

## Relationship between solid/liquid interface and crystal orientation for pure magnesium solidified in fashion of cellular crystal

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**Abstract:** The relationship between the solid/liquid interface and the crystal orientation for pure magnesium, which grows in fashion of cellular crystal in unidirectional solidification, was investigated. The results show that the energy of the solid/liquid interface is the lowest during cellular crystal growth of pure magnesium; and the solid/liquid interface is covered by the basal face  $\{0001\}$  and by the crystal face made up of three atoms located at the orientation  $\{0001\}\langle 0100 \rangle$  and two atoms located at the inner of magnesium crystal cell. The strongest bond is formed in the direction of  $61.9^\circ$  deviating from the growth direction, and the second strong bond is formed in the directions of  $8.5^\circ$  and  $47.7^\circ$ , respectively, deviating from the growth direction. The angle between the basal face  $\{0001\}$  and the growth direction is  $61.9^\circ$ . The theoretical analysis results are basically consistent with the experimental results from SUSUMU et al.

**Key words:** magnesium; solidification process; crystal growth; crystal orientation

### 1 Introduction

Pure magnesium is of the close-packed hexagonal structure, and its plastic deformation at room-temperature depends on the slipping of the basal face  $\{0001\}\langle 11\bar{2}0 \rangle$  and the twin of the pyramidal face  $\{10\bar{1}2\}\langle 10\bar{1}1 \rangle$  [1–2]. Two methods are generally applied to improving the plastic deformation ability of magnesium at room temperature. One is to decrease the axial ratio ( $c/a$ ) of magnesium crystal through adding alloying agents, such as Li, In and Ag[3]; the other is grain refinement to accommodate the slipping of the basal face and the twin of the pyramidal face[4]. The brittle-to-ductile transition temperature (BDTT) can be reduced to room-temperature when the grain size of pure magnesium is  $8\ \mu\text{m}$ [5]. The superplasticity is obtained when grain size is  $1\ \mu\text{m}$  at room temperature[6]. As the non-crystal magnesium is not easily obtained[7–11], the new processes are expected.

Because of the particularity of crystal structure of magnesium and magnesium alloys, the intragranular plastic deformation at room temperature takes on the directivity. In order to display sufficiently the effect of

basal face slipping on macroscopical plastic deformation at room temperature, the basal face of every grain should keep a suitable angle with the applied stress direction. It is very important to control grain orientation. For equiaxed crystal, it is impossible that the basal face of every grain is all parallel to each other. However, for columnar crystals obtained through unidirectional solidification, it is possible that the basal face of every grain is parallel to each other. So far, how to control definite relationship between the growth direction of columnar crystals and the grain orientation is less reported.

In this work, the growth processes of cellular crystal in the process of unidirectional solidification of pure magnesium were researched, and the relationship between growth direction of cellular crystal and crystal orientation was also investigated.

### 2 Relationship between growth direction and crystal orientation

Cellular or dendritic crystal can be obtained through unidirectional solidification. KURZ and FISAER[12] pointed out that the growth direction of cellular crystal

depends only on heat-flow direction and has no relation to crystal orientation in the solidification. The dendritic growth is controlled by both heat current direction and crystal orientation. Main arbors of dendrite are preferential growth directions of crystal, which are close to heat current direction. The relationship between growth direction of dendrite and crystal orientation is quite clear. However, for cellular crystal, the result that crystal growth has no relation to crystal structure is not proper. The experimental results show that the growth direction of cellular crystal is parallel to and reverse to the heat-flow direction. However, it cannot be proven that there are no relations between growth direction and crystal orientation in the process of the cellular crystal growth. It can be affirmed that there exist corresponding relationships among the growth direction of cellular crystal, the solid-liquid interface energy, the crystal orientation and the crystal face in the solidification.

