***In-situ* Observation of Growth and Melting of a Solid Particle Using Transparent Organic Alloys**

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Seed crystal for equiaxed grain may be suffered from the temperature change in the liquid phase. Seed crystal may grow and/or melt depending on the thermal field. In order to analyze the growth and melting of a solid particle, *in-situ* observation using succinonitrile-water alloys with the newly constructed experimental equipment have been performed. In the central region of the ring heater, a small spherical solid particle is held for a while. When the voltage for the ring heater was abruptly changed, the solid particle grew or melted. The morphological change was recorded and analyzed.

In case of growth, it indicated that the solid/liquid interface is dendritic. After stopping growth, the solid phase became round if the solute content is low. On the other hand, if the solute content is high, solid/liquid interface remained dendritic.

In case of melting, the solid/liquid interface is complex. If the solid phase is round after growth, it melted remaining round. If the solid/liquid interface was dendritic after growth, dendrite arms became slender and the tip of dendrite became pointed. Some secondary dendrite arms may have been detached.

It has been found that the melting velocity is lower than the growth velocity. Because of the difference in solid/liquid interfacial morphology and because of the difference in the traveling velocity of solid/liquid interface, the kinetics of growth and melting are different. One of the important reasons is the difference in operating point for growth and melting. In case of growth, the operating point is dendrite tip. On the other hand, in case of melting, it is rather wide area, which is inside of the envelope of the tips of the solid phase.

KEY WORDS: equiaxed grain; dendrite; growth; melting; *in-situ* observation.

1. Introduction

In a macroscopic point of view, it is known that a cast product consists three zones; chill, columnar and equiaxed zones.¹⁾ It is important to refine the macroscopic solidified structure in order to improve the mechanical properties of cast products. Especially, increasing the area of equiaxed grains is important for reducing the macroscopic segregation or internal cracks.

There have been several theories for the formation mechanism of equiaxed grains in the literatures.^{2–6)} They have been based on their own experimental results. Winegard and Chalmers thought that the equiaxed crystals may nucleate in the constitutionally undercooled melt, which is ahead of the columnar dendrite tips.²⁾ On the other hand, Jackson *et al.* proposed the detachment of secondary dendrite arms from the primary dendrite trunks. They carried out the observation of dendritic growth using a transparent organic materials.³⁾ There are other theories for the formation mechanism of equiaxed grains.^{4–6)} Though none of them is universal, any theory holds true, depending upon the solidification condition.

Before becoming a dominant equiaxed zone, it is necessary that copious small solid particles are in the liquid zone, which is independent of the formation mechanism.

Small solid particles grow into equiaxed crystals and finally they stop the growth of columnar dendrites. Then, a dominant equiaxed zone forms. Here a small solid particle in the liquid phase, which may be an equiaxed crystal, is named ‘seed crystal’ in this study.

Generally speaking, the density of solid phase is only a few percent larger than that of liquid phase. Thus, a seed crystal would move with liquid flow. The temperature in the liquid may be fluctuated place by place even though there is flow in the liquid. Therefore, the seed crystal is suffered the temperature change because of the movement in the liquid. The seed crystal may grow when the temperature is low, on the other hand, it may melt when the temperature is high.

Unfortunately, there has been little research works on the behavior of the small solid particle in case of thermal change around the particle.⁷⁾ Thus, *in-situ* observation of the solid/liquid interface using a transparent organic alloy has been carried out in this study. Without fluid flow, the thermal field is intentionally changed around the solid particle.

2. Experimental Procedure

In order to carry out the *in-situ* observation, succinonitrile-H₂O alloy system^{8,9)} has been selected in this study.

Table 1. Alloy used in this study.

Alloy A	SCN-0.1 mass% H_2O
Alloy B	SCN-2.0 mass% H_2O

Fig. 1. A schematic view of the principal part of experimental apparatus.

