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TITLE PAGE MISSING
DIRECTIONAL SOLIDIFICATION PROCESSING OF BYC OXIDES

by

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ABSTRACT

Directional solidification of yttrium-barium-copper oxides (YBCO) was investigated using a resistance heated furnace. Materials and solidification parameters were systematically varied and correlated to solidification morphologies. Thermal gradient was held constant at approximately 120 °C/cm.

Different types of growth morphologies were identified for samples with different compositions, solidified at different growth rates. The growth morphology changed from faceted plane front to dendritic/cellular and to equiaxed blocky with increasing growth rate. However, the maximum growth rates to get faceted plane front and dendritic/cellular were different for samples with different compositions. The maximum growth rate at which a single crystal could be obtained increased from 1 μm/s to 1.5 μm/s as excess $Y_2BaCuO_5$ (211) content increased from 0 to 20 % (wt). It then decreased to 1 μm/s again as excess 211 increased to 40 % (wt).

In the dendritic/cellular regime, dendrite growth with distinguishable secondary arms was observed in stoichiometric 123 samples. A qualitative dendrite growth model considering both yttrium and copper diffusion was developed to interpret the experimental observation. It is concluded that the formation of secondary dendrite arms was due to microsegregation in the ternary system.

A new quench technique developed in this study made it possible to perform detailed microstructural examination of the $YBa_2Cu_3O_{6+x}$ (123)/liquid growth interfaces. The examination revealed that the amount of excess $Y_2BaCuO_5$ (211) had a strong influence on the microscopic growth morphology of the $YBa_2Cu_3O_{6+x}$ (123) interface.
The microscopic 123 growth interface was flat at high excess 211 content, but not flat at low excess 211 content. A highly curved 123 envelope was formed on 211 particles located at the 123 growth interface at zero excess 211 content (stoichiometric 123 samples). Based on the detailed microscopic growth interface examinations, the relation between peritectic reaction and the engulfment of 211 particles into 123 matrix was discussed. It is concluded that the formation of a small highly curved 123 envelope on 211 particles for stoichiometric 123 samples was due to the large 211 particle spacing, making the interface temperature lower.

Solidification interface temperatures of YBa$_2$Cu$_3$O$_{7-8}$ (123) single crystals were measured systematically for samples with different amounts of excess Y$_2$BaCuO$_5$ (211) phase, solidified at different growth rates. The experimental results show that the solidification interface temperature depression $\Delta T_p$ increases with increasing the growth rate for samples with a given amount of excess 211. At a given growth rate, however, $\Delta T_p$ initially decreases and then increases with increasing the amount of excess 211. Using the peritectic solidification model, it is concluded that the initial decrease of $\Delta T_p$ with increasing the excess 211 content was due to the decrease of the 211 particle spacing, and the increase of $\Delta T_p$ at high excess 211 content was due to the lengthened diffusion path required for solute transport through the liquid.

Solute distributions in the semi-solid melt and the relation between growth rate and solidification temperature have been obtained for isothermal growth of 123 single crystals in the ternary system of Y-B-Cu-O. This was done by solving the full solute transport problem, both in the boundary layer near the growing crystal, and in the outer semi-solid region. Unlike the binary system, liquid composition in the semi-solid region is not uniform. The copper concentration decreases and yttrium concentration increases with increasing distance from the 123 growth interface. The 211 volume fraction in the semi-solid melt is approximately constant. Those conclusions agree well with the experimental measurements.

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Chapter 1
Introduction

§1.1 Application of High $T_c$ Superconductivity Technology in the Electric Power Industry

High $T_c$ superconductors have a variety of applications in different fields since their special characteristics of superconductivity. Figure 1.1 schematically illustrates the application fields of superconductivity technology in the electric power industry. It can be seen that the applications of high $T_c$ superconductors consist of two major categories:

![Diagram showing applications of high $T_c$ superconductivity technology in the electric power industry]

Figure 1.1 Application fields of superconductivity technology in the electric power industry
the new field which utilizes the special characteristics of superconductivity and the ordinary field where superconducting devices replace existing devices with spectacularly improved performance.

§1.1.1 New Fields Which Utilize the Special Characteristics of Superconductivity

Utilizing the quenching phenomena of AC superconducting wires, superconducting fault current limiter is one example of the applications of high Tc superconductors. Figure 1.2 shows the current limiting characteristics of a fault current limiter designed by TEPCO[1]. It can be seen that the resistance of coils occurs by quenching when the fault current reaches to 2756A, and the fault current is limited to
3464A at about 0.5 msec after quenching, which is much faster than ordinary current fuse.

Figure 1.3 shows a superconducting fault current system designed by TEPCO\textsuperscript{[1]}, which has three phase superconducting fault current limiter coils in a cryostat filled with liquid helium, three pair of current leads cooled by gas helium and/or liquid nitrogen, and two stage refrigerators. In order to make the refrigerator more compact, the reduction of heat flow through the current lead from atmosphere and the reduction of AC loss in superconducting coils are very important. The use of high Tc superconducting current leads may be essential because of their low thermal conductivity. Figure 1.4 is several different designs for the superconducting current lead\textsuperscript{[1]}. Therefore, the technology to manufacture superconducting fibers with high critical current density is essential in
making both the superconducting fault current limiter and the superconducting current lead.

A low temperature superconductor (LTS) cooled below $T_c$ generates an opposing surface current to shield its interior from the imposed field, a phenomenon referred to as Meissner effect\cite{2}. The thin sheath in which the shielding surface current circulates, the so-called penetration depth, are on the order of 1000 Å. This opposing current (or magnetization) is the origin of a repulsive magnetic force. However, LTS materials usually exhibit small critical field ($H_c$) above which they become normal metals\cite{3}. The

![Diagram of current leads configurations](image)

Figure 1.4 Configuration of current leads\cite{1}

critical magnetic pressure $P_c = \mu_0 \frac{H_c^2}{2}$ is only about 1 psi for a LTS with $\mu_0 H_c = 0.2$ Tesla (e.g., Nb at 4K). Such magnetic pressure is not high enough for realistic large-scale applications such as superconductivity levitated flywheel. Unlike the traditional LTS, high $T_c$ superconductors provides a much wider range of applicable magnetic fields. High $T_c$ superconductors can remain superconducting until an upper critical field ($H_{c2}$) is reached; $H_{c2}$ is about 10 Tesla at $T = 77K$ and about 100 Tesla at 4K. Figure 1.5 shows
the ability of high $T_c$ superconductors to levitate small magnets\cite{4}. However, applications such as superconductivity levitated flywheel require high critical current density.

§1.1.2 Spectacularly Improved Performance by Replacing Existing Devices with Superconducting Devices

Superconducting technology can improve the performance of existing device spectacularly such as underground cable. For example, since the electric power demand will be doubled within 25 years if it increases at a rate of 3\% per year, it is necessary to expand the cable ducts or tunnels in order to distribute these huge power by the conventional underground cable. It is very difficult to do so since the large construction cost. However, high $T_c$ superconducting power cable which has a large current capacity and a compact size can be installed in existing ducts of 150 mm in diameter thus the construction cost can be reduced substantially\cite{1}. Therefore, long superconducting cables with high critical current density are essential for the future electric power industry.

Figure 1.5 Photograph of a magnetically levitated rare earth magnet with a turbine disc above high-temperature superconducting materials (YBa$_2$Cu$_3$O$_7$)\cite{4}
§1.2 Objectives

As shown in §1.1, important potential applications of high $T_c$ superconducting oxides in the electric power industry require long (or large) conductors capable of carrying high current density in moderate to high magnetic fields. However, progress toward the much-expected major application of bulk $T_c$ superconductors has been hindered by their low critical current density ($J_c$), especially in high magnetic fields. By contrast, thin films epitaxially grown on single crystal substrates typically exhibit $J_c$ values in excess of $10^6$ A/cm$^2$ at 77 K. There are two major causes for the low critical current density at 77 K in bulk materials: weak links at the grain boundaries and flux line movement with the grains. The latter is due to insufficient flux pinning in Y-Ba-Cu-O.

Solidification processing of high temperature superconducting oxides is an effective method of eliminating weak links, by generating textured microstructures and introducing flux pinning by adding pinning centers through processing control. However, little understanding is available of how those processes affect the microstructure and hence the superconductivity.

The primary objective of the present research is to achieve better understanding of the solidification behavior of BYC materials and therefore to be able to control the solidified microstructures.

§1.3 Thesis Organization

This thesis is organized in 8 chapters. The literature is reviewed in Chapter 2. Different solidification processing methods of BYC superconducting oxides are reviewed. Also reviewed are the progresses in the growth mechanism of 123 single crystal.
Chapter 3 describes the experimental apparatus used in this study. Also reported are the general observations of the directionally solidified samples, including liquid migration, solidified microstructures, initial transient region.

Chapter 4 reports the effect of growth rate on the solidification interface morphology and microstructures. Different growth rates were applied to samples with different amount of excess 211 content. A dendrite growth model is developed to interpret the experimental results.

Chapter 5 reports the effect of the amount of excess 211 on the solidification interface morphology of single crystal 123, with emphases on the growth mechanism of the 123 phases and the peritectic reaction occurred during solidification.

Chapter 6 reports the interface temperature measurement and the bi-fiber growth experiments. Also discussed is the 123 growth mechanism at high excess 211 content.

Chapter 7 develops a ternary solidification model to describe the solidification behavior of this B-Y-C-O system. The solute distributions in the semi-solid melt is calculated according to this model and compared with the experimental measurement.

Conclusions from this research work are presented in chapter 8.

§1.4 Reference


§2.1 Phase Equilibrium in the Y-Ba-Cu-O System in Air

The pseudo-ternary section BaO-1/2(Y_2O_3)-CuO was determined by a number of investigators [1, 2, 3, 4, 5] in the temperature range of 800 °C - 900 °C. Published results are in general agreement concerning the phase relations but have disagreements on the exact temperature and composition for all invariant reactions. Figure 2.1 is the pseudo-ternary section at 875 °C determined by Roth et al [1]. Two ternary compounds exist in the region.