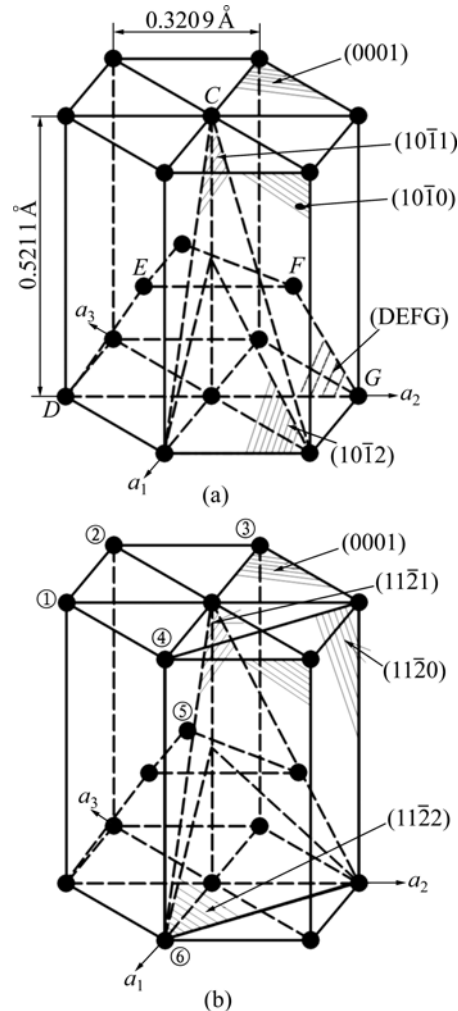
HARTMAN[13] pointed out that the crystal grew along the direction forming the strongest bond and was enclosed by low energy interface. According to the viewpoint, for cellular crystal growth, the positions forming the strongest bond in solid phase are firstly taken up when the atoms transfer from the liquid phase to the solid phase, and the solid/liquid interface must be the crystal face with the lowest energy. This request can be satisfied for certain crystals. For example, for simple cubic crystal, the bond of the orientation  $\langle 001 \rangle$  is the strongest, and the energy of the crystal face which is normal to the orientation  $\langle 001 \rangle$  is the lowest. It is very difficult that those two conditions are synchronously satisfied when the crystal structure is comparatively particular. For example, for the close-packed hexagonal structure, the strongest bond is the orientation  $\langle 11\bar{2}1 \rangle$ , and the energy of prism face normal to the orientation  $\langle 11\bar{2}1 \rangle$  is the largest. Under this condition, it is a conflict for cellular crystal to grow along the strongest bond and to make the energy of the solid/liquid interface the lowest, so it is not likely to grow in either of two fashions. It is possible that two fashions are harmonized, i.e., the growth direction of crystal is not along the direction forming the strongest bond, and the energy of the solid/liquid interface is also not the lowest.

### 3 Structure of solid/liquid interface for magnesium growing in cellular crystal

#### 3.1 Separation angle between typical crystal face and basal face for magnesium crystal

The crystal structure of magnesium is shown in Fig.1 from Ref.[1]. The calculation results of the separation angles between the typical crystal face and the basal face  $\{0001\}$ , and the atomic density of the crystal

face are shown in Table 1. It can be seen from Table 1 that the crystal face  $\{0001\}$  is a closest-packed face, and the crystal face  $\{DEFG\}$  is a secondary closest-packed face. Because the difference of the atomic densities between them is very small, the two crystal faces are



**Fig.1** Unit cell of magnesium (①–⑥ represent atom position numbers): (a) Unit cell; (b) Orientation relations of various crystal faces

**Table 1** Calculation results of relative parameters for magnesium crystal

Crystal face	Separation angle with basal face/(°)	Atomic density on crystal face/%
$\{0001\}$	0	91.644
$\{DEFG\}$	70.4	90.122
$\{10\bar{1}1\}$	61.9	82.325
$\{10\bar{1}0\}$	90.0	80.846
$\{11\bar{2}2\}$	58.4	71.777
$\{11\bar{2}1\}$	72.8	69.995
$\{10\bar{1}2\}$	43.2	63.806
$\{11\bar{2}0\}$	90.0	55.820

considered the closest-packed faces at the same time, and the energies of them are the lowest. In contrast, other crystal faces are not closest-packed faces.