Important parameters of this alloy system have been separately determined experimentally.¹⁰⁾ The liquidus slope, m , is $-0.4 \text{ K/mass\%}$ and the equilibrium distribution coefficient, k , is 0.1. H_2O content of alloys used in this study were 0.1 mass% and 2.0 mass% as shown in **Table 1**. Since the nominal purity of an as-received succinonitrile (hereafter SCN) was about 98 mass%, SCN has been distilled for 4 times. Then, alloys were prepared in argon atmosphere with distilled water. These alloys were filled in a glass cell and sealed with epoxy resin. The size of glass cell is $35 \text{ mm} \times 100 \text{ mm}$ and 0.15 mm in gap. A fine thermocouple (type-K, $25 \mu\text{m}\phi$) was placed in the center of the glass cell to measure the thermal history.

The principal part of experimental apparatus is shown in **Fig. 1**. The glass cell was put on the ring heater. The ring heater was made by copper plate, the outer and inner diameters of which were 20 mm and 10 mm, respectively. In order to facilitate the temperature control, it is better to increase the heat capacity to some extent, the thickness of copper plate was determined to be 1 mm. Kanthal wire was adhered on the lower side of the copper plate. The temperature in the central region of the ring heater is slightly lower than the other region. Thus, a small solid particle can be held in the liquid phase as shown in **Fig. 1**.

Temperature change that a seed crystal may suffer is quite complex and unknown. In this experiment therefore, the temperature in the central region of ring heater was changed by the abrupt change in voltage for the ring heater, in order to simplify the operation of experiment. Morphology of the seed crystal was observed directly with an optical microscope and recorded by a DVD recorder.

3. Experimental Results

3.1. Temperature Distribution of the Ring Heater

One example of the results for the temperature distribution of the ring heater is shown in **Fig. 2**. This temperature profile was measured by moving the glass cell unidirectionally at a constant velocity.

At first sight, the temperature distribution is a little asymmetric. The reason of this is that the temperature becomes higher at the entry position of resistant wire due to high

Fig. 2. Temperature distribution of the ring heater. **Fig. 3.** Enlarged temperature distribution of the ring heater. **Fig. 4.** Temperature change with time in case of decrease in voltage for the ring heater at 0.06 V.

density of heat flux. But this is not severe for the present study. Temperature distribution of the central region of the ring heater, which is the most important part in this study, is shown in **Fig. 3**. This experimental data indicates that the temperature is almost constant and symmetrical. A small solid particle, which was a seed crystal, was held in the liquid phase in the central region of the ring heater.

3.2. Temperature Change Due to Abrupt Change of Voltage

An example of temperature change after decreasing the voltage for the ring heater is shown in **Fig. 4**. This temperature change was measured by the thermocouple at a fixed position. In this case, change in voltage (ΔE) was 0.06 V. The temperature changed like an exponential function, and

Fig. 5. Temperature change with time in case of increase in voltage for the ring heater at 0.06 V.

Fig. 6. Relationship between change in voltage for the ring heater and change in temperature.

the temperature approached a constant value. It took some hundreds seconds to reach a constant temperature. In the same way, the temperature change after increasing the voltage for the ring heater is shown in Fig. 5. Here again, the temperature changed like an exponential function and it took some hundreds seconds to reach a certain value. The relation between the change in voltage for the ring heater (ΔE) and the change in temperature in the final stage (ΔT_1) is shown in Fig. 6. As shown, ΔT_1 is approximately proportional to ΔE . It has been found that this relation is independent of the solute content, or the temperature region, in the range of the present experiments.

3.3. Morphology Change during Growth

After holding a seed crystal in the central region of the ring heater for a while, the voltage for the ring heater was abruptly decreased a certain amount. During this process, the solid phase grew depending upon the solute content.

(1) Alloy A

Examples of the morphology change of the solid particle after decreasing the voltage with time found in alloy A are shown in Fig. 7. In this case, ΔE was equal to 0.06 V.

