**Three-dimensional α -Mg dendritic morphology and branching structure
transition in Mg-Zn alloys**

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Abstract

23 Three-dimensional dendritic morphology and branching structure of hexagonal
24 close-packed α -Mg in magnesium-zinc alloys possessing different zinc concentrations
25 were studied using synchrotron X-ray microtomography. Interestingly, dendrite
26 growth patterns were observed to undergo a morphologic transition with increasing
27 zinc addition. Dendrite arms in the basal plane of hexagonal close-packed α -Mg tend
28 to split and deviate from the basal plane continuously and symmetrically as a function
29 of zinc concentrations. A hyperbranched dendrite structure was also found with an
30 interim zinc concentration. Several types of dendrite growth patterns with different
31 morphologies and branching structure were proposed in order to reflect the evolution
32 of α -Mg dendrites with various zinc contents.

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34 **Keywords:** Magnesium alloy; X-ray tomography; solidification; dendritic growth;
35 morphology transition;

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37 **1 Introduction**

38 Dendrites are formed during a wide range of solidification processes like casting and
39 welding[1][2][3]. Primary formed dendrites constitute the skeletal network of
40 materials and significantly influence the final microstructure[4][5]. These
41 non-equilibrium patterns result from the instability of the solid-liquid interface exhibit
42 diverse morphological and hierarchical branching structures during solidification[2].
43 However, the fundamental elucidation of the formation of complicated dendritic
44 growth morphology and orientation remains limited. Dendrite morphology and
45 growth direction are mainly determined by diffusion of heat and solute, capillary
46 force due to surface energy effect and crystalline anisotropy, which reflects the
47 symmetrical of underlying crystal lattice[1][6]. These three distinct physical
48 phenomena and the competition between them, result in a much richer variety of
49 dendrite growth patterns in materials[2][6][7][8].

50 Magnesium is a typical hexagonal close-packed (hcp) structure metal which has
51 wide structural applications owing to its lightweight and good formability[9][10]. It
52 was reported that the anisotropy of the crystal-melt interfacial free energies γ_s for
53 magnesium in different high symmetry orientations was approximately 1% [11][12].
54 While for the hexagonal Zn, the anisotropy between the *c*-axis and basal plane was
55 shown to be as high as 30% [2][13]. α -Mg dendrite was found to grow as a snowflake
56 plate-like structure with the dendrite arms growing along $\langle 11\bar{2}0 \rangle$ directions in
57 Mg-9wt.%Al alloy [14][15][16]. Whilst in Mg-Zn [17][18], Mg-Sn [16] and Mg-Ca [19]
58 alloys, more complicated and richer dendrite morphologies and branching structures

were observed. Recently, the investigations by Gonzales *et al.*[13], Haxhimali *et al.*[2] and Rappaz *et al.*[20][21] reported that dendrite orientation of α -Al was observed to transition from $\langle 100 \rangle$ to $\langle 110 \rangle$ with an increasing concentration of Zn. Seaweed-structures without clear trunks and well-defined growth directions were also observed at interim composition of Zn from 25 wt. % to 55 wt. %. This dendrite orientation transition (DOT) was explained in terms of the influence of Zn on the solid-liquid interfacial free energy anisotropy of α -Al phase in Al-Zn alloys. Accordingly, similar to the DOT of weak anisotropy α -Al dendrites in Al-Zn alloys, it is reasonable to raises the question of whether the weak anisotropy hcp α -Mg dendrites in Mg-Zn (hcp-hcp) alloys will also experience a DOT with the increasing alloying addition of Zn.

In present work, the resultant 3D dendritic morphology and branching structure of primary α -Mg phase in Mg-Zn alloys possessing various concentrations of Zn were studied using high resolution synchrotron microtomography. The experimental results reveal a transition of α -Mg dendrite in morphology and branching structure with the increasing addition of Zn alloying element and they are of critical importance when tuning the composition of alloying elements, in order to control the microstructure and thus improve the mechanical properties of cast magnesium alloys.

2 Materials and methods

Mg-Zn alloys with different weight percent (10, 25, 38 and 50 wt. %) Zn were prepared by encapsulating cylindrical specimens with diameters of 1.5mm in quartz

tubes. Then the alloys were remelted and cooled from liquidus to approximately 20°C above the eutectic point at a cooling rate of 0.1°C/s, where equiaxed growth of dendrites were formed. Following this, the semi-solid alloys were quenched in ice water to freeze the dendritic microstructure. As the solidification experiments were conducted at a small to moderate growth rate, the contribution of attachment kinetics was minimised; and the difference in growth morphologies and orientation selection were thus mainly attributed to the influence of solute on the interfacial free energy γ_{sl} anisotropy in front of the solid-liquid interface of primary α -Mg phase[1][5][22][23].

