The effect of interfacial energy anisotropy on planar interface instability in a succinonitrile alloy under a small temperature gradient*

Wang Li-Lin(王理林), Wang Zhi-Jun(王志军), Lin Xin(林 鑫)†,
Wang Meng(王 猛), and Huang Wei-Dong(黄卫东)

State Key Laboratory of Solidification Processing, Northwestern Polytechnical University, Xi'an 710072, *China*

(Received 6 June 2011; revised manuscript received 13 December 2011)

The morphological stability of a planar interface with different crystallographic orientations is studied under a small positive temperature gradient using a transparent model alloy of succinonitrile. Novel experimental apparatus is constructed to provide a temperature gradient of about 0.37 K/mm. Under this small temperature gradient, the planar interface instability depends largely on the crystallographic orientation. It is shown experimentally that the effect of interfacial energy anisotropy on planar interface stability cannot be neglected even in a small temperature gradient system. Higher interfacial energy anisotropy leads the planar interface to become more unstable, which is different from the stabilizing effect of the interfacial energy on the planar interface. The experimental results are in agreement with previous theoretical calculations and phase field simulations.

Keywords: solid/liquid interfacial energy, anisotropy, planar interface instability, directional solidification

PACS: 68.08.De, 81.30.Fb, 47.20.Hw **DOI:** 10.1088/1674-1056/21/6/066801

1. Introduction

The growth interface of a non-faceted dilute alloy generally undergoes morphological instability from planar to cellular at the pulling velocity threshold in directional solidification.[1] This morphological instability has been explained well using the linear stability analysis by Mullins and Sekerka.[2] It is shown that the solute concentration gradient exerts a destabilizing effect on the planar interface, while the positive temperature gradient and the interfacial energy have a stabilizing effect. Furthermore, a physical explanation of the initial perturbation wavelength and the incubation time of the planar interface instability was developed by weakly nonlinear analysis[3] and non-steady-state analysis.[4−6] The validity of the above analyses have been examined by thin-sample directional solidification experiments using transparent model alloys as "analogs of metal", such as succinonitrile, pivalic acid, and CBr_4.[7−10] These theoretical and experimental researches contribute significantly to the understanding of morphological instability during directional solidification. However, in previous work interfacial energy anisotropy was not taken into account.

Interfacial energy anisotropy has been proven to play an important role in the growth dynamic process.[11] During the subsequent development, the morphological stability of a planar interface during directional solidification was modified by considering the effect of the anisotropy of interfacial energy and the interfacial kinetics through the linear analysis by Coriell and Sekerka[12] and the weak nonlinear analysis by Hoyle *et al.*,[13] and Golovin and Davis.[14] It was found that interfacial energy anisotropy can affect the threshold of planar interface instability. Recently, the effect of interfacial energy anisotropy on the onset of planar interface instability during directional solidification was further revealed using asymptotic analysis[15] and phase-field simulation.[16] It was found that the incubation time and the initial perturbation wavelength were strongly influenced by the interfacial energy anisotropy. To date, the experimental

*Project supported by the National Natural Science Foundation of China (Grant Nos. 50971102 and 50901061), the National Basic Research Program of China (Grant No. 2011CB610402), the Fund of the State Key Laboratory of Solidification Processing in Northwestern Polytechnical University, China (Grant Nos. 02-TZ-2008 and 36-TP-2009), the Programme of Introducing Talents of Discipline to Universities, China (Grant No. 08040), and the National Science Foundation for Post-doctoral Scientists of China (Grant No. 20110491689).

†Corresponding author. E-mail: xlin@nwpu.edu.cn

© 2012 Chinese Physical Society and IOP Publishing Ltd

evidence for the effect of interfacial energy anisotropy on planar interface instability is still lacking. Previous experiments on directional solidification cannot reflect the effect of interfacial energy anisotropy on the morphological instability, since the variation in instability threshold with interfacial energy anisotropy is small and hard to measure. It is worth noting that a small temperature gradient can increase the incubation time of planar interface instability, and the corresponding instability process also has a long duration. The grains with different crystallographic orientations under a small temperature gradient have different perturbation amplitudes during the planar interface instability. Therefore, the evolution of interfacial morphology under small temperature gradients can effectively describe the effects of interfacial energy anisotropy on planar interface instability.