After 33 s, the solid particle started to grow and there were a lot of perturbations on the all periphery. It was found that the protrusions are almost uniform. Namely, there is no remarkable protrusion or distinguished growth direction. At 50 s, some of perturbations grew remarkably and the tips of them look like parabolic. Furthermore, there are some side branches. Thus, it can be said that the morphology of the solid/liquid interface at this moment is dendrite. Some den-

Fig. 7. Morphological change of solid/liquid interface during growth, alloy A, $\Delta E=0.06$ V.

drites were growing into their preferred growth direction. After 90 s from the change in voltage, the dendritic growth is outstanding. Three or four dendrites trunks were growing into the preferred growth direction and an envelope of tips is distorted from the round shape. At 180 s, the growth of solid phase seemed to stop and the tips of dendrites became thick. Furthermore, the roots of dendrites continued to solidify and the amount of liquid phase in interdendritic region was decreasing. Finally, at 310 s, there were still some uneven on the periphery of solid phase, the solid phase indicated a round shape.

(2) Alloy B

The morphology changes with time found in alloy B are shown in Fig. 8. Here, the voltage applying to the ring heater abruptly decreased at 0.06 V.

After 100 s, the protrusions were growing and solid phase began to grow. After 180 s, some typical dendrites grew and some secondary dendrite arms formed. Here, the tip of dendrite indicated a parabolic shape. At 280 s, typical dendrites grew in the preferred growth direction and at 370 s some tertiary dendrite arms were also observed. After 500 s, dendrites stopped growing and the dendrite tip radius became coarse, but the tip of dendrite remained parabolic. Dendrite arms slightly ripened, however, liquid phase remained in the interdendritic region.

3.4. Morphology Change during Melting

After stopping the growth of a solid phase, the voltage for the ring heater was abruptly increased to a certain value. During this process, the solid phase melted depending upon the condition.

(1) Alloy A

The morphological changes with time in case of

Fig. 8. Morphological change of solid/liquid interface during growth, alloy B, $\Delta E=0.06$ V.

Fig. 10. Morphological change of solid/liquid interface during melting, alloy B, $\Delta E=0.06$ V.

Fig. 9. Morphological change of solid/liquid interface during melting, alloy A, $\Delta E=0.06$ V.

$\Delta E=0.06$ V are shown in Fig. 9. When the growth stopped, solid/liquid interface indicated the round shape as shown in Fig. 7. Thus, when the voltage for the ring heater increased ($t=0$), the solid/liquid interface was round. After some incubation period, the solid phase started to melt. The shapes of solid/liquid interface were always round ($t=150$ s, $t=300$ s). There should be some microsegregation in interdendritic region, though, the melting interface did not indicate an irregular line but always smooth round line. The melting shape is also independent of the crystallographic orientation. Namely, in case of growth dendrites tend to grow quickly along the preferred growth direction, though, it has been found that the melting velocity is the same in all direction in this experimental condition.

(2) Alloy B

After stopping growth of dendrite for a while, the voltage applying to the ring heater abruptly increased at 0.06 V. The morphology change after increase of voltage is shown in Fig. 10. After 60 s, melting of solid phase started and the

Fig. 11. Traveling velocity of dendrite tip as a function of time elapsed after changing voltage. Alloy A, $\Delta E=0.06$ V.

position of dendrite tip went back. Together with this, the secondary arms, which were far from the primary dendrite tip, became slender. After 140 s, melting further proceeded and the secondary arms as well as the primary arms became pointed. At 220 s, it was observed that the roots of secondary dendrite arms melted and some solid particles were detached from the primary dendrite trunk. The detachment of secondary dendrite arms was observed from 200 to 350 s in this experimental condition. At 570 s, there were still some protrusions on the solid phase, though, the process of melting was almost terminated.

3.5. Traveling Velocity of Dendrite Tip

The traveling velocity of dendrite tip as a function of time elapsed after changing voltage for the ring heater has been measured. Here, the dendrite, which grew in the preferred growth direction, was selected. The displacement of the dendrite tip was measured on the monitor every 10 s and then the traveling velocity was calculated. In order to easily compare each other, both velocities are indicated by the positive sign.

Fig. 12. Traveling velocity of dendrite tip as a function of time elapsed after changing voltage. Alloy B, $\Delta E=0.06$ V.

(1) Alloy A

The relationship between time elapsed after changing voltage and traveling velocity of dendrite is shown in Fig. 11, which correspond Figs. 7 and 9. Growth velocity and melting velocity are almost zero at $t=0$. After some incubation time, both velocities increase and indicate the maximum values. After the maximum, the velocities gradually decrease and approach to zero. The general behavior with time is similar.