**3.2 Valence electron structure of magnesium crystal**

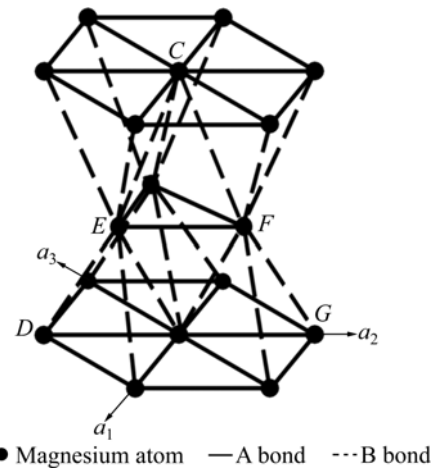
According to the calculation method of the valence electron structure (VES) of alloy proposed in Ref.[14], the VES of magnesium crystal cell is calculated on the basis of the structure and lattice constants of magnesium crystal shown in Fig.1, and the calculation results of the VES are shown in Table 2. In Table 2,  $\sigma_{Mg}$  is the hybridization state of Mg atom;  $n_{C3}^{Mg}$  and  $n_{L3}^{Mg}$  represent the numbers of covalent electron and lattice electron in the valence electron layer of Mg atom on the third hybridization state, respectively;  $R_3^{Mg}(1)$  is the single bond radius of Mg atom when it is in the third hybridization state;  $I_\alpha$  is the equivalent bond number of  $\alpha$  bond;  $D_{n\alpha}$  is the experimental length of  $\alpha$  bond;  $\bar{D}_{n\alpha}$  is the theoretical length of  $\alpha$  bond;  $\Delta D_{n\alpha}$  is the bond length difference between experimental bond length and the theoretical one;  $n_\alpha$  is the number of covalent electron pairs on the  $\alpha$  bond;  $\rho_V^L$  is the lattice electron number of unit volume;  $\rho_V^C$  is the covalent electron number of unit volume;  $\beta$  is a factor in the bond length difference of empirical electron theory of solids and molecules, which is 0.071 0 nm here;  $D_{nA}^{Mg-Mg}$  is the bond name of A bond formed by atoms ① and ② in Fig.1;  $D_{nB}^{Mg-Mg}$ ,  $D_{nC}^{Mg-Mg}$ ,  $D_{nD}^{Mg-Mg}$  and  $D_{nE}^{Mg-Mg}$  represent the bond names formed by atoms ② and ⑤, ④ and ⑤, ④ and ⑥, ① and ③, respectively. The space distributions of bonds A and B are shown in Fig.2.

**Table 2** Valence electron structure of magnesium unit cell

Bond	$I_\alpha$	$D_{n\alpha}/nm$	$\bar{D}_{n\alpha}/nm$	$n_\alpha$	$\Delta D_{n\alpha}/nm$
$D_{nA}^{Mg-Mg}$	36	0.319 706	0.320 186	0.109 814	
$D_{nB}^{Mg-Mg}$	36	0.320 900	0.321 380	0.105 64 7	
$D_{nC}^{Mg-Mg}$	36	0.452 978	0.453 458	0.001 458	$4.80 \times 10^{-4}$
$D_{nD}^{Mg-Mg}$	12	0.521 100	0.521 580	0.000 160	
$D_{nE}^{Mg-Mg}$	36	0.555 815	0.556 295	0.000 052	

$\sigma_{Mg}=3$ ;  $D_{C3}^{Mg}=1.302 2$ ;  $D_{L3}^{Mg}=0.697 8$ ;  $R_3^{Mg}(1)=1.258 0$  nm;  
 $\rho_V^L=34.891 5\%$ ;  $\rho_V^C=65.108 5\%$ ;  $\beta=0.071 0$  nm