![Diagram](image-url)

Figure 2.1 Pseudo-ternary section of the system 1/2(Y_2O_3)-BaO-CuO in air, at temperature around 850°C.
at barium content below 50 mole %: the superconducting phase YBa$_2$Cu$_3$O$_{6+d}$ (123) and the "green phase" Y$_2$BaCuO$_5$ (211), which is a non-superconducting phase.

Figure 2.2 is the temperature-composition section corresponding to the lines a1-a2 of the ternary section shown in figure 2.1. The compound 211 was found to melt incongruently at $1275 \pm 25 \, ^\circ C$ into Y$_2$O$_3$ plus liquid. The compound 123 decomposed into 211 plus liquid at $1000 \pm 2 \, ^\circ C$ and then became fully liquid at $1258 \pm 2 \, ^\circ C$. However, other researchers found a considerably higher liquidus temperature [2].

Figure 2.2 Temperature-composition section corresponding to the lines a1-a2 of the ternary section shown in figure 2.1.
Even though various sections of the ternary phase diagram of $\text{Y}_2\text{O}_3$-$\text{CuO}$-$\text{BaO}$ have been published in large number, only a few three dimensional views of the liquidus surface have been reported. Figure 2.3 is one determined by Kosmynin et al [6]. The eutectic, peritectic and melting point reactions in figure 2.3 are described in table 2.1:

<table>
<thead>
<tr>
<th>Type</th>
<th>Temperature</th>
<th>Phases Involved</th>
</tr>
</thead>
<tbody>
<tr>
<td>E</td>
<td>920</td>
<td>$\text{YBa}_2\text{Cu}<em>3\text{O}</em>{6+\delta}$ + $\text{BaCuO}_2$ +$\text{CuO}$ -&gt; Liquid</td>
</tr>
<tr>
<td>P1</td>
<td>992</td>
<td>$\text{YBa}_2\text{Cu}<em>3\text{O}</em>{6+\delta}$ + $\text{BaCuO}_2$ -&gt; $\text{Y}_2\text{BaCuO}_5$ + Liquid</td>
</tr>
<tr>
<td>P2</td>
<td>970</td>
<td>$\text{YBa}_2\text{Cu}<em>3\text{O}</em>{6+\delta}$ + $\text{CuO}$ -&gt; $\text{Y}_2\text{BaCuO}_5$ + Liquid</td>
</tr>
<tr>
<td>P3</td>
<td>1035</td>
<td>$\text{Y}_2\text{BaCuO}_5$ + $\text{CuO}$ -&gt; $\text{Y}_2\text{Cu}_2\text{O}_5$ + Liquid</td>
</tr>
<tr>
<td>P4</td>
<td>1068</td>
<td>$\text{Y}_2\text{BaCuO}_5$ + $\text{Y}_2\text{Cu}_2\text{O}_5$ -&gt; $\text{Y}_2\text{O}_3$ + Liquid</td>
</tr>
<tr>
<td>m1</td>
<td>1020</td>
<td>$\text{YBa}_2\text{Cu}<em>3\text{O}</em>{6+\delta}$ -&gt; $\text{Y}_2\text{BaCuO}_5$ + Liquid</td>
</tr>
<tr>
<td>m2</td>
<td>1295</td>
<td>$\text{Y}_2\text{BaCuO}_5$ -&gt; $\text{Y}_2\text{O}_3$ + Liquid</td>
</tr>
</tbody>
</table>

§2.2 Solidification Processing

Various processes have been employed for the fabrication of bulk high-temperature superconductors. Sintering is common in ceramic processing and has various advantages in making practical superconductors. However it has been unsuccessful in producing high-$J_c$ materials [7]. The weak links at grain boundaries in bulk sintered samples are believed to be the source of low $J_c$ values [8].

Solidification from the semi-solid melt (211 plus liquid) has been found to be an effective way of reducing weak links through gain alignment and improving $J_c$ values in YBCO, even at 77 K [9,10,11]. The various solidification processing methods can be
Figure 2.3 Top: Projection of the liquidus lines. Bottom: Three dimensional views of liquidus surface of Y-B-C-O system in air.
classed into two major categories, namely (i) non-directional solidification methods and (ii) directional solidification methods.

§2.2.1 Non-directional Solidification Methods

Since the initiation of melt processing of BYC materials, significant progress has been achieved in the development of non-directional solidification methods. The most commonly used non-directional solidification method in processing of BYC materials are melt-texturing methods. The resulting microstructures from melt-texturing method consist of multiple domains, which are randomly directed with respect to their neighbors\(^{[12]}\). The boundaries separating these domains are high-angle boundaries, which frequently contain secondary phases. Jin et al.\(^{[9]}\) developed the first method of melt texturing of 123 called melt-texture growth (MTG), where sintered YBaCuO was melted and slowly cooled in a thermal gradient. After melting, the sample was decomposed into liquid plus 211 particles. During the slow cooling process, 123 phase was formed

![Figure 2.4 Optical Micrograph of a MTG processed YBaCuO. Grains were highly textured, which can be confirmed by the orientation of the twin structures.](image)
through the peritectic reaction: liquid + 211 --> 123. A typical microstructure of MTG processed BYC materials is shown in figure 2.4. It can be seen that the resulting 123 grains were needle shaped, typically 100-300 μm long and 5-20 μm wide. The preferred orientation for the grain growth was known to be in the a-b plane and thus the grains were aligned along this direction. Due to the incompletion of the peritectic reaction, 211 particles of 2 - 20 μm size were typically observed in the microstructure. Transport $J_c$ values of the MTG sample exceed $10^4$ A/cm$^2$ at 77 K in zero field, indicating that grain alignment may have possibly eliminated the weak links. However, $J_c$ values were still small in magnetic fields, suggesting that flux pinning was insufficient.

There are two approaches used to achieve 211 + liquid phase for subsequent transformation to 123. One is decomposition of 123 phase, as in the case of the MTG process, and the other is reaction of $Y_2O_3$ with liquid of appropriate composition. In

![Schematic Illustration of MPMG process.](image)

Figure 2.5 Schematic Illustration of MPMG process. Corresponding microstructure at each stage (a, b, c, d) is also schematically shown.
order to decrease the 211 particle size and achieve a homogeneous distribution of 211 particles, Murakami et al.[13,14] developed processes termed quench and melt growth (QMG) and melt powder melt growth (MPMG). Figure 2.5 shows a schematic illustration of the MPMG (QMG) process. First the sintered sample was heated to the $Y_2O_3$ plus liquid phase region and then quenched to get a mixture of $Y_2O_3$ particles and a matrix consisting of quenched liquid. By crushing the quenched plates into powders and mixing them well, the $Y_2O_3$ particles can be made finer and distributions more homogeneous. Since $Y_2O_3$ was refined and its distribution is made more uniform, much smaller 211 particles were obtained in the solidified 123 matrix[15]. therefore, higher $J_c$ was achieved in MPMG samples.

Recently, other methods based on the principle of slow cooling have been developed. Several of these modifications were designed to compensate for the deficiency in the yttrium supply and provide for a more homogeneous distribution of 211 particles. These include the utilization of yttrium-rich starting composition and the addition of small amount of Pt to samples[16]. Solidified yttrium-rich samples have been found to be less micro-cracks. The presence of small amount of Pt was believed to alter the interfacial energy of the 211-liquid interface, resulting in a suppressed coarsening rate and a decrease of 211 particle size[17]. Another modification to the melt-texturing method involves MTG in the presence of a strong magnetic field in an effort to align the 123 nuclei with the melt during initial stage of solidification[18]. The results of this nuclei realignment was multiple-oriented domains that had smaller disorientation angles. Most recently, Jeong developed an infiltration-reaction process to obtain microstructures with a fine dispersion of 211 particles in the 123 grains without residual liquid phase[19]. 211 powder compacts were placed on the top of 123 powder compact and heated at 1030 °C. The liquid appearing in the 123 compact infiltrated into the 211 compact and the peritectic occurring during cooling resulting in uniform distribution of 211 particles and much higher pinning effect than conventionally melt-grown specimens.
For most applications, one needs bulk materials fabricated in usable shapes of large size. The control of crystal orientation is also desirable since the superconductivity of oxide superconductors is highly anisotropic. It has been demonstrated that other rare earth 123 crystals such as SmBa$_2$Cu$_3$O$_x$, which have higher melting points than Y123, can work as seeds for the crystal growth of 123 and thus make it possible to control the product crystal's orientation. When a small amount of these materials is placed on top of a sintered 123 sample, which is then subjected to non-directional melt texturing, grain growth of 123 around the seeding crystal is greatly enhanced. During the slow cooling process, they can act as heterogeneous nucleation centers. Larger crystals with controlled orientation have been fabricated by this technique.$^{[20,21,22]}$

§2.2.2 Directional Solidification

Melt-texturing methods can be used to produce regions of aligned grains (or "domain" of texture) in the absence of a temperature gradient. However, without a temperature gradient, domains tend to nucleate and grow at multiple sites throughout a sample. Although large textured regions can be produced and then sectioned from a sample for characterization and testing, there will be high-angle boundaries and copper rich phases between domains which limits the transport of current between domains even though the transport properties of individual domains are extremely good. On the other hand, although the seeding method can produce relatively large single crystal, the sizes attainable may be limited.