In this paper, the small temperature gradient apparatus is assembled, and three grains with different crystallographic orientations are prepared in a sample cell. The morphologies of the planar interface instability under a small temperature gradient for the three grains are observed. The variation in perturbation amplitude with crystallographic orientation is analysed and then the contribution of interfacial energy anisotropy to the stability of the planar interface is discussed.

2. Experimental apparatus and procedure

The sample alloy used in the experiment was a transparent model alloy of succinonitrile. The solute concentration of the alloy was estimated from the measured equilibrium solid/liquid interface temperature. The sample alloy was filled into a two-dimensional capillary sample cell with a sample space of 80 μm, which was made of two glass plates with dimensions 50 mm×32 mm×0.17 mm glued by epoxy resin adhesive. The sample cell was placed on a temperature platform consisting of two copper plates, whose temperatures were controlled by circulating water from two thermostats, respectively, as shown in Fig. 1. The temperature stability of each thermostat was ±0.02 K. The copper plates were fixed in a plexiglass box and the gap between them could be adjusted. The solid/liquid interface morphology was observed with a microscope (Nikon AZ100) and recorded using a 5 mega pixel digital CCD (Olympus DP25). The interface morphology was then characterized through the digital processing of images based on Matlab's image processing toolbox. The temperature distribution between the copper plates was measured accurately with a calibrated K-type thermocouple, a multimeter (Agilent 34420A) with a temperature resolution of 1 mK and a zero-point source.

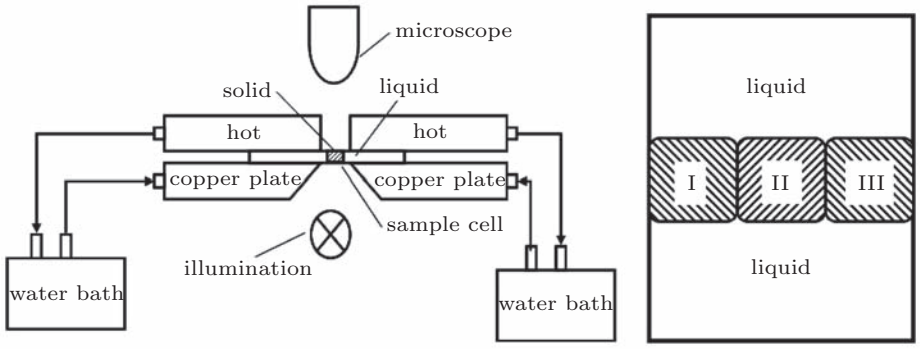


Fig. 1. Schematic diagram of the temperature platform and sample cell.

Three crystal grains with different crystallographic orientations were kept in a sample cell through careful crystal selection. Then the prepared sample cell was fixed on the temperature platform and covered by glass windows at the top and the bottom of the copper plates to insulate the perturbation from the ambient airflow. The temperatures of both copper plates were set to be slightly above the liquidus temperature of the sample so that a U-shaped temperature profile with small temperature gradient forms between the copper plates due to a small heat loss through the glass windows. In this case, a solid band was trapped in the gap, and two solid/liquid interfaces formed near the edges of the copper plates, as

shown in Fig. 1. After the sample was annealed for at least 12 h, the solid/liquid interface morphology was acquired with the microscope and CCD. For the transparent model alloy, the crystallographic orientation of the crystal grain was assessed approximately from the characteristics of its rapid growth morphology, such as the preferred growth direction and crystallographic symmetry of the dendritic arms, owing to the lack of other measurement techniques. Thus, the growth morphology that was rapidly growing into the undercooled melt was also recorded when the water thermostats were turned off.

3. Results and discussion

3.1. The crystallographic orientation of crystal grains

A body-centred cubic (BCC) succinonitrile crystal has a six-fold symmetry in its three-dimensional interfacial energy plot, and its crystalline pattern will adopt an orientation which follows the preferred growth axes: ⟨100⟩ crystalline axes when it grows far from the limit of stability of the planar front. Thus, the six ⟨100⟩ axes form a six-armed dendritic pattern in three-dimensional free growth. In the case of quasi-two-dimensional thin sample growth, the sample is constrained to grow within a particular plane, and its growth morphology depends on the in-plane interfacial energy polar plot, just like a two-dimensional slice cut down from the three-dimensional interfacial energy polar plot. Brener *et al.*,[17] and Utter and Bodenschatz[11] proposed dendritic structures with a stable parabolic tip shape at high in-plane anisotropy of interfacial energy, and seaweed structures with a frequent splitting tip shape at low in-plane anisotropy in two-dimensional diffused growth. For a BCC structure, the dendritic growth occurs in the {100} plane with the highest anisotropic interfacial energy, and the seaweed growth occurs in the {111} plane with nearly isotropic interfacial energy.