In the view of Ref.[14], the larger the  $n_\alpha$  is, the stronger the bond strength is. From Table 2, it can be seen that the  $n_\alpha$  value of bond A is the largest, which indicates that bond A is the strongest bond, and bond B is the second strong bond. It can also be found that the strengths of bonds A and B are nearly identical; however, the  $n_\alpha$  values of bonds C, D and E are quite smaller than those of bonds A and B. The bond strengths of bonds C, D and E are very small, so it is easy to grow along the direction of bond A, and it is also possible to grow along



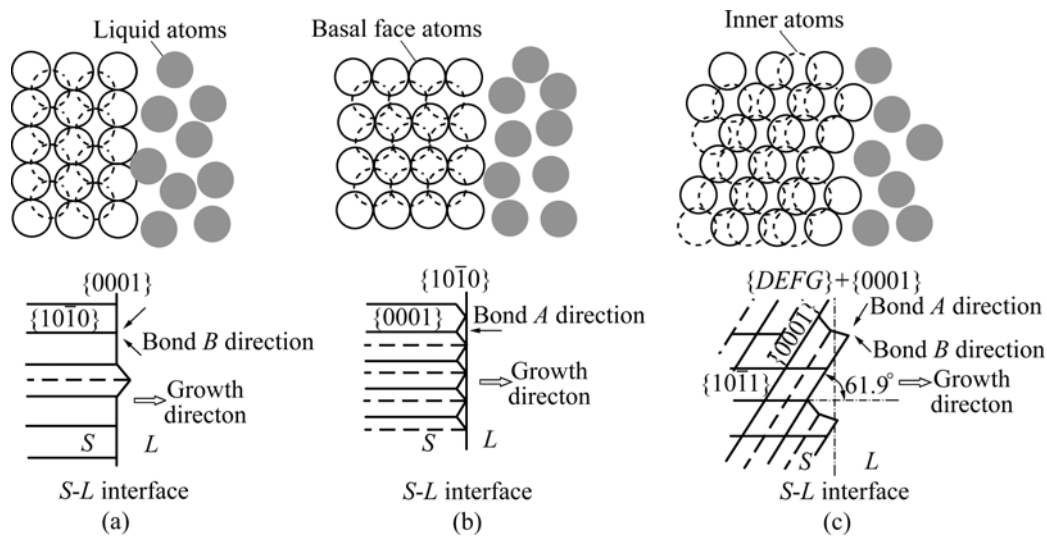
**Fig.2** Space distributions of bonds A and B in magnesium crystal cell

the direction of bond B during the growth process of crystal. The final growth direction depends upon the energy of the solid/liquid interface.

**3.3 Crystal face on solid/liquid interface of magnesium solidified in cellular crystal**

According to Hartman theory, by combining Fig.1, Fig.2 and Table 2, and considering the synthetical factors the bonding direction and the energy of the solid/liquid interface, the relationship between crystal orientation on the solid/liquid interface and the bonding direction, of which liquid atoms are changed into solid state, is shown in Fig.3.

Fig.3(a) shows that the solid/liquid interface is covered by the basal face {0001} of magnesium, where bond B is formed in the direction of 19.6° deviating the growth direction, and bond A depending on bond B is formed in the direction normal to the crystal growth direction. The crystal face {DEFG} is formed as a result of the atom stacking on the crystal face {0001}. The solid/liquid interface is together covered by the crystal faces {0001} and {DEFG}. Under this condition, the energy of the solid/liquid interface is the lowest, in despite of the fact that the second strong bond B can be formed; however, the strongest bond A cannot be directly formed. So, this mode cannot exist in the process of solidification. The strongest bond A can be easily formed according to the atom occupying mode from Fig.3(b), and the low-energy crystal face {DEFG} can also appear on the solid/liquid interface in the solidification. The simultaneous appearance for the crystal faces {10 $\bar{1}$ 0} and {DEFG} will result in the fact that the solid/liquid interface is covered by the prism face and its energy is the largest. So, it is not easy to exist for this kind of mode. Fig.3(c) is the middle state between Fig.3(a) and Fig.3(b). The crystal face {10 $\bar{1}$ 1} is parallel to the



