***In situ* observation of $\text{NaBi}(\text{WO}_4)_2$ dendrite growth and the study on microstructure of solidification**

AI Fei[†], HONG Yong, JIN WeiQing, LUO HaoSu, LIU Yan & PAN XiuHong

Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, China

The dendrite growth process of transparent $\text{NaBi}(\text{WO}_4)_2$ with small prandtl and high melting point was studied by using the *in-situ* observation system. According to the dynamic images and detailed information, there are two kinds of restriction effect on the dendrite growth, the competition between arms and branches and the convection in the melt. The dendrite growth rate was time dependent, and the rate of arm growth reached the maximum 5.8 mm/s in the diffusive-advective region and rapidly decreased in the diffusive-convective region. The growth rate of branch had the same change trends as the arm's. Based on the EPMA-EDS data of solidification structure of quenched $\text{NaBi}(\text{WO}_4)_2$ melt, it was found that there were component differences from stoichiometric concentration in the melt near the interface during the growth process.

oxide, dendrite, *in-situ* observation, solidification structure

1 Introduction

Rosenberger^[1,2] has pointed out the relations between Rayleigh, Prandtl numbers of melts and flow conditions, that is, it is easy for the flow of big Prandtl number melts (oxide, etc.) to keep steady, while the flow of small Prandtl number melts (metal, semiconductor, etc.) is usually turbulent. It means that the solidification of metals is often a nonequilibrium process and can result in dendrite structures. It is difficult to observe the convection and microstructures of the metal solidification for the optics opacity of metal melts, and therefore, transparent metal-like materials are used for simulating the metal solidification.

In crystal growth, cell and dendrite induced by the interface instability are the familiar crystal structures under the nonequilibrium conditions^[3]. There are many reports about the study of the

Received February 12, 2007; accepted April 16, 2007

doi: 10.1007/s11433-007-0050-x

[†]Corresponding author (email: aifei@mail.sic.ac.cn)

Supported by the National Natural Science Foundation of China (Grant No. 50331040) and the Innovation Funds from Shanghai Institute of Ceramics, Chinese Academy of Sciences (Grant No. SCX0623)

cell and dendrite of low temperature metal-like materials such as succinonitrile^[4,5], however, these materials cannot completely simulate the actual solidification characteristics of the metal system because of the significant difference between the experimental temperature of such materials and the high melting points of metals.

In this work, we considered the materials of small Prandtl number and high melting points and chose transparent NaBi(WO₄)₂ oxide crystal as a research object which was close to metal in Prandtl number (~5), with 1000°C melting point. High-temperature *in-situ* observation instrument was used in the study of the dendrite growth for further research of oxide crystal growth and better experimental reference for metal solidification.

2 Experiments

The dendrite growth experiments were carried out by using high-temperature *in-situ* observation instrument^[6]. The crystal growth unit was composed of a heating chamber and a loop-shaped Pt wire heater, as shown in Figure 1. The Pt wire ($\Phi 0.20$ mm) was employed to heat and suspend the melt, and the temperature of the heater could be controlled by power supply during the *in-situ* observation experiment. A V-type of electrode was used to defend the loop-shaped heater from deformation. A Pt-10% Rh thermocouple ($\Phi 0.08$ mm) was used to measure the temperature of the loop. The temperature distribution along the radial direction of the thin melt film was measured by a non-contact method^[7], as shown in Figure 2.

Figure 1 Photo of crystal growth unit. a, Loop-shaped heater; b, thermocouple.

The main experimental procedure was carried out as follows. Put NBWO crystal sample into the loop-shaped heater mentioned above. When the temperature increased to 1150 K, the crystal melted, and a thin film (about 0.2 mm in thickness) formed in the heater due to surface tension. After several times of melting and solidification, a homogeneous mixture was obtained. With the increase in temperature, a small crystal seed formed, and then with the decrease in temperature, the melt solidified gradually. Schlieren technique coupled with the differential interference microscope was applied to visualizing the solid-liquid interface motion. The images were recorded into a computer by using a CCD camera for further analysis.

The element component analysis of quenched NBWO melts was carried out by Shimadzu EPMA-8705QH. In order to reduce the error rate, each point was measured at least three times and the average data were used for analysis.

3 Results and discussion

The whole process of NBWO dendrite growth was observed, and typical pictures during the process are shown in Figure 3, where (a)–(d) represent the picture at $t = 0.3, 0.5, 0.7, 0.9$ s, respectively. We can obtain detailed information of NBWO dendrite growth according to Figure 3. It was found that there are two kinds of restriction effect on the dendrite growth, that is, competition and convection.