However, the change in growth velocity and melting velocity with time are different in detail. The maximum in growth velocity is larger than that in melting velocity and the time that gives the maximum value for growth velocity is shorter than that for melting velocity. Furthermore, the time that gives the maximum value for the melting velocity is broad and the peak is not sharp.

(2) Alloy B

The relationship between time elapsed after changing voltage and traveling velocity of dendrite is shown in Fig. 12. These experimental results correspond to Figs. 8 and 10. Here again, the general tendency is the same as Fig. 11. However, the incubation times for growth and melting found in alloy B are longer than these found in alloy A. It is remarkable that the incubation time for growth becomes long in alloy B.

4. Discussions

4.1. Incubation Time for Growth and Melting

Comparing with Figs. 11 and 12, the incubation time for growth depends on the solute content and it is longer when the solute content is high. In this experiment, because the temperature decreases from the liquidus temperature to a certain temperature, the solid particle solidifies, or increases its volume. The change in volume of solid as a function of decrease in temperature is analyzed in equilibrium state. Assuming that the Lever rule can be applied, the fraction solid can be calculated using a following equation.

$$f_s = \frac{\Delta T_U}{(mC_0 - \Delta T_U)(1 - k)} \quad \text{.....(1)}$$

where ΔT_U is undercooling ($=T_L - T$), m is the liquidus

Fig. 13. Relation between the undercooling and fraction solid in succinonitrile-water alloy system.

Fig. 14. Procedure for obtaining a relationship between undercooling and growth velocity.

slope, k is the equilibrium distribution coefficient and C_0 is solute content. The relations between C_0 and f_s at some values of undercooling for succinonitrile-water alloy system are shown in Fig. 13. As seen, the fraction solid increases with increasing undercooling, ΔT_U . However, at the same undercooling, the fraction solid strongly depends on the solute content, namely f_s decreases as C_0 increases. In other words, to obtain the same amount of solid fraction, it is necessary to increase the undercooling when the solute content is high. Therefore, the incubation time for initiation of growth in high solute content alloy becomes longer, because the cooling rates are almost the same.

Furthermore, the incubation time for melting is shorter than that for growth. The reason of this may be related with a fact that it is difficult to obtain the superheated solid. When the temperature increases beyond the liquidus temperature, the solid phase easily melts.

4.2. Growth Velocity as a Function of Undercooling

When the voltage for the ring heater abruptly changed, the temperature changed according with an exponential function as shown in Figs. 4 and 5. The amount of change in temperature at the fixed position may be related to undercooling and superheating, in cases of growth and melting, respectively. Before reaching the maximum in the traveling velocity, it can be related with the undercooling or superheating. The procedure for determining temperature change is schematically shown in Fig. 14. Here, the difference between the holding temperature and the temperature at any moment, which is indicated by a dotted line in Fig. 14, is defined as a undercooling. The growth velocity at this mo-

Fig. 15. Relation between undercooling and growth velocity obtained in Alloy B before reaching the maximum velocity.

ment is known using the time–velocity relationship as shown in Fig. 14. Thus, the relation between undercooling and growth velocity can be obtained. The traveling velocity has been analyzed when the solid/liquid interface is dendritic in this study.

The relation between ΔT_U and the growth velocity of dendrite tip (V_G) found in Alloy B is shown in Fig. 15. There are three series of experiments at different levels of ΔE . Though there are some scatters, these experimental data lie on the unique line. The regression analysis indicates that the slope of this line is 1.30. Thus, it has been found in the present study that V_G is proportional to $\Delta T_U^{1.30}$.