Directional solidification of the Y-Ba-Cu-O system has been investigated by a number of researchers over the past a few years because of its unique advantages of producing well textured microstructures or even single crystals and the ability to fabricate long conductors as required in application. Directional solidification is a versatile melt-texturing process which employs the motion of a sample relative to a temperature
gradient to achieve textured microstructures \cite{23}. The movement of the sample is desirable from a commercial standpoint, because it permits long samples to be processed in a semi-continuous fashion. A variety of means have been used to generate the temperature gradient, including laser and resistance heated furnaces. In the zone melting method used by McGinn et al\cite{24}, thin extruded samples were sintered and directionally solidified in a vertical tube furnace in air. Localized heating of the sample was provided by a resistance coil where typical hot-zone temperature is between 950 °C to 1050 °C, and the solidification rate was controlled by the traveling rate of the sample. A-b plane alignment along the sample axis had been achieved for samples of this size. Superconductors of larger cross-sectional area have been directionally solidified by Meng et al \cite{25}. In their semi-continuous method, a multi-zone horizontal tube furnace with a prescribed temperature profiles employed. A sintered 123 sample was transported through the furnace at a travel rate that was chosen according to the temperature profile. By doing so, various parts of the sample were heated to 1100°C for a short duration, rapidly cooled to 1050 °C and slow cooled at different times. Samples of 2.5×5×40 mm$^3$ have been fabricated by this method.

Figueroedo et al.\cite{26} has successfully grown 123 single crystal using a laser-heated floating zone furnace, which consists of a 100-W CO2 laser, two-beam heating optics, and a controlled atmosphere crystal grower with a cold wall chamber, operated at pressures ranging from vacuum to 1.3 atm. Direct and indirect current density measurements yielded current density value along the ab planes in excess of $10^5$ A/cm$^2$ at 77.3 K.

Most recently, Shiohara et al.\cite{36} developed a crystal-pulling process (Solute Rich Liquid Crystal Pulling, SRL-CP method) to grow a single crystal continuously along either a-axis or c-axis and reported that large faceted (1.6 cm×1.6 cm×0.9 cm) YBCO crystals were continuously pulled at about 0.1 mm/h of the pulling rate. In doing this experiment, the 211 phase powder was first placed as a solute at the bottom of the
crucible which are made of polycrystalline $\text{Y}_2\text{O}_3$ or single or polycrystalline MgO. According to the mass balance, the solvent of 3Bao-5CuO or Bao-3CuO was put on the layer of the solute. Heating was supplied by a resistance heater to keep a constant temperature gradient, which is several degrees higher at the bottom than the surface of the melted solvent and the surface temperature was kept constant at about 900-1050 °C, depending on the growth direction and growth rate. The seed crystals used are a single crystal MgO with appropriate surface treatment or 123 single crystal produced separately. Rotation of the seed crystal was 20-150 rpm which is relatively fast to other crystal pulling techniques. The typical pulling rate was about 0.1 mm/hour.

§2.3 Growth Mechanism of 123 Phase and Peritectic Reaction

From the beginning of the investigations on solidification processing of 123, the peritectic growth mechanism of 123 crystal has been one of the main topics. Both directional and non-directional solidification techniques have been used to investigate the growth mechanism of 123 and the peritectic reaction occurred during solidification process.

Melt-texturing methods usually involve the heating of 123 above its peritectic temperature, which is approximately 1000 °C in air. When 123 is heated above this temperature, it incongruently melts into 211 and a liquid phase according to the reaction

$$123 \rightarrow 211 + \text{liquid} \quad (2.1)$$

On subsequent slow cooling of the semi-solid melt, oriented-grains of 123 form with 211 inclusions distributed throughout the superconducting matrix. The microstructure of melt-textured 123 obtained by slow cooling through the peritectic temperature, however, is different from the typical microstructures resulting from traditional peritectic reaction and
transformation. Instead of small randomly oriented grains due to multiple nucleation sites in the high temperature 211 phase, melt-textured 123 grains are extensive in the a-b direction. Rodriguez et al. [27] analyzed the formation of textured 123 from the liquid using real-time analysis techniques of high temperature x-ray diffraction, high temperature optical microscopy and environmental scanning electron microscopy. They concluded that the presence of crystalline 211 primarily acts as a source of yttrium, and that the slow dissolution of 211 into the yttrium deficient liquid phase is the rate controlling step in the formation and growth of textured 123. Morita et al. [28] investigated the growth process, crystallization and growth mechanism of 123 using a seeding technique and found that there was anisotropy of the growth rate between a and c axis. They considered that yttrium were diffusing along the facets rather than diffusing in the liquid phase from 211 to 123 while the growth of QMG crystal proceeds.

From the yttrium diffusion controlled growth mechanism of 123, Cima et al.[29] developed a solidification model which not only is able to interpret this experimental observation but also shows that growth rate strongly affects the ability to obtain the desirable plane front interface, and that thermal gradient has only a small effect. Izumi et al.[30] proposed a simple solidification model considering the interface curvature of 211 as the only driving force for the growth of 123 phase. Schmitz et al.[31] proposed a diffusion model for the growth of 123 taking into account the engulfment process of the 211 particles by the solidifying 123 interface. Bateman et al.[32] proposed that the aligned grain structure is formed by sympathetic nucleation of new 123 grains on existing grains. Recently, Chen[33] reported that the undercooling temperature is a critical parameter which controls the final morphology of 123 in the case of non-directional solidification. Large amounts of undercooling result in a microstructure characterized by randomly-oriented dendrite needles or plates, while a low degree of undercooling yields large, blocky domains of oriented 123.
Cima et al. [29] measured the solidification interface temperature for samples directionally solidified at different growth rates (from 0.1 to 0.5 µm/s). They found the interface temperature depression ΔT_p (= 1000 °C - T_{interface}) was about 33 °C at 0.5 µm/s. Endo et al. [21] measured the growth rate for samples isothermally solidified at different temperatures. They found that ΔT_p was about 15 °C at 0.09 µm/s. The magnitude of the interface temperature depression is large, given what is known about the phase equilibrium in the BYCO system. Cima et al. [29] shows that the maximum constitutional undercooling ΔT_s in the semi-solid melt may be much less than ΔT_p. This may be seen by following equation [29]:

\[
ΔT_p = \left(\frac{m_{Lα}}{m_{Lα} - m_{Lγ}}\right)ΔT_s + G l
\]  

(2.2)

where \( m_{Lα} \) and \( m_{Lγ} \) are the slopes of the equilibrium γ (123) and metastable α (211) liquidus; \( G \) is the thermal gradient; \( l \) is half spacing of 211 particles. It can be seen that \( ΔT_p \) is much larger than \( ΔT_s \) when \( m_{Lα} \rightarrow m_{Lγ} \). Therefore, single crystal growth can be achieved even at large interface temperature depression such as 33 °C since the constitutional undercooling \( ΔT_s \) is actually very small.

Although 123 can grow rapidly in the [110] direction, growth along the C axis appears to be much slower. Scheel et al. [34] studied the growth mechanism of (100) and (001) faces, especially near edges and corners using a scanning tunneling microscope combined with SEM and found these two faces of 123 have a different growth mechanism. Lin et al. [35] studied the crystallographic defects in (001), (100)/(010) and (011) faces of 123 single crystal by chemical etching with acetic acid, as well as mixed solutions of acetic acid, nitric acid and methanol. and found clear evidence for growth hillocks and steps on these faces. Three types of etch pits are observed: type I is a square pyramid with growth steps along the <100> and <010> directions; type II is an octagonal pattern of the above square truncated along the <110> direction, and type III is a shallow
ellipse with long and short axes in the $<100>/<010>$ and $<001>$ direction, respectively. Due to their spiral growth feature types I and II are designated screw dislocation etch pits and type III is to be of Hopper-like morphology, on the basis of the growth mechanism.

§2.4 Reference


[31] G.J. Schmitz, J. Laakmann, Ch. Wolters and R. Rex,
Chapter 3
Experiments

§3.1 Experimental Apparatus

Figure 3.1 is a schematic diagram of the apparatus built for this study. It consists of a motion system and a zone melting furnace. The details of the furnace are shown in figure 3.2. Two conventional electrical heating elements with length of 5 cm and inside

![Diagram of experimental apparatus]

Figure 3.1 The apparatus for directional solidification
diameter 1.5 cm were arranged end-to-end and insulated. Located between the upper and lower heating elements was a smaller local heater used to control the shape of the temperature profile. The local heater was made by a coiled electric resistance wire which is commercially available (Kanthal®). A heating element with the same inside diameter (1.5 cm) and longer length (20 cm) was placed below those two heating elements and one local heater to prevent heat convection. The maximum temperature was controlled to be in the range 1030 °C to 1100°C and the thermal gradient in the freezing range was between 90°C/cm to 200°C/cm. The motion controlling system was purchased from Areotech Company®. It has the accuracy of 1 µm/s per 25 mm. The motion speed can be varied from 0.01 µm/s to 1000 µm/s.

§3.2 Sample Preparation

The preparation of polycrystalline precursor samples used in a previous laser furnace study can be found elsewhere[1]. However, since the solidification processing
using resistance heated furnace required much longer samples than those employed in the laser furnace, a technique to produce much longer samples was developed. Briefly, commercial 123 and 211 powders (SSC, INC., Woodinville, WA) synthesized by a spray pyrolysis process were weighted in the desired proposition and mixed well with a prepared polymer solution. After extensive grinding in an agate mortar using a pestle, the mixtures were heated on a hot-plate to evaporate the excess solvent. Then the clay-like mixture was extruded to 200 - 300 μm sample on top of a glass plate. After removing most of the solvent by heating these wet samples in a vacuum furnace, they were sintered in flowing oxygen. Polycrystalline precursor samples with lengths of more than 25 cm were successfully produced using this method. Figure 3.3 is an optical microscopic picture of a stoichiometric sample after sintering. It can be seen that the microstructure of the as-sintered sample was polycrystalline.

Figure 3.3 The optical microscopic picture of a stoichiometric sample after sintering. It can be seen that the microstructure of the as-sintered sample was polycrystalline.

