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Divorced Eutectic Solidification of Mg-Al Alloys

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Abstract

We present simulations of the nucleation and equiaxed dendritic growth of the primary HCP α -Mg phase followed by the nucleation of the β -phase in interdendritic regions. A zoomed-in region of a melt channel under eutectic conditions is investigated and compared to experiments. The presented simulations allow to predict final properties of an alloy based on process parameters. The obtained results give insight into the solidification processes governing the microstructure formation of Mg-Al alloys allowing their targeted design for different applications.

Introduction

Due to their low density, magnesium alloys are of high importance for modern lightweight structures and are widely used for various applications in automotive and aerospace industries as well as consumer electronics. The most applied alloying element in Mg alloys is aluminum which is used for AZ91, AM50 (cast) or AZ31 (wrought) technical alloys. The mechanical properties of Mg-Al alloys are primarily determined by their microstructure which consists of two main phases: the Mg-rich hexagonal close-packed (HCP) α -phase and a near stoichiometric $Mg_{17}Al_{12}$ β -phase, and further minor secondary phases due to third alloying elements. The addition of Al in small concentrations has a positive effect on the corrosion properties of the Mg-Al alloys mainly due to the formation of a percolating β -phase network [1] which is less electrochemically active compared to the α -phase. Experiments e.g. in [2] revealed that the formation of a closed shell of β -phase, preventing α -phase dendrites from building networks, is a good strategy to significantly increase the corrosion resistance of cast Mg-Al alloys. Furthermore, it severely hinders the galvanic corrosion if Mg-alloys are brought into contact with more noble metals. Thus, tailoring the Mg-Al alloy microstructure is of great importance for controlling its corrosion resistance [3]. In this work we apply the phase-field method [4, 5, 6] to simulate the solidification microstructure of Mg-Al alloys. Besides primary solidification, which has been presented in 2 and 3 dimensions by several authors [4, 5, 6, 7], eutectic solidification of the residual melt between the dendrites, which is assumed to happen in a divorced mode, is the focus of the present paper. The information about the as cast morphology and in particular the distribution of secondary β -phase shall point towards improved materials and process design also in terms of corrosion. The proposed approach enables metallurgical process control by correlation of metallurgical parameters to metallic phase fractions and, in a subsequent step, to corrosion rates. This will significantly

contribute to the development of Integrated-Computational-Materials-Engineering (ICME) by adding service-life aspects to computational materials design.

Experimental details

A pure magnesium ingot (99.95 %, 1kg weight) and pure Al buttons were given into a carbon crucible according to the given compositions (Mg-5Al, Mg-15Al, and Mg-25Al in wt%) and heated to 973 K using an induction furnace under CO_2 and SF_6 protective atmosphere. The melt was poured into a rectangular mould, preheated to 573 K ($10 \text{ mm} \times 100 \text{ mm} \times 150 \text{ mm}$). In order to record the temperature during the whole solidification process a K-type thermocouple was placed at the center of the mould. Microstructures were observed next to the thermocouple using scanning electron microscope (SEM) in order to obtain microstructures with the corresponding cooling history given in Fig. 1. The resulting experimental microstructures are shown in Fig. 2.

Figure 1: Experimentally measured cooling curves for different alloy compositions: Mg-5wt.%Al, Mg-15wt.%Al and Mg-25wt.%Al.

Figure 2: SEM images of as cast Mg-Al microstructures for different alloy compositions (from left to right): Mg-5wt.%Al, Mg-15wt.%Al and Mg-25wt.%Al.

Phase-field model

In this study we apply the multi-phase-field method on a meso-scale with locally linearized phase diagram information [8]. In this method each grain of a distinct crystallographic phase

is attributed by its own phase-field variable $\phi_p(\vec{x}, t) \in [0, 1]$. Three distinct crystallographic phases are considered: liquid melt, Mg-rich α -phase and a near stoichiometric $Mg_{17}Al_{12}$ β -phase, where each solid grain is attributed by an identifier of the crystallographic phase and its orientation in space (for details see [5, 8]). For the interface between melt and the α -phase an anisotropic interface energy $\sigma_{pq} = \sigma_{pq}(\vec{n})$ as a function of the interface normal $\vec{n}$ with respect to the crystallographic orientation of each grain is used [8]. The interface energy between the melt and β -phase as well as between the solid α - and β -phases is assumed isotropic. In order to consider the effect of external cooling rate on nucleation and growth of solid phases we solve the heat balance in average over the whole domain with n_{xyz} discrete elements:

$$\rho c_p \dot{T} = \sum_{n_{xyz}} \sum_{p \neq q} \dot{\psi}_{pq} L_{pq} + \dot{Q}_{ext}, \quad (1)$$

where T is the temperature of the system, $\dot{Q}_{ext}$ is the heat extraction rate, ρ and c_p are the specific heat and the mass density which are taken constant throughout the simulation. $\dot{\psi}_{pq}$ are the local transformation rates between pairs of phases which sum up to the total transformation rate of individual phases $\dot{\phi}_p = \sum_{q \neq p}^N \dot{\psi}_{pq}$ in the interface or a junction point with N phases (for details see [9]). L_{pq} is the latent heat associated with the individual transformations between phases p and q . In the present study we treat all possible transformations between liquid $\leftrightarrow \alpha$, liquid $\leftrightarrow \beta$ and $\alpha \leftrightarrow \beta$ phases.

Phase diagram

In order to obtain the phase diagram along with the exact transformation temperatures and slopes for our calculations the CalPhaD method was used via the Thermocalc TCS 4.0 database TCBIN. For convenience the obtained phase diagram was linearized for the simulations as it is shown in Fig. 3

Figure 3: Mg-Al binary phase diagram with linearization (red)

All slopes but $m_{liq \leftrightarrow \alpha}$ and $m_{\alpha \leftrightarrow liq}$ are taken at eutectic temperature of 709.4K. Solidus- and liquidus-slopes are the slopes between the points (923.15K; 0.0%Al) and (709.4K; 31.0%Al) [eutectic point] or (709.4K; 11.6%Al) respectively.

Table 1: Parameters of the linearized Mg-Al phase diagram as shown in red on Fig. 3

intersection concentration	$C_{\alpha \leftrightarrow liq.}$	0.00 %	slope (liquidus)	$m_{liq. \leftrightarrow \alpha}$	-6.90 K/%
intersection temperature	$T_{\alpha \leftrightarrow liq.}$	923.15 K	slope (solidus)	$m_{\alpha \leftrightarrow liq.}$	-27.58 K/%
intersection concentration	$C_{\beta \leftrightarrow liq.}$	45.64 %	slope (liquidus)	$m_{liq. \leftrightarrow \beta}$	3.50 K/%
intersection temperature	$T_{\beta \leftrightarrow liq.}$	760.60 K	slope (solidus)	$m_{\beta \leftrightarrow liq.}$	9.00 K/%
intersection concentration	$C_{\alpha \leftrightarrow \beta}$	34.20 %	slope (solvus)	$m_{\alpha \leftrightarrow \beta}$	22.40 K/%
intersection temperature	$T_{\alpha \leftrightarrow \beta}$	1301.84 K	slope (solvus)	$m_{\beta \leftrightarrow \alpha}$	-103.00 K/%

The linearization alters the point of maximum solubility in the α from 11.6% to 7.75% to match the area of the original $liquid \leftrightarrow \alpha$ two-phase area in the phase diagram. Thus the solidus slope ($m_{\alpha \leftrightarrow liq.}$) was adjusted from the original -18.43 K/% to -27.58 K/%. Also $C_{\alpha \leftrightarrow \beta}$ and $T_{\alpha \leftrightarrow \beta}$ were adjusted to retain $m_{\alpha \leftrightarrow \beta}$. Consequently the original $\alpha \leftrightarrow \beta$ intersection-point (1229.84K ; 34.83%Al) was adjusted to (1301.84K ; 34.20%Al). All values used for the characterization of the phase diagram are summarized in table 1.

Nucleation model

In order to capture the dependence of the nucleation density on the cooling rate we employ the so-called “free growth model” by Greer and coworkers [11]. This model is based on a given distribution of seed particles of different size. Assuming perfect wetting condition between the primary α -phase and the seed particles, the hemispheric cap of α -phase on the seed particles defines the critical undercooling for free growth of the nucleating phase which is inversely proportional to the size of the seed particles [10]. In our simulations we start from a random distribution of particles with a given density and size distribution over the entire simulation domain initially filled with liquid melt. The utilized normal distribution is given by

$$N(d) = K \cdot \frac{1}{b\sqrt{2\pi}} \exp \left[- (d - a)^2 / 2b^2 \right]. \quad (2)$$

Each particle is assigned an effective size d which determines the critical undercooling for its activation. The resulting number of particles is typically higher than the actual number of the activated particles (active nucleation sites). Activation happens if a grid cell, which contains a particle, reaches it's critical undercooling, i.e. if the difference between actual temperature and melting temperature dependent on the local alloy concentration exceeds the local critical undercooling. A similar model has also been applied by Eiken et al. [8]. The parameters of the utilized nucleation model are summarized in table 2. Note that while parameter a is negative only the positive tail of a normal distribution is used. We also assume significantly higher nucleation density of the β -phase in the melt channels between the primary α -phase dendrites.