The synchrotron X-ray microtomography was carried out on BL13W1 in SSRF (Shanghai Synchrotron Radiation Facility, China). A monochromatic beam with energy of 28 keV was used to penetrate the specimens and 720 projections were taken for each scan over 180° with a voxel size of 0.74×0.74×0.74 μm^3 . Images were processed and rendered with ImageJ (NIH, US) and Avizo[®] (FEI, France). A 3-D median filter was used for noise reduction and a 3-D region growing algorithm for segmentation of solid and liquid phases.

3 results and discussions

3.1 α -Mg dendrite morphology and orientation transition

Isolated dendrites located in the centre of four samples were extracted from the ensemble of dendrites for analysis. The selected dendrites were representative of the typical microstructures observed for corresponding compositions. Three-dimensional morphologies of α -Mg dendrites in Mg-Zn alloys with different additions of Zn are presented in Figure 1. It is clearly observed, that the α -Mg dendrites evolved with

different morphologies and branching structures with increasing Zn concentrations.

Section 1 and section 2 in Figure 1a, b, c and d are two clip planes parallel to the supposed basal plane and the prismatic central plane, respectively.

Figure 1 Three-dimensional dendritic morphologies and branching mechanism of α -Mg dendrites in Mg-Zn alloys with various additions of Zn; section 1 and section 2 are supposed to be the basal plane and prismatic central plane, respectively. (a, a1, a2) Mg-10wt.%Zn; (b, b1, b2) Mg-25wt.%Zn; (c, c1, c2) Mg-38wt.%Zn; (d, d1, d2) Mg-50wt.%Zn. (a1) and (a2), (b1) and (b2), (c1) and (c2), (d1) and (d2) share the same scale bar, respectively.

When analysing the lowest Zn concentration (10 wt. %) of which primary α -Mg phase is less developed, as depicted in Figure 1(a), 1(a1) and 1(a2), a snowflake plate-like structure with six-fold symmetrical growth form was observed. No branch arms are observed to grow deviate from the basal plane. This type of growth morphology is similar to what observed in Mg-9wt. %Al alloys[14][15][16]. The growth directions of the six branching arms are likely to be the preferential $\langle 1120 \rangle$ on the basal plane (0001) since $\langle 1120 \rangle$ is commonly reported to be the preferred orientation in Mg[1][3][15].

It was found that when the addition of Zn was increased to 25 wt. %, the dendrites kept forming a six-fold symmetric morphology from the perspective of the basal plane (section 1), while on the prismatic section, as seen in Figure 1 (b2), these dendrite arms split into two symmetric directions with respect to the basal plane. Furthermore, based on the topological analysis in present study and results from

previous researches[14][15][16][17], the growth directions of the split arms are supposed to be $\langle 11\bar{2}0 \rangle$ directions which are between $\langle 1120 \rangle$ and $\langle 0001 \rangle$.

When increasing the concentration of Zn to 38 wt. %, the dendrite growth directions were not clearly determined, however, a dim six-fold symmetric was still recognizable from the basal plane (Figure 1(c1)). Dendrites appeared to be more like hyperbranched structures with plentiful split dendrite tips formed and their growth directions were so ill-defined that it was difficult to precisely identify crystallographic directions. This is likely due to the interfacial free energy anisotropy alteration caused by the addition of zinc, which favored more growth directions and resulted in a hyperbranch structure. The seaweed-like dendrite morphology was also observed experimentally in Al-Zn alloys, with the Zn concentration between 25 and 55 wt. %[13][20] and simulated numerically with phase-field models[2][6].

When considering the relatively high concentration of Zn (50 wt. %), which is close to the eutectic composition, the morphology of dendrites exhibited a six-fold symmetry as those observed in Mg-10/25wt. %Zn from the view of the basal plane (Figure 1(d1)). However, it was evident that the $\langle 1120 \rangle$ branching arms on the basal plane disappeared and only dendrite arms growing along directions between a axis on basal plane and c axis on central prismatic plane were observed, as illustrated in section 2 (Figure 1(d2)). In order to confirm our assumption of the growth orientation, EBSD measurement was performed on the α -Mg dendrite arms in Mg-50wt.%Zn alloy and the results are shown in Figure 2. Interestingly, α -Mg dendrite arms in Mg-50wt.%Zn alloy are demonstrated to grow along $\langle 11\bar{2}1 \rangle$. The

result clearly indicates that in Mg-Zn alloys, with the increase of zinc concentration from 10 wt.% to 50 wt.%, the dendrite preferred orientation undergoes a transition from $\langle 1120 \rangle$ to $\langle 1121 \rangle$.