§3.3 General Observations
§3.3.1 Liquid Migration

In conventional zone melting solidification, it is important to maintain the stability of the molten zone and to avoid the liquid migration from the molten zone. This requires that the molten zone length be approximately same as the sample diameter. However, in this study, the molten zone length was about 10 mm and the sample diameter was only 0.2 mm. Therefore liquid migration was severe when both the temperature profile inside the furnace and the pulling rate were not properly controlled. Figure 3.4(a) shows the solidified sample surface, which is not smooth because of liquid migration. Figure 3.4(b) is the optical microscopic picture of a polished sample, which shows that the migrated liquid accumulated near the molten zone.

Liquid migration not only changed the overall composition of the molten zone but also increased the coarsening rate of 211 particles in the molten zone. Therefore, it was necessary to find the optimum condition to avoid the liquid migration.

After a series of trial and error experiments, it was found that to avoid surface liquid migration, the maximum temperature of the molten zone should not exceed 1080 °C and the minimum growth rate should not be below 0.2 μm/s. Figure 3.5 is a sample surface solidified at $T_{\text{max}} = 1050$ °C and growth rate $R = 1$ μm/s without polishing. It can be seen that the surface of the sample is smooth and the solidification interface is clear.

§3.3.2 The Microstructures in the Molten Zone and Solidified Portion

The molten zone contains 211 particles and liquid phase. Figure 3.6 is a SEM picture of the molten zone for a sample with 20%(wt) excess 211. It can be seen that 211 particles were distributed in the liquid phases. After solidification, the microstructure consisted of 123 phase with 211 inclusions. Figure 3.7 shows optical microscopic picture of solidified portion for samples with different amount of excess 211. It can be seen that 211 particles are distributed in the 123 single crystal matrix. The 211 particle spacing decreases with increasing amount of excess 211.
Figure 3.4 Liquid migration along a sample surface solidified at $T_{\text{max}} = 1100 \, ^\circ\text{C}$. (a) The solidified sample surface, which is not smooth because of liquid migration. (b) The optical microscopic picture of a polished sample, which shows that the migrated liquid accumulated near the molten zone.
Figure 3.5 A sample surface solidified at $T_{\text{max}} = 1050 \, ^{\circ}\text{C}$ and at a growth rate of 1 $\mu$m/s. The solidification interface can be seen very clearly.

Figure 3.6 A SEM picture of the molten zone in a sample with 20% (wt) excess 211. It can be seen that 211 particles were distributed in the liquid phase.
§3.3.3 Initial Transient Region

In directional solidification processing, an initial transient region exists before a steady state is reached. The length of the initial transient region depends on growth rate, initial composition and thermal gradient. In this experiment, it was found that there is an initial transient region in which much more 211 particle inclusions existed. Figure 3.8(a) shows the solidified microstructures of a sample with 20%(wt) excess 211 along the sample length and figure 3.8(b) shows the corresponding 211 volume fraction. It can be seen that the initial solidified region (approximately one zone length) contained much more 211 particles than the rest of the sample. Composition measurement confirmed that the microstructures were 123 matrix with 211 particle inclusions. After this initial transient region, 211 volume fraction became constant.

The existence of this initial transition region was caused by the non-complete densification of the sintered BYC samples. Figure 3.9 shows schematically what happened during initial stage of the zone melting solidification processing when the sintered sample had approximately 80-90% green density. At the beginning of the solidification, a molten zone formed and its volume was less than that before melting. Since the sample both above and below this molten zone had about 10-20% porosity, part of the liquid in the molten zone migrated in both directions through the pores existing in those regions (figure 3.9b). Therefore, there were many more 211 particles in the initial molten zone, and hence many more 211 particles in the initially solidified 123. With the formation a 123 crystal above the molten zone (since the sample was pulled upward), liquid from the molten zone could no longer migrate upwards to the un-melted region. Furthermore, the liquid from the molten zone could not migrated downward to the un-melted region either, since the solid here was now 100% dense. Therefore, the initial transient region containing a high concentration of 211 particles had a length approximately the same as the zone length.
Samples used for microstructural and interface morphology examination in this work were taken at or beyond 20 mm from the start of solidification (twice the molten zone length).

§3.4 Reference

Figure 3.7 Solidified microstructures for samples with different amount of excess 211. It can be seen that the 211 particle spacing decreased with the increase of the amount of excess 211.
Figure 3.8 (a) Solidified microstructures of a sample with 20% (wt) excess 211 at different distance from the start point of solidification. (b) Plot of the 211 volume fraction and the distance from the start point of solidification.
Figure 3.9 (a) Before solidification, the sample has about 80-90% green density. (b) At the beginning of the solidification, a molten zone formed and its volume was less than before melting. The liquid in this molten zone migrated to non-fully dense portion both above and below the molten zone, making the molten zone have much more 211 volume fraction. Therefore, more 211 particles remained after solidification. (c) After a small portion of the sample was solidified, the liquid in the molten zone can not migrate upward since the existed fully dense solidified portion. The liquid can not migrate downward either since a small portion below the molten zone was fully densified due to high temperature (near the melting point) sintering. Therefore, the intial transition region was only about one molten zone length.
Chapter 4
Effect of Growth Rate on the Solidification Interface Morphology and Microstructure of YBa$_2$Cu$_3$O$_{6+\delta}$

§4.1 Abstract

Directional solidification was used to study the effect of growth rate on the solidification interface morphology and microstructure of YBa$_2$Cu$_3$O$_{6+\delta}$ (123). Different growth rates were applied to the YBCO samples which had different amounts of excess Y$_2$BaCuO$_5$ (211). It was found that the maximum growth rate at which a single crystal could be obtained increased from 1 $\mu$m/s to 1.5 $\mu$m/s as excess 211 content increased from 0 to 20% (wt). It then decreased again to 1 $\mu$m/s as excess 211 increased to 40% (wt). In the regime of cellular/dendritic, dendrite growth with distinguishable secondary arms occurred for samples with stoichiometric 123; a qualitative dendrite growth model was developed to interpret the experimental observation.

§4.2 Introduction

For practical applications of oxide ceramic high temperature superconductors, the bulk transport critical current density $J_c$ must be higher than that obtained from the polycrystalline microstructures. Experimental evidence indicates that the lower $J_c$ is caused by weak links between high $J_c$ grains or regions. The weak link behavior leading to low $J_c$ values in those compounds is attributed to a number of factors [1,2,3]: (a) anisotropy in conductivity in the crystal resulting in weak link at high angle grain boundaries, (b) micro-cracking resulting from anisotropy thermal expansion, (c) impurity layers along the grain boundaries and (d) non-
stoichiometry near grain boundaries. Recently, melt-processing methods\cite{4, 5, 6, 7, 8} have been successfully used to eliminate the weak-link behavior of bulk materials by grain alignment. The critical current density $J_c$ can thereby be enhanced dramatically. However, $J_c$ in those melt processed bulk materials is still two orders less than that in the thin films, and the production rate is extremely low due to the slow solute transport process in the melt. Therefore, the fundamental understanding of the growth behavior of 123 single crystals is important in order not only to obtain much higher $J_c$ but also to increase the growth rate of those textured microstructures.

This chapter will report the effect of growth rate on the solidification interface morphology and solidified microstructures. Directional solidification was used to solidify pre-sintered samples. Different growth rates were applied on samples which had different amount of excess 211. The maximum growth rates to obtain 123 single crystal were investigated. A qualitative dendrite growth model was developed to interpret the experimental observation.

**§4.3 Experiment**

Details of the electrically heated resistance furnace used to directionally solidify samples can be found in Chapter 2. Briefly, two conventional electrical heating elements with length of 5 cm and inside diameter 1.5 cm were arranged end-to-end and insulated. Located between the upper and lower heating elements were a smaller local heater used to control the shape of the temperature profile. The local heater was made by a coiled electric resistance wire which is commercially available (Kanthal®). A heating element with the same inside diameter (1.5 cm) and longer length (20 cm) was placed below those two heating elements and one local heater to prevent heat convection. The maximum temperature was controlled to be between 1030°C at low growth rate (0.25 μm/s) and 1050 °C at high growth rate (1.5 μm/s or above). The corresponding thermal gradient in the freezing range was 90 °C and 120°C/cm, respectively.

Pre-sintered YBCO fibers were prepared from commercially available 123 and 211 powders (SSC, Inc.) by pressing through a die and followed by vacuum drying at 120°C for 20
hours. The dried samples were then sintered at 975 °C for 20 hours. The final diameter was about 200 - 250 µm and they were normally 15 cm long. In making a run, the sample was glued to a ceramic tube with inside diameter about 1000 µm by Ceramabond (#569, Aremco Products, Inc.). The ceramic tube was then placed on a sample holder. The sample holder was then fixed to the motion device which was commercially available (Aerotech®). The sample was lowered into the furnace until the joint between sample and the ceramic tube was about 1 cm above the hot zone. The sample was then pulled up through the hot zone at a rate from 0.025 to 10 µm/s for directional solidification.

Since the sintered samples had a diameter of about 200 - 250 µm, the solidification interface could be easily quenched by pulling the sample out of the furnace by hands very quickly. The cooling rate was very high since the sample diameter was very small. Since this quench process did not involve any water or oil, the solidification interface was kept intact.

The quenched solidification interfaces were carefully polished by diamond paste, requiring about 2 - 3 hours for each sample. The microstructures were examined by optical microscopy, SEM and microprobe.

§4.4 Experimental Results

A total of 64 successful runs were completed and reported in table 4.1, where interface morphology "a" refers to "single crystal growth"; interface morphology "b" refers to "cellular/dendritic growth"; interface morphology "c" refers to "equiaxed blocky growth". Details of the interface temperature measurement are reported in Chapter 6.