In the initial stage of dendrite growth, arms K, L, M develop independently, as shown in Figure 3(a). From Figure 3(b) to (c), arm K and M restrain the growth of L for the competition effect among them. Arms L and K unite finally due to their similar crystallographic direction, as shown in Figure 3(d). Competition also exists in the branches perpendicular to the arms. In Figure 3, the space between branches in front of the same interface is very narrow, also their crystallographic directions are similar, so the competition growth is greatly severe. As a result, those branches with the minimum width gradually disappear because they are affected fiercely by the neighboring branches. For example, branches K_1, K_2 and K_3 limit the growth of K_4 and K_5 , as shown in Figure 3(c) and (d). Competition growth between arms and branches is a familiar phenomenon in the metal solidification^[8,9].

In this paper, the temperature distribution in the loop-shaped heater can be considered as a near-axis symmetrical one, as shown in Figure 2. In area E which is close to the center of the heater and about 0.6 mm in diameter, the temperature difference is so small that we can regard that the mass transfer in area E is dominated by diffusion-advection^[1]. On the contrary, in area F which is near the edge of the heater, the temperature difference is big and there are strong buoyancy and marangoni convection, so the mass transfer is dominated by diffusion-convection. From Figure 3, arm K and its branches grow sufficiently, while arm M in the diffusive-convective area F grows slowly and its branches can hardly be observed. This indicates that convection has restraint effect on the dendrite growth. Another phenomenon is the dissymmetry of arm K , that is, underside branches are located in the diffusive-convective area and both their length and width are smaller than the upside ones', which also shows the restraint effect of convection.

In addition, the selective growth under the competition was observed. In Figure 3(b), the length and width of branch K_1 are smaller than those of K_2 and K_3 , but it grows fast and its size has exceeded K_2 and K_3 , as shown in Figure 3(d). The temperature in the center of the heater is lowest and

Figure 2 Temperature difference along the radial direction (Temperature difference $\Delta T = T_{d_l} - T_O$).

Figure 3 Typical pictures during the process of NBWO dendrite growth. (a)–(d) represent the picture at $t = 0.3, 0.5, 0.7, 0.9$ s, respectively.

the super-cooling is bigger. K_1 in this area grows rapidly and reaches to the super-cooling melts, which further promote the growth of K_1 , and moreover, the secondary branch perpendicular to K_1 forms in the low temperature area.

Arm K which has a good shape and branch K_1 near the center area were chosen as the object for further research. The growth rate of arms and branches can be measured based on the displacement per second of the tip of dendrite in the video. In Figure 4, the growth rate of dendrite is time dependent, which can be explained as follows: the dendrite growth is a nonequilibrium process and the drive force changes with time, so the growth rate also changes with time.

The relations between the growth rate of arm K , branch K_1 and time are shown in Figure 4(a). The growth rate of arm K increases with time, reaches the maximum 5.8 mm/s and then decreases. At its drop point, branch K_1 appears, and the growth rate of K_1 decreases with time. According to

Figure 4 Analysis of the NBWO dendrite growth rate. (a) Change of the growth rate of arm K and branch K_1 against time; (b) change of the growth rate of arm K against radial position d_1 ; (c) change of the growth rate of branch K_1 against radial position d_2 .

Figures 2 and 3, arm K grows from position A to C , and branch K_1 grows from position D to B . K and K_1 arrive at different positions at different time, so the relations between the growth rate of arm K , branch K_1 and radial position can be figured out. As shown in Figure 4(b) and (c), d_1 , d_2 represent the radial position along AC and BD , respectively. In Figure 4(b), R_K , the growth rate of arm K , reaches the maximum value in the diffusive-advective area E (about 0.6 mm in diameter) close to the center of the heater, and decreases in the diffusive-convective area F . R_{K_1} , the growth rate of branch K_1 , has the maximum value about 3.2 mm/s near the diffusive-advective area, and decreases with the distance apart from the center. The data from Figure 4 prove the restraint effect of convection on the dendrite growth and demonstrate that one of the characteristics of this effect is the decrease in the dendrite growth rate in the diffusive-convective area.

After the *in-situ* observation experiment, the analysis data and pictures from EPMA of the quenched NBWO melts are shown in Figure 5. In Figure 5(a), area ① is the structures of super-cooling melts, while ② the typical dendrite structures. It can be seen that the dendrite can easily form under a bigger decreasing rate of temperature. In the underside part of Figure 5(a), there is a dendrite structure different from that in area ②, which is probably related to the locally deep super-cooling. Its typical characteristic is the striation structure perpendicular to the growth direction, as shown by arrow S , which may be the special configuration of structure superposition under deep super-cooling. For element analysis in front of the solid-melt interface, the EDS analysis of four points along a line parallel to the growth direction of branch P was carried out and compared with stoichiometric concentration, as shown in Table 1.

