Zn content and higher cooling rates favor formation of the thermally stable I(Mg_3Zn_6Gd) phase, while higher Gd content and lower cooling rates promote formation of the W($Mg_3Gd_2Zn_3$) phase.

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