The rapid growth morphologies of the three grains chosen in our sample cell are shown in Fig. 2. Grain I has a typical seaweed pattern with a frequent splitting tip, which indicates that Grain I is crystallographically oriented close to the {111} plane in the two-dimensional sample plane and its in-plane anisotropy is nearly isotropic. Grain II has a typical dendritic pattern with stable parabolic tip, a dendritic trunk opposite to the imposed heat flow direction and sidebranches perpendicular to the dendritic trunk, which indicates that Grain II is crystallographically oriented close to the {100} plane and its in-plane anisotropy is 0.55%.[18] Grain III has a dendritic pattern with critical stable tip and sidebranches tilting to the dendrite trunk, which indicates that the crystallographical orientation of Grain III deviates from the {100} plane slightly and its in-plane anisotropy is between those of Grain I and Grain II. Therefore, based on the relationship between rapid growth morphology in two-dimensional diffused growth and in-plane anisotropy of interfacial energy, the qualitative relationship to the extent of in-plane anisotropy among three the grains chosen in the present experiment is Grain II>Grain III>Grain I.

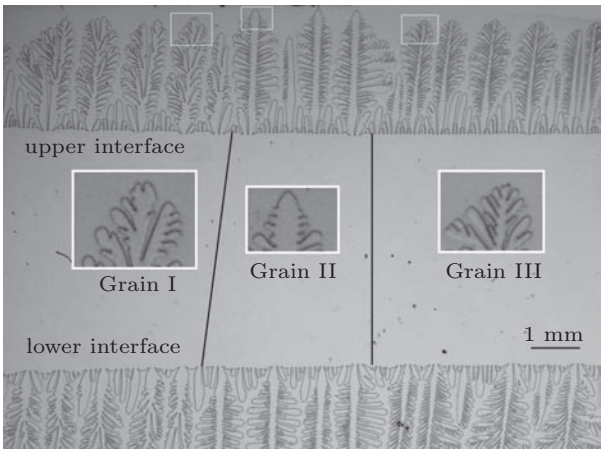


Fig. 2. The rapid growth morphologies of the three grains growing into undercooled melt.

3.2. Temperature profile measurement and solute concentration estimation

A U-shaped temperature profile with a small temperature gradient was constructed to study the interface stabilities of different oriented grains. The temperature profile was obtained by using a K-type thermocouple to accurately measure temperatures at different positions in the same sample after the observation of the interface stability as shown in Fig. 3. From Fig. 2 it can be seen that an about 4.5 mm wide solid is trapped in the centre of this temperature profile and two parallel solid/liquid interfaces marked as upper and lower exist. According to the positions of the upper and lower interfaces in the temperature profile, the equilibrium temperature and temperature gradient at the solid/liquid interface are evaluated through a parabolic fitting to the measured temperature points. The equilibrium solid/liquid interface temperature is 56.01 °C, the temperature gradient at the upper interface (as marked in Fig. 3) is 0.369 K/mm, and the temperature gradient at the

lower interface (as marked in Fig. 3) is 0.373 K/mm. The temperature gradient at the lower interface is slightly larger than that at the upper interface.

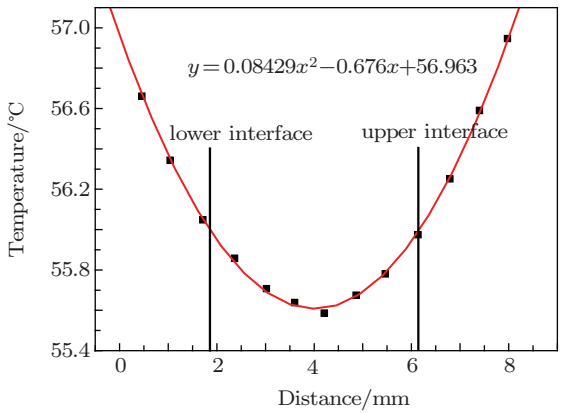


Fig. 3. (colour online) Temperature distribution between copper plates. The solid squares are for the measured temperature, and the solid line is for a parabolic fit and yields $y = 0.08429x^2 - 0.676x + 56.963$, where y denotes temperature and x the distance from the copper plate edge.