Results

Although, the primary solidification in three-dimensional domains can be investigated in order to reveal the effect of cooling rate on the nucleation density of α -phase dendrites (see

Table 2: Nucleation model parameters

particle density for α -phase nucleation, K_α	$0.2 \cdot 10^{14} m^{-3}$
particle density for β -phase nucleation, K_β	$1.5 \cdot 10^{16} m^{-3}$
parameter a of the normal size-distribution	$-1.5 \cdot 10^{-7} m$
parameter b of the normal size-distribution	$1.0 \cdot 10^{-7} m$

Fig. 4), it is computationally demanding to study the entire solidification process in 3D over the temperature range of more than $200K$ even with high cooling rates. In contrast, in the 2D simulations it is possible to investigate the entire solidification process starting from the primary α -phase dendritic solidification and continuing with the eutectic solidification of secondary β -phase upon cooling below the eutectic point.

Figure 4: Results of a 3D simulation of primary α -phase nucleation and growth

The heat extraction rate is assumed constant, which relates to an applied cooling rate (neglecting release of latent heat) $CR = \frac{\dot{Q}}{\rho c_p}$. We note that this cooling rate is different from the cooling rate evaluated from the experiments. We will compare both entities by comparing the solidification time (see below). All simulations of primary α -phase solidification are performed in a domain with periodic boundary conditions initially filled with homogeneous melt.

Figure 5: 2D solidification simulation at different time-steps. From left to right: α -phase dendrites (blue) nucleate and grow in the melt (white) and are surrounded by a secondary β -phase (orange) in the late stage.

Simulations of consecutive α - and β -phase nucleation and their divorced eutectic growth were carried out in 2D. The applied cooling rates were varied from $10K/s$ to $25K/s$. The resulting temperature profiles are shown in Fig. 6. The obtained solidification microstructure along with its evolution at a cooling rate of $10K/s$ is presented in Fig. 5. At first, the domain is filled with liquid Mg-5at.%Al slightly above $T_{solidus}$ and cooled down linearly, extracting the same amount of heat every time. As the undercooling gets large enough for the largest of the hard inclusions to get activated as nucleation sites, seeds are placed

Figure 6: Simulated coling curves

creating the nucleation events. Growth of primary α -phase releases latent heat leading to a recoalescence, as frequently observed in experiments. Thus all of the smaller not activated particles never reach the necessary undercooling and thus remain inactive. The system is continuously cooled down to the eutectic temperature of 709.4 K. After cooling down below the eutectic temperature, the β -phase nucleates in the interdendritic region. The particle density for β -phase nucleation is assumed to be three orders of magnitude higher than for the α -phase because of the segregation of particles in the interdendritic regions. The final microstructure consists of a primary α -phase dendrites (blue) surrounded by the thin channels of β -phase (orange). The final volume fraction of the β -phase obtained in the simulations is about 5%. Comparing simulation results shown in Fig. 5 with experimental observations shown in Fig. 2 a good qualitative agreement between the obtained microstructure can be noted. There is a slight difference in the initial alloy composition between experiment (5wt.% Al) and simulation (5at.% Al $\approx$ 5.52wt.% Al) which is responsible for a visibly higher β -phase volume fraction in the simulation. A clear trend of increasing β -phase fraction with increasing Al-concentration is also seen in the experiment (see Fig. 2).

The difference in the applied cooling rates (which results in a solidification time of about 20 s in the 25K/s simulation but only about 13 s in the experiment) leads to almost twice as coarse microstructure in the simulation which is the result of a recoalescence effect (compare Figs. 2 and 7).

A similar trend is observed in the simulations results shown in Fig. 7.

Figure 7: 2D simulated microstructures of Mg-Al alloy solidified at different cooling rates

It shall be noted, that on a scale of primary α -phase dendrites the eutectic structure in the interdendritic region cannot be resolved and as the result the secondary β -phase builds a bulk structure between the primary dendrites as can be seen in Fig. 5. In order to

investigate in detail the β -phase nucleation and growth kinetics the simulation was performed in 3D. We zoom into the channel between two primary dendrites upon reaching the eutectic temperature. Here we select the scale of the simulations by a factor of 5 finer than the scale of primary α -phase dendritic solidification simulations. The channel width between α -dendrites was chosen large enough to see the eutectic structure. The simulations start from a concentration profile taken around the melt channel of a 2D simulation of primary α -phase growth. Then a second particle distribution for β -phase nucleation is generated using the parameters given in Table 2. The results of eutectic solidification simulation are shown in Fig. 8.