§4.4.1 Solidification Interface Morphology and Microstructure for Stoichiometric 123 Samples at Different Growth Rates

Figure 4.1 to figure 4.5 show the solidification interface morphologies and solidified microstructures of stoichiometric 123 samples solidified at different growth rates. At a growth
rate of 2 μm/s and above, there was a region ahead of the growth interface where small grains co-existed with the semi-solid melt. Figures 1(a) and 1(b) show the solidification interfaces and microstructures at a growth rate of 2 μm/s and 10 μm/s, respectively. It can be seen that the solidified microstructures comprise equiaxed grains. 211 particles exist inside the

<table>
<thead>
<tr>
<th>Run Number</th>
<th>Weight % of excess 211</th>
<th>Growth Rate (μm/s)</th>
<th>Interface Morphology</th>
<th>Interface Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>11</td>
<td>20</td>
<td>1.25</td>
<td>a</td>
</tr>
<tr>
<td>2</td>
<td>12</td>
<td>20</td>
<td>2</td>
<td>b</td>
</tr>
<tr>
<td>3</td>
<td>16</td>
<td>20</td>
<td>2.8</td>
<td>b</td>
</tr>
<tr>
<td>4</td>
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solidified 123 grains even though the initial composition was stoichiometric 123. Copper rich phase exists at the grain boundary.

Figure 4.2 shows the solidification interface morphology and the solidified microstructure at a growth rate of 1.75 µm/s. It can be seen that it is cellular/dendritic: many small grains with faceted interfaces grew along the sample axis. Unlike equiaxed microstructures obtained at a growth rate of 2 µm/s and above, no new grains nucleated ahead of the solidification interface at this growth rate. Again, copper rich phase exists at the grain boundary.

Figure 4.3 shows the solidification interface and microstructure at a growth rate of 1.5 µm/s. It can be seen that there were fewer grains in the solidified region than that at a growth rate of 1.75 µm/s. The growth pattern was similar to dendrite growth in metal system, with primary dendrites approximately parallel to the sample axis and secondary arms grown from the primary arms. Copper rich phase was trapped between both primary arms and secondary arms. Figure 4.4 is a high magnification picture of the dendrite growth in another sample. It can be seen that the trapped copper rich phase is parallel to the growth interface. The orientation of the secondary arms reflects the orientation of the faceted interface.
At a growth rate below 1 µm/s, single crystal 123 was obtained. Figure 4.5 shows the solidification interface and solidified microstructure at a growth rate of 1 µm/s.

§4.4.2 Solidification Interface Morphology and Microstructures of Samples with Excess 211 at Different Growth Rates

Figure 4.6 is an optical microscopic picture of the solidification interface of a sample with 10%(wt) excess 211 solidified at a growth rate of 1 µm/s. It can be seen that the interface is faceted. Figure 4.7 is an optical microscopic picture of the solidification interface and microstructure at a growth rate of 3 µm/s. It can be seen that it is cellular/dendritic: the solidification interface contains a few small grains which grew parallel to the sample axis. At much higher growth rate, new grains were nucleated ahead of the solidification interface and the solidified microstructure comprises equiaxed grains. Figure 4.8 shows the solidification interface at 10 µm/s.

The solidification interface morphology and microstructures of samples with 20%(wt) excess 211 are similar to that with 10%(wt) excess 211. However, single crystals were obtained at a growth rate up to 1.5 µm/s. Figure 4.9 shows the solidification interface at a growth rate of 1.5 µm/s. It can be seen that not only it is a single crystal, but also the solidification interface is flat. Figure 4.10 shows the solidification interface at a growth rate of 10 µm/s. Again, it can be seen that new grains were nucleated ahead of the growth interface and the solidified microstructure comprises equiaxed grains.

§4.4.3 Solidification Interface Morphology and Microstructures of Samples with Stoichiometric 123 plus 40%(wt) 211 at Different Growth Rates

At high weight fraction of excess 211 (40%(wt)), the maximum growth rate to achieve single crystal 123 is about 1 µm/s and the solidification interface was not flat. Figure 4.11 shows the solidification interface of a sample at a growth rate of 1 µm/s. It can be seen that many
211 particles exist in the semi-solid melt and are aggregated to each other. At a growth rate higher than 1 μm/s, equiaxed microstructures were obtained; cellular/dendrite growth was not achieved for samples with 40% (wt) excess 211.

§4.5 Discussion

§4.5.1 Solidification Interface Morphology at Different Conditions

Figure 4.12 summarizes the interface morphologies obtained at different growth rates for samples with different amounts of excess 211 (wt%). The volume fraction of 211 in figure 4.12 was measured from quenched semi-solid melt. Three different growth regimes are seen. Similar to the definition given by Cima et al. [9], the three types of interfaces are termed, "single crystal growth", "cellular/dendritic" and "equiaxed blocky". Note that "cellular/dendritic with distinguishable secondary arms" were only formed in samples with stoichiometric 123.

The experimental results shown in figure 4.12 indicate that the maximum velocity for continuous growth of 123 crystals varies with the amount of excess 211. With increasing amount of excess 211 (from 0 to 20% (wt)), the maximum growth rate to obtain a single crystal increases from 1 μm/s to 1.5 μm/s. The maximum growth rate to obtain cellular growth increases from 1.5 μm/s to 3 μm/s. According to the growth model by Cima et al.[9], the maximum growth rate to obtain continuous growth of 123 crystals was

\[ R_{\text{max}} = \frac{D_L}{l(C_{211} - C_{LP})} \left[ \frac{(\Delta T_s)_{\text{max}} + G l}{m_{LY}} \right] \]  

(4.1)

where \( D_L \) is the yttrium diffusivity in the melt, \( C_{211} \) is the yttrium concentration in 123, \( C_{LP} \) is the yttrium concentration in the liquid at peritectic temperature, \( (\Delta T_s)_{\text{max}} \) is the maximum undercooling in the semi-solid melt, \( G \) is the thermal gradient, \( l \) is the 211 particle spacing and \( m_{LY} \) is the slope of the liquidus. As discussed by Cima et al.[9], since \( l \) is of the order of the particle dimension, equation (4.1) indicates that the maximum growth rate is insensitive to the
temperature gradient and increases with the decrease of the 211 particle spacing. Therefore, the experimental results in figure 4.12 are in agreement with the growth model\textsuperscript{9} at low excess 211 content. At high 211 content, however, the maximum growth rate to obtain 123 single crystal decreases. Chapter 6 will discuss the growth mechanism of 123 phase in samples with high excess 211 content.

\section*{§4.5.2 Dendrite Growth for Samples with Stoichiometric 123}

When the growth rate exceeds the maximum growth rate, \( R_{\text{max}} \), plane front single crystal growth breaks down and cellular/dendritic growth occurs. However, only samples with stoichiometric 123 had cellular/dendritic growth in which the secondary arms were distinguishable. Figure 4.13 shows schematically primary and secondary dendrite arms based on figure 4.3 and 4.4. It can be seen that quenched copper rich liquid phase was trapped in the solidified 123 phase and distributed parallel to the solidification interface. 211 particles existed in the solidified 123 phase even though the initial composition was stoichiometric 123. More 211 particles were found along the growth path of the dendrite tip.

EDAX composition measurements were performed in the semi-solid melt ahead of the growth interface of the sample shown in figure 4.3. Figure 4.14 shows both the location and the results of the measurements. EDAX measured an area approximately 30×25 \( \mu \text{m}^2 \) at each measurements. Therefore, the composition shown in figure 4.14 is an average composition of 211 particles and quenched liquid phase. Since the volume fraction of 211 particles was approximately constant in each measurement, the average composition difference in figure 4.14 reflects the composition difference in the quenched liquid. It can be seen that the copper concentration near the dendrite root in the semi-solid melt was higher than that near the dendrite tip. Since YBCO is a ternary system as to be discussed in Chapter 7, the growth of 123 phase involves both the diffusion of yttrium from 211 particles to the 123 growth interface and the diffusion of copper from the 123 growth interface to the semi-solid melt, as shown in figure 4.16. The liquid ahead of the growth interface is copper rich but yttrium poor. In the liquid near the
dendrite root, dendritic microsegregation results in accumulation of rejected copper, as shown in
figure 4.15(a), as expected from the ternary phase diagram (figure 4.17), in which the
equilibrium peritectic reaction temperature decreases with the increase of copper concentration.

After passing over the copper rich region ahead of the dendrite root, the growth interface
was able to grow in both directions: along the primary direction and along the interface direction,
as shown in figure 4.15(c) schematically and figure 4.4 experimentally, with copper rich liquid
trapped between dendrite arms. With the advance of the growth interface along the primary
dendrite direction, the growth pattern from figure 4.15(a) to figure 4.15(d) was repeated until the
end of the solidification.

Since the liquid at the dendrite tip is yttrium rich, the growth of the dendrite tip does not
consume as much of the yttrium particles as in other area of the growth interface. Therefore,
more un-dissolved 211 particles are trapped after solidification along the growth path of the
dendrite tip, as observed in figure 4.4 and schematically shown in figure 4.13.

§4.6 Summary

Different growth rates have been applied to BYC samples with different amounts of
excess 211. It was found that the maximum growth rate to obtain single crystal growth was 1.5
µm/s for samples with 20% (wt) excess 211. Dendritic growth with distinguishable secondary
arms occurred for samples with stoichiometric 123 samples. A qualitative dendrite growth model
was developed to interpret the experimental observations.

§4.7 Reference

current and microstructure of uniaxially aligned, polycrystalline YBa$_2$Cu$_3$O$_{7-δ}$", J. Mater.