The impurity in commercial succinonitrile was removed by purification processing before use. The solute in the sample was probably water, which could be absorbed from air during the sample filling process. Assuming that the solute is water, the solute concentration is estimated to be about 1.26 mol% based on the measured equilibrium interface temperature and the phase diagram of succinonitrile-water alloy.[19]

3.3. Interface stability of different oriented grains under a small temperature gradient

The high magnification images of the solid/liquid interface morphologies after annealing for 12 h under the above-mentioned temperature field are shown in Fig. 4. Images N1 and N2 correspond to the upper interface, and images N3 and N4 correspond to the lower interface. The grain boundaries between two grains were observed clearly in the centre of the images. It is found that the solid/liquid interface of Grain I is stable, while the interfaces of Grain II and Grain III are undulated. The difference in interface morphology between Grain II and Grain III is small. In order to distinguish precisely the difference between Grain II and Grain III, the ratio r of real interface length and straight-line distance between two points on the interface edge is used to evaluate the interface instability. The $r = 1$ value denotes the planar interface without undulation, $r > 1$ denotes the undulated interface: the larger the r value, the stronger the interface undulation. The images were processed to obtain the digital edges of the solid/liquid interface using the image processing toolbox in Matlab, and then the ratio r of three grains were calculated as shown in Fig. 5. It is shown that the qualitative relationship of the ratio r of three grains is Grain II>Grain III>Grain I=1 at the upper interface, as is the case at the lower interface. The values of r for three grains indicate that the solid/liquid interface of Grain II is more unstable than that of Grain III, and the interface of Grain I is stable at the upper and lower interface under the current temperature gradient. Combining the qualitative relationships of the in-plane interfacial energy anisotropy for the three grains, it can be concluded that the higher the interfacial energy anisotropy, the more unstable the solid/liquid interface becomes under a small temperature gradient.

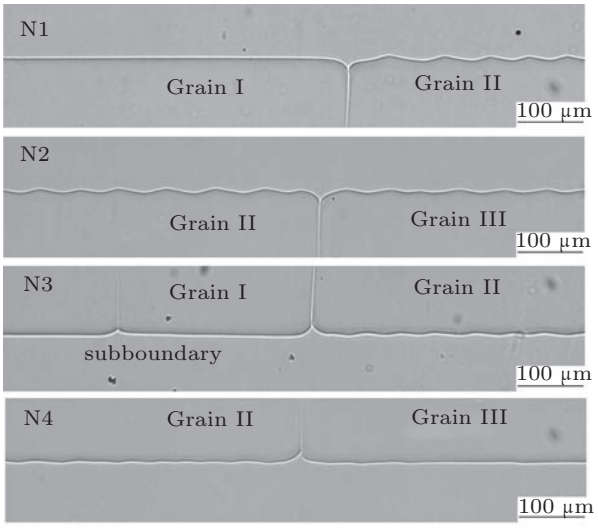


Fig. 4. The solid/liquid interface morphologies of the grains after annealing.

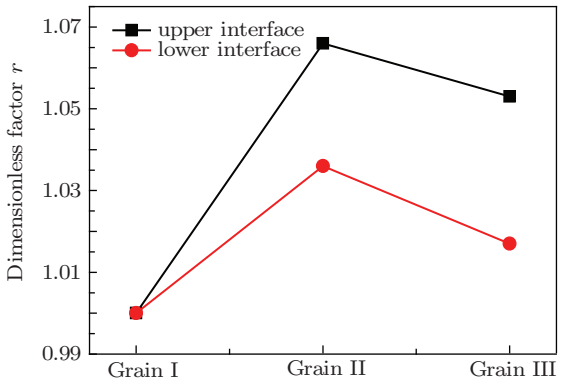


Fig. 5. (colour online) The solid/liquid interface instability degrees of the three grains.

It is also found that the undulation amplitudes of Grain II and Grain III at the upper interface are larger than those at the lower interface. This may result from a stronger stabilizing effect of a positive

temperature gradient on the interface undulation at the lower interface because of a slightly larger temperature gradient at the lower interface than at the upper interface.