Figure 5 EPMA pictures of NBWO solidification structures. (b) is the enlarged view of the rectangle area in (a).

Table 1 The component analysis of NBWO dendrite near the solid-liquid interface

Element	Mass percent (%)				Stoichiometric ratio	In dendrite
	I	II	III	IV		
Na	7.43	5.53	5.03	4.22	3.16	4.17
W	55.88	50.15	50.10	50.02	50.53	50.48
Bi	17.50	26.28	26.94	28.02	28.72	27.56
O	19.18	18.04	17.93	17.74	17.59	17.79

For quenched samples, mass transfer cannot go along sufficiently because the temperature decreases so quickly, and thus it is reasonable to consider that the concentration distribution in the solidification samples keeps the conditions of growth. It was found that there are component differences from stoichiometric concentration in the melt near the interface during the growth proc-

ess by comparing Figure 5(b) with Table 1. In the initial stage of dendrite growth, the element Na and W are rich while Bi is absent in the melt in front of the interface (point I). While in the dendrite, the element Na is rich and Bi is absent. These component differences possibly result from segregation effect and convection. Along with the dendrite growth, the component ratio in the melts in front of the interface (points II, III, IV) is gradually close to the stoichiometric concentration, which can be explained by the convective transfer effect. From point *T* to IV, the tip of the dendrite arrives at the diffusive-convective region, and the component ratio at point IV is close to the stoichiometric concentration, which illustrates that the convective transfer makes the concentration in the melts uniform^[10]. However, as to the problem on how the heat transfer, mass transfer and momentum transfer affect the growth rate, structures and components in the dendrite growth, much more thorough work will be required.

4 Conclusions

The NBWO dendrite growth process was observed. It was found that not only the competition between arms and branches but also the convection in the melt near the edge of the heater has the restriction effect on the dendrite growth. The maximum growth rate of arm reached 5.8 mm/s in the diffusive-advective region near the center of the heater and rapidly decreased in the diffusive-convective region. The growth rate of the branch had the same change trend as that of the arm. Based on the EPMA-EDS data of solidification structure of quenched NaBi(WO₄)₂ melt, in the initial stage of dendrite growth, the element Na and W were rich while Bi was absent in the melt in front of the interface. Along with the dendrite growth, the component ratio was gradually close to the stoichiometric concentration. It is indicated from our work that the research on NBWO dendrite growth can not only guide thorough discussion on the crystal growth of high temperature oxide but also provide experimental reference for the study of metal solidification as a good simulative material.

- 1 Rosenberg F. Interfacial transport in crystal growth, a parametric comparison of convective effects. *J Cryst Growth*, 1983, 65: 91–104
- 2 Rosenberg F. Boundary layers in crystal growth-facts and fancy. *Progr Crystal Growth Charact Mater*, 1993, 26: 87–98
- 3 Huang Q, Zhao S R. Development and progress of the research of dendrite growth. *J Synth Cryst*, 2002, 31: 486–489
- 4 Kauerauf B, Zimmermann G. Planar to cellular transition in the system succinonitrile-acetone during directional solidification of a bulk sample. *J Cryst Growth*, 1998, 193: 701–711
- 5 Pan X H, Hong Y, Jin W Q. *In situ* observation of cell-to-dendrite transition. *Chin Phys Lett*, 2005, 22: 2966–2968
- 6 Jin W Q, Liu Z H, Pan Z L, et al. High temperature *in situ* observation technique for space experiments. *Microgravity Sci Tech*, 1997, 4: 194–196
- 7 Liang X A, Jin W Q, Pan Z L. Experimental measurement of temperature distribution across a loop-like heater. *Progr Crystal Growth Charact Mater*, 2000, 40: 301–307
- 8 Ding G L, Huang W D, Lin X. Prediction of average spacing for constrained cellular/dendritic growth. *J Cryst Growth*, 1997, 177: 281–288
- 9 Cadirli E, Karaca I, Kaya H. Effect of growth rate and composition on the primary spacing, the dendrite tip radius and mushy zone depth in the directionally solidified succinonitrile-salol alloys. *J Cryst Growth*, 2003, 255: 190–203
- 10 Cai L X, Jin W Q, Yoda S. The convective effect on the morphological instability of KNbO₃ crystals. *J Cryst Growth*, 2001, 231: 230–234