Figure 4.1 The solidification interfaces and microstructures of samples with stoichiometric 123 at a growth rate of (a) top: 2 mm/s and (b) bottom: 10 μm/s. It can be seen that the solidified microstructures were equiaxed grains.
Figure 4.2 The solidification interface and solidified microstructures of a sample with stoichiometric 123 at a growth rate of 1.75 μm/s. It can be seen that solidified microstructures were long grains parallel to the growth direction.
Figure 4.3 The solidification interface and microstructure of a sample with stoichiometric 123 at a growth rate of 1.5 μm/s. It can be seen that it is dendrite growth.
Figure 4.4 High magnification picture of the dendritic growth. It can be seen that the trapped liquid phases were parallel to the growth interface. The secondary arm marked "A" just started to grow along the growth interface of the primary arm. More 211 particles were trapped along the growth path of the dendrite tip after solidification.
Figure 4.5 Solidification interface and solidified microstructures of a stoichiometric 123 sample at a growth rate of 1 μm/s. It can be seen that it was a single crystal.
Figure 4.6 The solidification interface of a sample with 10% (wt) excess 211 at a growth rate of 1 μm/s. It can be seen that the interface was faceted.
Figure 4.7 The solidification interface and microstructure of a sample with 10% (wt) 211 at a growth rate of 3 μm/s. It can be seen that textured microstructures were obtained.

Figure 4.8 The solidification interface of a sample with 10% (wt) excess 211 at a growth rate of 10 μm/s. It can be seen that the solidified microstructure was equiaxed.
Figure 4.9  The solidification interface of a sample with 20% (wt) 211 at a growth rate of 1.5 μm/s. It can be seen that it was a single crystal.

Figure 4.10  The solidification interface and microstructure of a sample with 20% (wt) 211 at a growth rate of 10 μm/s. It can be seen that the solidified microstructure was equiaxed.
Figure 4.11  The solidification interface of a sample with 40% (wt) 211 at a growth rate of 1 μm/s. It can be seen that the solidification interface was not flat and 211 particles in the melt were aggregated.
211 volume fraction in the semi-solid melt

- **Single crystal growth**
- **Cellular/Dendrite growth**
- **Equiaxed blocky**

I Equiaxed blocky

O Maximum growth rate to get single crystal by Izumi et al. [10]. Thermal gradient = 180 °C/cm. Tmax = 1040 °C.

The weight % of excess 211

Figure 4.12 The effect of growth rate and the amount of excess 211 on the morphology of the solidification interface.
More 211 particles were trapped along the growth path of the dendrite tip.

Trapped copper rich liquid phases

Copper rich liquid phases were also existed between the grain boundary.

Solidified 123 phase

Figure 4.13 Schematic illustration of the primary and secondary dendrite arms based on figure 4.3 and figure 4.4.
Figure 4.14 (a) CuO concentration in the semi-solid melt. It can be seen that copper concentrations at the dendrite root (A, D and E) are higher than that at the dendrite tip (B and C). (b) Illustration of the positions where the EDAX measurements were made. Curve shows anticipated for based on data and structure, with low concentrations at dendrite tips.
Stoichiometric 123 samples have a 211 devoid region ahead of the growth interface. Composition measurement found that the copper concentration in the liquid at the dendrite root (marked "A") is much higher than that at the dendrite tip (marked "B").

After passing over the copper rich region ahead of the dendrite root, the dendrite tip will grow both directions: along the sample axis and parallel to the growth interface. Therefore, a pocket of copper rich liquid was trapped inside the 123 dendrite.

After growing a certain distance, copper rich region ahead of the dendrite tip will occur again. The formation of the dendrite growth will repeat until the end of the solidification.

Figure 4.15 The dendrite growth model for samples with stoichiometric 123
Figure 4.16 Solute distributions (yttrium and copper) in the semi-solid melt. It can be seen that yttrium diffuses from 211 particles to the 123 growth interface and copper diffuses from the 123 growth interface to the semi-solid melt. The liquid ahead of the 123 growth interface is copper rich but yttrium poor.
Figure 4.17 Ternary phase diagram. It can be seen that with the increase of copper concentration in the liquidus line from m1 to p2, the liquidus temperature on this line decreases from 1020 °C to 970°C.
Chapter 5
Effect of Excess $Y_2BaCuO_5$ on the Microscopic Solidification Interface Morphology of Single Crystal $YBa_2Cu_3O_{6+\delta}$

§5.1 Abstract

A new quench technique was used for detailed microstructural examination of quenched $YBa_2Cu_3O_{6+\delta}$/liquid interfaces. The examination revealed that the amount of excess $Y_2BaCuO_5$ (211) had a strong influence on the microscopic growth morphology of single crystal $YBa_2Cu_3O_{6+\delta}$ (123) interface. The microscopic 123 growth interface was flat at high excess 211 content, but not flat at low excess 211 content. A highly curved 123 envelope was formed on 211 particles located at the 123 growth interface at zero excess 211 content (stoichiometric 123 samples). Based on detailed microscopic growth interface examination, the relation between peritectic reaction and the engulfment of 211 particles into 123 matrix is discussed. It is found that the formation of a small highly curved 123 envelope on 211 particles for stoichiometric 123 samples was due to the large 211 particle spacing, making the interface temperature lower.

§5.2 Introduction

The growth mechanism of the 123 superconductor from a semi-solid melt (211 plus liquid) via the peritectic reaction has been the subject of many recent studies [1,2,3,4,5,6]. Interest in understanding this growth mechanism is largely with the aim improving the superconducting...
properties and facilitating the manufacturing process. The peritectic reaction which occurs at the 123 solidification interface can be described approximately by the following reaction\(^7\)

\[
\text{BaY}_2\text{CuO}_5(s) + [3\text{BaCuO}_2 + 2\text{CuO}](l) = 2\text{Ba}_2\text{YCu}_3\text{O}_{6.5}(s)
\]  

(5.1)

Based on experimental observation, it has been concluded that the growth of 123 proceeds primarily by a liquid diffusion mechanism \(^7,8\). Yttrium diffuses from the dissolving 211/liquid interface to the 123/liquid growth front through the liquid and copper diffuses in the opposite direction. The driving force for the diffusion is provided by the concentration gradient due to growth interface undercooling\(^7\) and 211 particle curvature \(^8,9\). Neglecting curvature and taking yttrium diffusion as controlling process\(^7\) and assuming a pseudo-binary phase diagram, the temperature depression at the growth interface was obtained as

\[
\Delta T_P = \frac{R}{{D_L}}\left[ {C_{sy} - C_{LP} - \frac{G}{m_{Ly}} \frac{m_{Ly}}{m_{L\alpha}} \frac{m_{L\alpha}}{m_{Ly}}} \right]
\]  

(5.2)

where \(D_L\) is the yttrium diffusion coefficient, \(G\) is the temperature gradient at the liquid/123 interface, \(l\) is the half 211 particle spacing, \(m_{Ly}\) and \(m_{L\alpha}\) are the slopes of the equilibrium 123 and 211 liquidus, respectively. \(R\) is the growth rate, \(C_{sy}\) is the yttrium concentration in 123 and \(C_{LP}\) is the peritectic liquid composition. The model shows, in agreement with experiment, that growth rate of the low temperature solid phase (123) has a strong effect on the ability to obtain a desirable faceted plane front, and interface temperature depression is proportional to the 211 particle spacing. Recently, Schmitz et al.\(^9\) proposed a solidification model of 123 taking into account the engulfment process of the 211 particles into the solidifying 123 interface. This model proposes that as the growth front approaches the 211 particles, the yttrium diffusion mechanism is followed sequentially by 123 bridge formation, a classical peritectic reaction and peritectic transformation.

Chapter 4 reported the effect of growth rate on the growth morphology and microstructure. It was found that a single crystal could be obtained for all samples with different amounts of excess
211 (0%, 10%, 20% and 40%) solidified at a growth rate below 1μm/s. This Chapter reports the effect of the amount of excess 211 on the microscopic interface morphologies in the single crystal growth regime (1 μm/s), using an improved quench technique. It will be shown that the amount of excess 211 has a strong influence on the growth interface morphology of 123 single crystals. Based on these experimental observations, the relation between the peritectic reaction and the engulfing process of 211 particles into 123 matrix will be discussed.

§5.3 Experiment

Details of the electrically heated resistance furnace used to directionally solidify samples can be found elsewhere[7]. Briefly, two conventional electrical heating elements with length of 5 cm and inside diameter 1.5 cm were arranged end-to-end and insulated. Located between the upper and lower heating elements were a smaller local heater used to control the shape of the temperature profile. The local heater was made by a coiled electric resistance wire which is commercially available (Kanthal®). A heating element with the same inside diameter (1.5 cm) and longer length (20 cm) was placed below those two heating elements and one local heater to prevent heat convection. The maximum temperature was controlled to be between 1030°C at low growth rates (0.25 μm/s) and 1050 °C at high growth rates (1.5 μm/s or above). The corresponding thermal gradients in the freezing range were 90 °C and 120°C/cm, respectively.

Pre-sintered BYCO fibers were prepared from commercially available 123 and 211 powers (SSC, Inc.) by pressing through a die and followed by vacuum drying at 120°C for 20 hours. The dried samples were then sintered at 975 °C for 20 hours. The final diameter was about 200 - 250 μm and they were normally 15 cm long. In making a run, the sample was glued to a ceramic tube with inside diameter about 1000 μm by Ceramabond (#569, Aremco Products, Inc.). The ceramic tube was then placed on a sample holder. The sample holder was then fixed to the motion device which was commercially available (Aerotech®). The sample was lowered into the furnace until the
joint between sample and the ceramic tube was about 1 cm above the hot zone. The sample was then pulled up through the hot zone at a rate from 0.025 to 10 μm/s for directional solidification.