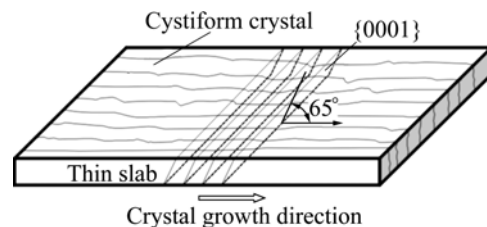
**Fig.3** Sketch map of solid/liquid interface structure and crystal orientation: (a)  $S$ - $L$  interface covered by  $\{0001\}$ ; (b)  $S$ - $L$  interface covered by  $\{10\bar{1}0\}$ ; (c)  $S$ - $L$  interface covered by both  $\{0001\}$  and  $\{DEFG\}$

crystal growth direction, and the solid/liquid interface is covered by the basal faces  $\{0001\}$  and crystal face  $\{DEFG\}$ . From atoms scale, the solid/liquid interface is in rugosity and it is easy to receive the liquid atoms. Bond  $A$  will be formed in the direction of  $61.9^\circ$  deviating from the growth direction, and bond  $B$  will be formed in the directions of  $8.5^\circ$  and  $47.7^\circ$ , respectively, deviating from the growth. Because the energy of crystal face  $\{DEFG\}$  is also the lowest, the energy of the solid/liquid interface is the lowest and the separation angle between the basal face  $\{0001\}$  and the growth direction is  $61.9^\circ$ . By analyzing, we can draw conclusion that the solid/liquid interface cannot be covered by other crystal faces, which is not in agreement with Hartman theory. It can be deduced that Fig.3(c) is the easiest way to exist when magnesium grows in fashion of cellular crystal.

The grain arrangement is fixed in the solidification structure after the solidification, namely, the separation angle between the basal face and the growth direction is  $61.9^\circ$  when magnesium grows in fashion of cellular crystal.

The slab of pure magnesium was prepared through Ohno continuous casting method by SUSUMU et al[15], and the separation angle between crystal face  $\{0001\}$  and crystal growth direction was measured through X-ray diffraction analysis; and the results are shown in Fig.4. The crystal face  $\{0001\}$  is parallel to the width direction of the slab, and the angle with the crystal growth direction is  $65^\circ$ . As mentioned above, the grain arrangement is fixed in the solidification structure after the solidification, so the grain arrangement in the solidification structure represents indirectly the crystal face arrangement on the solid/liquid interface in the solidification. Hence, the experimental results of

SUSUMU et al can be used to verify the results of the theoretical analysis above. By comparison, the theoretical analysis, i.e., the segregation angle between the basal face and the crystal growth direction is  $61.9^\circ$  when magnesium grows in fashion of cellular crystal, is consistent with the experimental result of SUSUMU et al. The difference of  $3^\circ$  exists between the experimental result and the theoretical one, which is thought to be the result of the existence of the sub-boundary in pure magnesium structure.



**Fig.4** Sketch map of relation between  $\{0001\}$  and growth direction of cellular crystal for pure magnesium slab

## 4 Conclusions

1) The solid/liquid interface is covered by the basal face  $\{0001\}$  and the crystal face  $\{DEFG\}$ , which is made up of three atoms located at the orientation  $\{0001\}\langle 0100\rangle$  and two atoms located at the inner of crystal cell, so the energy of the solid/liquid is the lowest. Bond  $A$  is formed in the direction of  $61.9^\circ$  deviating the growth direction; bond  $B$  is formed in the direction of  $8.5^\circ$  and  $47.7^\circ$  deviating the growth direction; and the separation angle between the basal face  $\{0001\}$  and the growth direction is  $61.9^\circ$ .

2) Theoretical analysis is basically consistent with the experimental result of SUSUMU et al.

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