Figure 2 EBSD result showing the dendrite growth direction of branch arms in Mg-50wt.%Zn alloy: (a) SEM image of the measured dendrite; (b) EBSD orientation mapping; (c) pole figure showing the orientation of the dendrite.

Based on the analysis above, dendrite morphology and orientation transition are observed in Mg-Zn alloys with the zinc addition ranging from 10wt.% to 50wt.%. Similarly, a dendrite orientation transition (DOT) was also revealed in Al-Zn alloys alloying element of zinc increased from 20wt.% to 90wt.%[2][13]. In addition, dendrites evolved with seaweed morphology are found in both alloys with interim concentration of zinc solute. Thus, it is reasonable to attribute the dendrite morphology transition to the increasing addition of zinc which continuously alter the surface energy anisotropy in front of the dendrite growth interface as suggested by Haxhimali and Rappaz et al[2][13]. Apart from the surface tension anisotropy modified by the addition of Zn solute, the effect of Zn content on the crystallography of Mg is also likely to be a potential explanation since there is a significant difference of c/a ratio between these two structures.

3.2 Misorientation of primary dendrite arms from basal plane

The experimental results clearly demonstrate that growth morphologies and branching structures of α -Mg dendrites, experienced a transition from anisotropic to relatively isotropic and then back to anisotropic with the gradual increase in Zn concentration.

Dendrite arms split and deviated from the basal plane gradually and grew along directions with an angle (ϕ) between the basal plane. The approximate misorientations between the growth direction of dendrites and the principle crystal axis ($\langle 1120 \rangle$ direction on basal plane) were roughly measured and plotted with different Zn concentrations in Figure 3. It is shown that the deviation angles (ϕ) between branching arms and the basal plane increase from 0° to about 35° , with an increase in Zn concentration from 10 wt.% to 50 wt.%. This is most likely attributed to the continuously small changes in solid-liquid interfacial free energy anisotropy, as caused by the addition of different concentrations of Zn. With Zn dissolved into magnesium alloys, on one aspect, due to the difference in atom size, the hcp Mg lattice distortion may occur when magnesium atoms in the lattice structure are substituted by hcp Zn and thus close-packed planes are prone to change, and the preferential orientations are likely to convert accordingly. Moreover, anisotropy between c and a in magnesium was reported to be relatively low (typically 1 %)[11], however, the anisotropy between c and a for Zn is as high as 30%[13]. Haxhimali and Rappaz *et al.*[2][13] suggested that the dendrite growth direction would undergo a continuous change over a narrow range of anisotropy parameters. Therefore, it is reasonable to consider that the addition of Zn would affect the solid-liquid interfacial free energy of α -Mg phase and then an orientation transition commenced.

Figure 3 Misorientation (ϕ) between the split dendrite arms and the principle crystal axis (supposed $\langle 1120 \rangle$ in the basal plane) as a function of Zn addition.

3.3 Branching structure of primary α -Mg dendrites in Mg-Zn alloys

Apart from the seaweed structure found in Mg-38wt.%Zn alloy, three distinctive types of dendrite growth patterns could be deduced based on the observed dendritic morphology and branching structure. These disparate growth patterns were illustrated in Figure 4a, b and c. Figure 4a presented the snowflake plate-like structure with 6 preferential orientations on the basal plane growing along commonly believed $\langle 1120 \rangle$ [3][15]. For the growth pattern depicted in Mg-25wt.%Zn, roughly, 24 dendrite arms off the basal plane were observed and twelve of them growing along the supposed $\langle 112X \rangle$ (blue) and the remaining twelve (pale green) along $\langle 112Y \rangle$ ($X \neq Y$), as shown in Figure 4b. Figure 4c illustrated the dendrite growth pattern reflecting the branching structure of α -Mg dendrite in Mg-50wt.%Zn. All of the twelve branch arms were found to deviate from the basal plane with the orientation of $\langle 1121 \rangle$ and evolve symmetrically with respect to the basal plane. It was clearly demonstrated that from the Mg-25wt.%Zn onwards, the well-recognized preferred orientation $\langle 1120 \rangle$ was no longer presented, instead, the orientations off the basal plane started to take over and thus dendritic morphology and branching structure transition performed.