The microscopic solidification interface morphology of 123 has been reported by many investigators using quench techniques involving water or oil quenching. Since the liquid in the semi-solid melt has a very good fluidity and easily reacts with water, the solidification interfaces were eroded during quenching. Thus the microstructures of the 123 solidification interface which have been reported so far have lacked clearness, making it difficult to obtain details such as the engulfment process of 211 into the 123 matrix. In our experiments, since the sintered samples had a diameter of about 200 - 250 μm, the solidification interface could be rapidly quenched by simply pulling the sample from the furnace and allowing it to cool in air. Since this quench process did not involve any water or oil, the solidification interface was kept intact.

The quenched solidification interfaces were carefully polished by diamond paste, requiring about 2 - 3 hours for each sample. The microstructures were examined by optical microscopy, SEM and microprobe.

§5.4 Experimental Results

§5.4.1 Effect of the Amount of Excess 211 on the Microscopic Solidification Morphology of Single Crystal 123

Chapter 4 showed that single crystals could be obtained for all samples with different amounts of excess 211 (0%, 10%, 20% and 40%) at a growth rate of at least 1 μm/s. Figure 5.1(a) shows the optical microscopic picture of the solidification interface of a sample with 20%(wt) excess 211 at a growth rate of 1 μm/s. The region on the left is single crystal 123 with small 211 inclusions. The 211 particles represent un-reacted material within the 123 crystal. The right portion consists of quenched semi-solid material. This region comprises a high concentration of 211 particles in the quenched liquid matrix. It can be seen that a 211 depleted layer existed ahead of the
growth interface and the growth interface is flat, without apparent curvature on the scale of the 211 particle size or above.

Figure 5.1(b) is a high magnification picture of the solidification interface of the same sample. It can be seen that a large 211 particle was lying across and perpendicular to the solidification interface between quenched liquid and solidified 123 phase. The rectangular angle between the 211 particle and 123 interface indicates that no visible 123 "envelope" was formed at the triple area of the 211 particle, quenched liquid and 123 growth interface.

Figure 5.2 shows the solidification interface of a sample with 10% excess 211, solidified at a growth rate of 1 µm/s. Again the region on the left is single crystal 123 with small 211 inclusions and the region on the right is quenched semi-solid material. It can be seen that a 211 depleted layer exists ahead of the growth interface. In contrast to the sample with 20%(wt) 211, the interface of this sample is seen not to be perfectly flat on the scale of 211 particle sizes. Instead, the interface trends to lags in the region where 211 particles are depleted.

Figure 5.3 shows the solidification interface of a stoichiometric 123 sample (0% excess 211). Figure 5.4 and 5.5 are high magnification pictures of the solidification interface in two different areas of the same sample. Close examination of figure 5.4 and 5.5 reveals that a 211 depleted layer exists ahead of the growth interface and the growth interface is not flat. Similar to samples with 10%(wt) excess 211, the growth interface lags in regions depleted in 211 particles.

It can be seen from figure 5.5 that there was a large particle lying across the solidification interface between quenched liquid and solidified 123 phase. Microprobe measurements confirmed that this particle was 211. Close examination of figure 5.3 and 5.5 shows that a small 123 "envelope" is formed on this 211 particle at the triple area of the 211 particle, quenched liquid and 123 growth interface. This small 123 envelope has a highly curved shape. Such highly curved 123 envelopes were observed in all samples with stoichiometric 123 at a growth rate of 1 µm/s, but not in samples with 10% and 20% excess 211 at same growth rate.

At much higher excess 211 content, the growth interface of 123 was also not flat. Figure 6 shows the interface of a sample with 40% excess 211. At 40% (wt) excess 211, the volume
fraction of 211 in the semi-solid melt is about 55%. As can be seen from figure 5.6, the growth interface was not as flat as in samples with 20% excess 211 and 211 depleted layer cannot be seen ahead of the growth interface. Close examination of those pictures revealed that the 123 growth interface was a relatively rough, with a curved 123 interface between 211 particles. Figure 5.7 summarizes the solidification interface morphologies of samples with different amounts of excess 211 at a growth rate of 1 μm/s:

1. The solidification interfaces were apparently flat for samples with 20% (wt) excess 211; but not flat for samples with 0% (wt), 10% (wt) and 40% (wt) excess 211.
2. 211 depleted layers can be seen in samples with 0% (wt), 10% (wt) and 20% (wt) excess 211; but not in samples with 40% (wt) excess 211.
3. In stoichiometric 123 samples, the 211 depleted layer was relatively large. However, if there was a 211 particle lying across the solidification interface, a small 123 "envelope" was always formed at the triple area of the 211 particle, quenched liquid and 123 growth interface. On the contrary, 211 particles lying across the solidification interface in samples with 10% (wt) and 20% (wt) excess 211 did not form visible 123 "envelope".

§5.4.2 Effect of the 211 Particle Orientation on the Microscopic Solidification Interface Morphology of 123

It has been found that the geometric orientation of 211 particles influences the solidification interface morphology of single crystal 123. Figure 5.8 is part of the 123 growth interface of a sample with 10% excess 211 at a growth rate of 1 μm/s. Figure 5.9 schematically shows the 123 growth interface in figure 5.8. It can be seen that a small region in the 123 growth interface which saw a 211 particle (marked B) parallel to the growth interface grown slower than other area. Even though the 211 particle was very close to the 123 growth interface, locally this part of the interface grown slower. This kind of phenomena can be seen very often in all samples at different growth rate. The 211 particle marked A in figure 5.8 and 5.9 was also parallel to the growth interface but
perpendicular to the picture. It can be seen that this 211 particle also decreased the interface growth rate locally.

§5.5 Discussion

§5.5.1 Peritectic Reaction and Peritectic Transformation

In order to understand the experimental results, a peritectic transformation process near the growth interface for directional solidification is considered, assuming a "pseudo-binary" peritectic reaction. Figure 5.10 shows the situation near the solid/liquid interface where the peritectic transformation occurs. As can be seen in figure 5.10, the high temperature phase (211) exists ahead of the solid/liquid interface where the temperature is higher than the peritectic reaction temperature. The peritectic reaction can take place by diffusion of solute from the 211 (α) phase to 123 (γ) phase by one or more of the paths p1, p2, p3, and p4:

(a) Path p1 is through the liquid to the planar interface.
(b) Path p2 is through the liquid to curved (protruding) section of the γ interface adjacent to the α phase.
(c) Path p3 is by diffusion through the protruding section of the γ, and/or along the grain boundary between α and γ. This path results in size diminishment of α particle in the solid state.
(d) Surface diffusion along path p4 between the liquid and γ phase. Path p4 is neglected in the discussion, assuming that surface diffusion is small compared with that through the bulk liquid.

The mechanism of path p3 is mainly observed in metal systems, where the peritectic transformation takes place by "surrounding" and subsequent solid diffusion. Taking p3 as the
transport path, St. John et al.\textsuperscript{[11,12]} obtained that the thickening rate of the \(\gamma\) phase envelop by solid diffusion from \(\alpha\) to \(\gamma\) is:

\[
\frac{d(\Delta x)}{dt} = \left( D \frac{(C_\alpha - C_L)(C_{\gamma 2} - C_{\gamma 1})}{(C_\gamma - C_L)(C_\alpha - C_\gamma)} \right)^{1/2} \sqrt{ \frac{2t}{c} } \tag{5.3}
\]

where \(\Delta x\) is the thickness of the \(\gamma\) phase envelop, \(t\) is the time, \(D\) is the diffusivity of the solute, \(C_\alpha\) is the solute concentration in the \(\alpha\) phase, \(C_L\) is the solute concentration in the liquid, \(C_\gamma\) is the average solute concentration in \(\gamma\) phase, \(C_{\gamma 2}\) and \(C_{\gamma 1}\) is the solute concentrations at the \(\alpha/\gamma\) and \(\gamma/\text{Liquid}\) interfaces respectively. In the Y-B-C-O system, since 123 are line compound, \(C_{\gamma 2}\) is very close to \(C_{\gamma 1}\). Thus, the thickening rate of \(\gamma\) phase by the solid diffusion mechanism should be very slow according to equation (5.3) and we may expect the peritectic transformation to occur mainly by liquid diffusion.

§5.5.2 Effect of 211 Particles on the Microscopic Solidification Interface Morphology of 123 Single Crystal before Engulfment

At the beginning of the engulfment, the 123 growth interface does not contact the 211 particle. The growth of the 123 interface is accomplished by the diffusion path p1: solute diffusion from 211 particles to the growth front through liquid. For samples with small amount of excess 211, as in samples with stoichiometric 123 and samples with 10\%(wt) 211, the solute concentration gradient in front of the solidification interface is not uniform. Figure 5.11(a) shows schematically the iso-concentration line ahead of the solidification interface. The concentration gradient is perpendicular to those iso-concentration lines and larger where the iso-concentration lines are denser. Therefore, the solute concentration gradient ahead of the interface which was close to the 211 particles is higher than that which was not close to the 211 particles. This means that certain areas of the solidification interface trend to lag behind others, in spite of the strong faceting tendency, as observed in figure 5.2 and figure 5.3. For samples with large amounts of...
excess 211 (as in samples with 20% excess 211), the 211 particle spacing is smaller and so the solute concentration gradient is more uniform and the interface are flatter. Figure 5.11(b) shows the iso-concentration lines ahead of the solidification interface of higher excess 211 samples. A flat faceted solidification interface is obtained, as observed in figure 5.1.

When the 123 solidification interface approaches a 211 particle, the local growth rate of the interface increase since the solute concentration gradient increases. However, when the interface is very close to the 211 particles, the growth rate of the interface will not always increase as suggested by Schmitz\textsuperscript{[9]} to form a 123 bridge between the 211 particles and 123 growth interface. On the contrary, the growth rate of the interface decreases as it approaches a 211 particle which presents a large face to the growth front, as shown in figure 5.8 and schematically in figure 5.9. This observation can be explained by the lengthened diffusion path required for solute transport through the liquid to the region under the particle. Slowing of the interface such as this can be expected when the diffusion distance under the large particle (approximately one-half of the 211 diameter) is larger than the regime average diffusion distance (approximately one half the 211 particle spacing). Details will be discussed in Chapter 6.4.3.