Huang and Glicksman studied on the relationship between undercooling and growth velocity of thermal dendrite using pure succinonitrile.^{11,12)} Using their experimental data, the relation between the undercooling and growth velocity is found to be expressed by a following equation.

$$V \propto \Delta T_U^{2.4} \dots\dots\dots (2)$$

This relationship agreed well with the theory of dendritic growth. In case of alloys, the growth velocity depends on the solute content, though, the relation between ΔT_U and V is close to that found in pure substance.¹³⁾

As shown in Fig. 15, the power is much smaller than that found by Huang and Glicksman. This may be due to the difference in thermal field. Namely, in case of Huang and Glicksman, the dendrite grew in a fairly large bath, which was kept at a constant temperature. On the other hand, in the case of the present experiment, the bath was large enough for the dendritic growth but small. Furthermore, the temperature was not constant but decreasing with time. Thus, the effect of temperature change on the growth velocity may be limited and thus the power on ΔT becomes small. However, the growth of equiaxed grains in a real casting can not take place in an undercooled bath at a constant temperature. The temperature in the liquid should change locally and thus the seed crystal undergoes gradual change in temperature. Therefore, it is reasonable that the effect of undercooling on the growth velocity becomes small, when the equiaxed grains grow in the liquid phase becoming cooler slowly.

Fig. 16. Relation between superheating and melting velocity obtained in Alloy B before reaching the maximum velocity.

4.3. Melting Velocity as a Function of Superheating

In the same way as Sec. 4.2, the relation between superheating (ΔT_h) and melting velocity of dendrite tip (V_M) can be obtained. The relation between ΔT_h and V_M found in Alloy B is shown in Fig. 16. There are again three series of experiments. There are some scatters, though, it is found that V_M is proportional to $\Delta T_h^{0.20}$.

The kinetics for melting has never been investigated. The present study is the first one that describes the relation between superheating and melting velocity. As indicated in Fig. 16, the power on the temperature change is 0.20, which is much smaller than that for the growth. This means that the effect of temperature change on the melting velocity is small. In other words, the melting velocity does not increase according to the amount of temperature increase. Since the heat flux is transferred through the solid/liquid interface, the solid grows or melts. As the thermal conductivity of solid phase and heat transfer coefficient between the solid and liquid interface are the same when the solid grows or melts. Thus, these physical parameters do not affect the velocity of the solid liquid interface. In case of melting, melting takes place on secondary dendrite arms and primary dendrite trunk as well as on dendrite tips. The former area is rather far from the dendrite tip and the dendrite trunk becomes slender and the dendrite tip is pointed sharp as shown in Fig. 10. The difference in morphology in solid/liquid interface indicates that the operating point for melting is not dendrite tip but solid/liquid interface near the dendrite tip. Therefore, if the melting velocity is defined as the moving velocity of the dendrite tip, the melting velocity is affected to a small extent by the amount of temperature change.

4.4. Formation Mechanism of Equiaxed Grains

In this experiment, the detached secondary dendrite arms melted away where they were because the liquid was stagnant. If there were some flow in the liquid phase, these detached arms may be transported to another area and would be seed crystals for equiaxed grains.

Jackson *et al.* made an *in-situ* observation using a transparent substance in an isothermal condition.³⁾ They observed some secondary dendrite arms detaching from the primary arms during holding at the constant temperature.

Sato *et al.* also performed an *in-situ* observation in unidirectional solidification condition.¹⁴⁾ They once solidified partially the organic substance and then they drew back their glass cell to melt the solid phase. Sato *et al.* reported that the detachment of secondary dendrite arms took place when the temperature increased in the columnar solidification condition.

In this study, on the other hand, it is found that the secondary dendrite arms can be detached in the equiaxed solidification condition when the temperature increases. Therefore, the multiplication takes place in not only columnar dendrite zone but also in equiaxed dendrite zone.

5. Conclusions

In order to analyze the growth and melting of a solid particle in the liquid, *in-situ* observation using succinonitrile-water alloys have been performed. The morphological changes have been quantitatively analyzed.

(1) In case of growth, dendrites grow from a solid particle. After stopping growth, the solid phase became round if the solute content is low. On the other hand, if the solute content is high, solid/liquid interface remained dendritic.

(2) In case of melting, solid/liquid interface is complex. If the solid phase is round after growth, it melted remaining round. If the solid/liquid interface is dendritic after growth, dendrite arms become pointed and secondary dendrite arms may be detached.

(3) Growth velocity is larger than melting velocity in case of the same temperature change. This may be due to the difference in operating point for growth and melting.

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