Figure 8: Zoomed in region of the residual eutectic melt channel between two α -phase (blue) dendrites at different time-steps. Undercooling causes the β -phase (orange) to nucleate at randomly chosen positions in the melt and grow until the α -phase boundary is fully covered. Then residual melt is depleted which would allow a tertiary α -phase to nucleate and grow again.

At the beginning of the simulation a residual melt channel has the eutectic composition of 31% with a nearly eutectic α -phase at the bottom and the top of the simulation volume. The system is cooled down starting from 712.0 K, slightly above the eutectic temperature. The α -phase is still slowly growing on this scale. As soon as the undercooling is sufficient, nucleation automatically takes place and generates a large number of β -grains in the residual melt. The high nucleation density of 3×10^{13} particles m^3 was chosen because it is expected for the particles to be aggregated in the residual melt. In our simulation we get around 50 nuclei within the channel. A strong tendency of β -phase growth towards the α -liquid interface can be observed. This is because Al is strongly segregated by the growing α -phase into the melt close to the interface, since the solubility for Al in α is only 11.6% at the eutectic temperature of 709.4 K. This leads to a higher concentration of Al in the melt close to the slowly growing α -phase. The β -phase, consisting of about 40% Al grows preferably in the area of the increased concentration. Due to this circumstances a rapid full enclosure of the α -phase by the β -phase can be observed. Thus, further growth of the α -phase is hindered. Continuing β -phase growth further depletes the concentration in the residual melt. This brings the system into the state where a tertiary α -phase nucleation is necessary for complete solidification.

Similar tendencies are also observed in experimental results shown in Fig. 9 where the β -phase covers the primary α -phase dendrites. The rest of the channel is filled with a fine divorced eutectic microstructure consisting of α - and β -phase.

As it is shown above the growth of β -phase show tendency for the formation of a closed shell around the α -phase dendrites which is responsible for increasing the corrosion-resistance of Mg-Al alloys. The good agreement of the simulation results with experimental observations allows using the proposed simulation method for computationally assisted design of corrosion resistant Mg-alloys. Of course there is a trade off between fine grain structure (better mechanical properties) and low connectivity of primary α -phase dendrites (better

Figure 9: Higher resolution SEM images of a channel between primary α -dendrites in the Mg-15wt.%Al alloy.

corrosion properties). The balance between mechanical and corrosion properties can be further tuned and investigated by the proposed method.

Outlook: sedimenting dendrites

The simulations were performed under purely diffusive conditions. Under experimental conditions, however, there will always be convection in the melt, either caused by long range thermal gradients, short range solutal gradients or by the density difference between the solid and the melt: No dendrite will stay at the location it has been nucleated, nor keep its orientation. Also the segregated alloying components will be transported by advection. A phase-field model to treat this effect has been established [13]. It has been first applied to a ripening study in a binary mush [14]. An application to directional solidification demonstrated the strong dependence of the primary spacing of directionally solidified dendrites on the orientation in the gravity field [15]. The OpenPhase[12] code with MPI parallelization opens the possibility to perform large scale dendritic solidification including melt flow in 3D (Fig. 10). It shall be applied in the future to get even more realistic description of the morphology of as cast dendritic structures.

Figure 10: α -Mg dendrite growing in liquid melt, rotating due to applied shear flow.

Summary

In this paper a phase-field approach for Mg-Al alloy solidification was presented. The free open source library OpenPhase together with a linearized phase diagram based on Thermo-calc TCS 4.0 database TCBDIN was used to simulate 3D primary dendritic solidification as well as the full solidification cycle in 2D for different cooling conditions. The “free growth” model, which allows to simulate the recoalescence effect, was used in order to model the correct nucleation kinetics as it is seen in experiments. In order to fully describe the kinetics of final eutectic solidification in interdendritic regions a dual-scale approach was employed. The resulting microstructure shows the tendency of rapid, complete coverage of primary dendrites with β -phase and was verified with experimental data with remarkable agreement. Divorced eutectic solidification mode was reproduced showing a tendency for tertiary nucleation of α -phase due to full shielding of primary dendrites after a short period of time.

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