Figure 4 Growth patterns reflecting the α -Mg dendrite branching structure in Mg-Zn alloys with different zinc concentrations

3.4 Anisotropy function reflecting the morphology and branching structure of α -Mg dendrites in Mg-Zn alloys

Dendrites have been observed to grow along the direction with maxima surface energy or minima stiffness[6]. Thus, the surface free energy anisotropy, with the use

213 of a function (Equation 1) based on the spherical harmonics which represents the
 214 space group of the hcp crystal lattice was introduced, in order to interpret the
 215 morphology of α -Mg dendrite observed in present study:

$$216 \quad \gamma_{sl\theta,\varphi}\gamma_{sl0}=1+e_1n_x^6-15n_x^4n_y^2+15n_x^2n_y^4-n_y^6+e_25n_z^2-5n_z^4-n_z^6 \quad (1)$$

217 Where γ_{sl0} is the mean value of surface free energy $\gamma_{sl\theta,\varphi}$, ni is a unit vector given
 218 by $ni=\partial\varphi\partial i/(\partial\varphi\partial x)^2+(\partial\varphi\partial y)^2+(\partial\varphi\partial z)^2$ and i represents x, y, z respectively. e_1
 219 and e_2 favour the dendrite growth directions on and deviate from the basal plane,
 220 respectively. With different pairs of (e_1, e_2) parameters individually found for
 221 different alloys (Mg-10wt. %, 25wt. %Zn and 50wt. %Zn), the anisotropy function
 222 values are presented in Figure 5. The red/orange areas indicate the directions toward
 223 which dendrites arms are more likely to grow. The 3D graph results from a high ratio
 224 (i.e. 10) of e_1/e_2 , as shown in Figure 5a, predicting similar dendrite morphology as
 225 observed in Mg-10 wt. %Zn alloy. When decreasing the ratio of e_1/e_2 to a lower
 226 value (i.e. 2.5), the graph presented in Figure 5b shows that the areas possessing the
 227 maximum value, distribute along the longitude near the basal plane. The distribution
 228 in this case predicted a comparable dendrite growth pattern in Mg-25 wt. %Zn alloy.
 229 The areas having maximum value move towards a direction between $\langle 1120 \rangle$ and
 230 $\langle 0001 \rangle$ with identical values of e_1 and e_2 (Figure 5c), suggesting a dendrite
 231 morphology feature similar to what observed in Mg-50wt. %Zn alloy. The proposed
 232 anisotropy function along its calculated values with various ratios of e_1 and e_2
 233 strongly indicated that the transition of the dendritic morphology of α -Mg observed in

the solidified microstructures of Mg-Zn alloys, is closely associated with an anisotropic property change due to the Zn addition. It also suggests a potential application of the proposed anisotropic function incorporated into phase-field models, to perform more detailed studies of the evolution of the α -Mg dendrite morphologies in the Mg alloys.

Figure 5 3D graphs showing the distribution of anisotropic function values with different e_1/e_2 parameters.

4 Conclusion

In summary, we have studied the dendritic morphologies and branching structures of primary α -Mg phase in Mg-Zn alloys possessing different Zn concentrations using 3D synchrotron X-ray microtomography. The results indicate that the α -Mg dendritic morphology and branching structure will undergo a transition with the increasing addition of high anisotropy Zn alloying element into magnesium alloys. Three distinctive growth patterns of α -Mg dendrites were presented when the zinc additions increase from 10wt.% to 50wt.% except for hyperbranch structure in the 38wt.%. The growth patterns was observed to transform from anisotropy (low Zn addition) with six symmetric snow-flake structure to relative isotropy (intermediate Zn addition) where seaweed morphology presented and then back to anisotropy (high Zn addition) when only 12 branches with preferred $\langle 11\bar{2}1 \rangle$ orientations were observed. These findings provide the possibility to control the formation pattern of dendrites in light magnesium alloys, through the addition of specific alloying elements. These results

have important implications for predicting and controlling the microstructure formation during solidification, and thus could serve to broaden the application of magnesium alloys.

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Figures Captions

Figure 1 Three-dimensional dendritic morphologies and branching mechanism of α -Mg dendrites in Mg-Zn alloys with various additions of Zn; section 1 and section 2 are supposed to be the basal plane and prismatic central plane, respectively. (a, a1, a2) Mg-10wt.%Zn; (b, b1, b2) Mg-25wt.%Zn; (c, c1, c2) Mg-38wt.%Zn; (d, d1, d2) Mg-50wt.%Zn. (a1) and (a2), (b1) and (b2), (c1) and (c2), (d1) and (d2) share the same scale bar, respectively.

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