3.4. Discussion

In conventional directional solidification, planar interface instability occurs under a high positive temperature gradient and high pulling velocity, in which the effect of interfacial energy anisotropy on planar interface instability is hard to show. In the present experiment, a small positive temperature gradient is adopted, whose interface stabilizing effect is very weak. The solid/liquid interface drifted back and forth at a velocity of about 10^{-2} μm/s because of ambient temperature disturbance and the temperature fluctuation in water thermostats. According to constitutional supercooling theory, the interface drifting velocity can lead to the planar interface instability. Under a small temperature gradient and a low interface velocity, the effect of interfacial energy anisotropy on the planar interface instability is shown clearly in Fig. 4, although it is very small (about 0.55%).[18] The higher interfacial energy anisotropy causes a more unstable planar interface when it breaks the limit of the stability of the planar front. This experimental conclusion is consistent with previous theoretical calculations[14] and phase field simulation results.[16]

It has been found theoretically[20] and experimentally[21] that the initial perturbation does not emerge on the entire planar interface simultaneously, but a small perturbation appears first at the grain boundary, sub-boundary or defects and then propagates to the entire interface. Therefore, in the present experiment, the interface instability occurring first at the grain boundary groove probably becomes the origin of the entire planar interface instability. We reckon that the stability of the curved interface at the grain boundary groove might be associated with the continuous change in crystallographic orientation at the interface, which strongly attracts our attention to study this further in future work.

4. Conclusion

A small temperature gradient system is built to provide a temperature gradient of about 0.37 K/mm at the solid/liquid interface, under which the effect of solid/liquid interfacial energy anisotropy on the planar interfacial instability is investigated. Because the stability effect of the small temperature gradient is weak, the solid/liquid interface motion at a velocity of about 10^{-2} μm/s, which results from the ambient temperature disturbance and the temperature fluctuation in the water thermostats, is responsible for the planar interface instability. Under a small temperature gradient and a low interface velocity, the effect of interfacial energy anisotropy on the planar interface instability is shown clearly for the first time in this experimental observation. It is found that the higher interfacial energy anisotropy causes a more unstable planar interface when it breaks the limit of the stability of the planar front. This experimental conclusion is consistent with previous theoretical calculations[14] and phase field simulation results.[16]

References

[1] Trivedi R and Somboonsuk K 1985 *Acta Metall.* **33** 1061

[2] Mullins W W and Sekerka R F 1964 *J. Appl. Phys.* **35** 444

[3] Wollkind D J and Segel L A 1970 *Phil. Trans. R. Soc. Lond.* A **268** 351

[4] Warren J A and Langer J S 1993 *Phys. Rev.* E **47** 2702

[5] Lin X, Li T, Wang L L, Su Y P and Huang W D 2004 *Acta Phys. Sin.* **53** 3971 (in Chinese)

[6] Huang W D, Lin X, Li T, Wang L L and Inatomi Y 2004 *Acta Phys. Sin.* **53** 3978 (in Chinese)

[7] Eshelman M A and Trivedi R 1987 *Acta Metall.* **35** 2443

[8] De Cheveign S, Guthmann C and Lebrun M M 1985 *J. Cryst. Growth* **73** 242

[9] Liu L X and Kirkaldy J S 1994 *J. Cryst. Growth* **144** 335

[10] Huang W D, Shang B L and Zhou Y H 1991 *Acta Phys. Sin.* **40** 323 (in Chinese)

[11] Utter B and Bodenschatz E 2002 *Phys. Rev.* E **66** 051604

[12] Coriell S R and Sekerka R F 1976 *J. Cryst. Growth* **34** 157

[13] Hoyle R B, McFadden G B and Davis S H 1996 *Phil. Trans. R. Soc. Lond.* A **354** 2915

[14] Golovin A A and Davis S H 1998 *Physica* D **116** 363

[15] Wang Z J, Wang J C and Yang G C 2008 *Acta Phys. Sin.* **57** 1246 (in Chinese)

[16] Wang Z J, Wang J C and Yang G C 2009 *Phys. Rev.* E **80** 052603

[17] Brener E, Muller-Krumbhaar H and Temkin D 1996 *Phys. Rev.* E **54** 2714

[18] Muschol M, Liu D and Cummins H Z 1992 *Phys. Rev.* A **46** 1038

[19] Smith J E Jr, Frazier D O and Kaukler W F 1984 *Scr. Metall.* **18** 677

[20] Coriell S R and Sekerya R F 1973 *J. Cryst. Growth* **19** 285

[21] Ding G L, Lin X, Huang W D and Zhou Y H 1997 *Acta Phys. Sin.* **46** 1243 (in Chinese)