§5.5.3 Effect of Excess 211 Particles on the Microscopic Solidification Interface Morphology of 123 Single Crystals during the Engulfment

When the 123 growth interface contacts a 211 particle, peritectic reaction occurs at the triple point of liquid, α and γ phases, as shown in figure 5.10. As the result, a small 123 layer is formed on 211 particles at the triple area. After a small 123 layer is formed by peritectic reaction, its growth is realized by the diffusion path p2: solute diffusion through liquid from the 211/liquid interface to the front of the 123 layer, as discussed above.

When solidification interfaces grow at a same growth rate, the interface temperature for the stoichiometric 123 sample was lower than that for the sample with excess 211 according to equation (5.2) and the interface temperature measurement in Chapter 6, since stoichiometric 123 samples have large 211 particle spacing. On the other hand, since the peritectic reaction is a kinetics
process, the reaction rate very strongly depends on the interface temperature. Therefore, the formation of the small 123 layers on the 211 particles for stoichiometric 123 samples was faster than that for samples with excess 211. As the result, a small 123 "envelope" can be seen in stoichiometric 123 sample, but not in samples with excess 211.

When the 211 particle spacing was very small, as in samples with 40% (wt) excess 211, the growth interface of 123 was not flat either. This observation can also be explained by the lengthened diffusion path required for cooper transport through the liquid away from the 123 growth interface. The lengthened copper diffusion distance slows the growth of 123 interface and makes 123 interface temperature lower than that for stoichiometric 123 samples at a same growth rate. Details will be discussed in Chapter 6.4.3.

§5.6 Summary

A new quench technique has been used to produce detailed quenched solid/liquid interface. These detailed 123 and liquid interface revealed that the effect of excess 211 particles on the microscopic solidification morphology of 123 single crystal:

(a) When the amount of excess 211 contents was high, the 123 growth interface was flat due to the small 211 particle spacing, making the solute concentration gradient ahead of the growth interface relatively uniform.

(b) When the amount of excess 211 is zero (stoichiometric 123), the 123 growth interface is not flat and a small 123 envelope was visible on 211 particles at the 123 growth interface due to the large 211 particle spacing, making the interface temperature lower at a given growth rate and therefore increasing the peritectic reaction rate.

(c) The geometric orientation of 211 particles had a strong influence on the growth morphology of 123. 211 particles parallel to the growth interface decrease the growth rate of the 123 interface due to the lengthened solute diffusion path.
When the amount of excess 211 was very high, the 123 growth interface is not flat either also due to the lengthened solute diffusion path.

§5.7 Reference


Figure 5.1(a) Solidification interface morphology of a sample with 20% (wt) excess 211 at a growth rate of 1 μm/s. It can be seen that the solidification interface was flat.
Figure 5.1(b) A high magnification picture of the solidification interface in figure 1(a). It can be seen that a large 211 particle was lying across and perpendicular to the solidification interface between the quenched liquid and solidified 123 phase. The rectangular angle between the 211 particle and 123 interface indicates that no 123 "envelope" was formed at the triple area of the 211 particle, quenched liquid and 123 growth interface. It has to be noticed that the gray area near the large 211 particle at the growth interface was not 123 phase but liquid phase, which can be easily distinguished in the optical microscope but not be seen easily in the picture.
Figure 5.2 Solidification interface morphology of a sample with 10\% (wt) excess 211 at a growth rate of 1 \( \mu \text{m/s} \). It can be seen that the solidification interface was not flat but curved.
Figure 5.3 Solidification interface morphology of a sample with 0\%(wt) excess 211 at a growth rate of 1 \(\mu\text{m/s}\) (stoichiometric 123). It can be seen that there were small 123 envelopes on the 211 particles located at the solidification interface. Those small 123 envelopes had highly curved shape.
Figure 5.4 High magnification SEM picture of the solidification interface of the sample in figure 5.3. On the left is the solidified 123 and on the right is liquid plus 211 particles. It can be seen clearly that the solidification interface was not flat and part of the interface which was close to 211 particles grown faster than other part of the interface which had no 211 particles in its vicinity.
Figure 5.5 High magnification SEM picture of the solidification interface of the sample in figure 5.3. On the left is the solidified 123 and on the right is liquid plus 211 particles. It can be seen that a big 211 particles was located in both sides of the solidification interface. Close examination of this picture and figure 5.3 shows that there was a small 123 envelope on this 211 particles at the solidification interface.
Figure 5.6 Solidification interface morphology of a sample with 40% (wt) excess 211 at a growth rate of 1 μm/s. On the left is the solidified 123 matrix plus 211 particles. On the right is liquid plus 211 particles. It can be seen that the solidification interface was not flat. (a) Top: Optical microscopic picture. (b) Bottom: SEM picture.
<table>
<thead>
<tr>
<th></th>
<th>0% (wt) excess 211</th>
<th>10% (wt) excess 211</th>
<th>20% (wt) excess 211</th>
<th>40% (wt) excess 211</th>
</tr>
</thead>
<tbody>
<tr>
<td>Growth interface</td>
<td>Not flat</td>
<td>Not flat</td>
<td>Flat</td>
<td>Not flat</td>
</tr>
<tr>
<td>211 depleted zone</td>
<td>Visible</td>
<td>Visible</td>
<td>Visible</td>
<td>Not visible</td>
</tr>
<tr>
<td>123 envelope on 211 particles at the growth interface</td>
<td>Visible</td>
<td>Not visible</td>
<td>Not visible</td>
<td>Not visible</td>
</tr>
<tr>
<td>Typical solidification interface morphology</td>
<td><img src="image.png" alt="Diagram" /></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 5.7 The relation between the microscopic solidification interface morphology and the amount of excess 211.
Figure 5.8 The growth interface of a sample with 10\% (wt) excess 211 at a growth rate of 1 \mu m/s. On the top is quenched liquid plus 211 particles and on the bottom is solidified 123 single crystal with 211 inclusions. It can be seen that the 211 particles marked "A" acted as an obstacle to the growth of the 123 interface. It can also be seen that the 123 growth interface which saw a 211 particle (marked "B") parallel to the growth interface grown slower than other part of the interface. Even though this 211 particles was very close to the 123 interface, locally this part of the interface grown slower because it is difficult for the copper to diffuse away from the 123 interface through a small channel between the 123 interface and the 211 particle.
Figure 5.9 Schematic illustration of figure 5.8.
Figure 5.10 Peritectic reaction and transformation at the solidification interface. At temperature $T$, the $\gamma$ phase envelope is formed on $\alpha$ phase particles. The thickening of the $\gamma$ phase envelope and the growth of the liquid/g interface are accomplished by solute diffusion through four paths: $p_1$ is through the liquid to the planar interface; $p_2$ is through the liquid to the curved (protruding) section of $\gamma$ phase adjacent to $\alpha$ phase; $p_3$ is by diffusion through the protruding section of the $\gamma$, and/or along the grain boundary between $\alpha$ and $\gamma$. Only this path among the four paths results in size diminishment of the $\alpha$ particle in solid state; surface diffusion along the path 4 between the liquid and $\gamma$ phase. This path is neglected in the discussion, assuming that transport by this path is small compared with that through the bulk liquid.
Figure 5.11 Iso-concentration lines ahead of the 123 growth interface. (a) top: samples with less excess 211 have different concentration gradient ahead of the growth interface. (b) bottom: samples with more excess 211 have approximately the same concentration gradient ahead of the grown interface.
Chapter 6
Solidification Interface Temperature
of YBa$_2$Cu$_3$O$_{6+\delta}$ Single Crystal

§6.1 Abstract

Solidification interface temperatures of YBa$_2$Cu$_3$O$_{7-\delta}$ (123) single crystals were measured for samples with different amounts of excess Y$_2$BaCuO$_5$ (211) phase solidified at different growth rates. The experimental results show that the solidification interface temperature depression $\Delta T_P$ increases with increasing growth rate for samples with a given amount of excess 211. At a given growth rate, however, $\Delta T_P$ initially decreases and then increases with increasing the amount of excess 211. Using the peritectic solidification model, it is concluded that the initial decrease of $\Delta T_P$ with increasing the amount of excess 211 is due to the decrease of the 211 particle spacing, and the increase of $\Delta T_P$ at high excess 211 is due to the lengthened diffusion path required for solute transport.

§6.2 Introduction

Enhancement of the critical current density $J_c$ for ceramic superconductors has created the possibility of practical usage in industry. Conventionally processed YBa$_2$Cu$_3$O$_{7-\delta}$ shows a low current density due to weak-links related to high angle grain boundaries. Those difficulties may be overcome by processing techniques such as directional solidification [1, 2]. In order to obtain optimum microstructures, it is necessary to understand how processing affects the microstructure and hence the superconductivity. One issue of great importance is the growth
interface temperature of the 123 phase, since this is a key to understanding the growth mechanism.

Despite the numerous experimental studies reported on the growth mechanism of 123 phase\cite{3,4,5}, little conclusive information is available regarding the interface temperature of 123 phase during growth from semi-solid melt. Intrinsic experimental difficulties in studying this YBCO system are its opacity (which prevents from direct determination of the interface morphology and location), its high melting temperature and its reaction with other elements.

Several methods of direct and indirect measurement of the solid/liquid interface temperature have been used in the past for metal system\cite{6}. The indirect method of obtaining the interface temperature depends on mathematical analysis of heat-flow at the solid/liquid interface. A few heat transfer models have been developed for unconstrained growth into a supercooled melt to relate the interface temperature to the bulk liquid temperature\cite{7}. However, the result of this method depends on the accuracy of the physical property data, which are not available for this YBCO system. The most commonly used direct technique consists of embedding a thermocouple probe into the crystal or the melt. However, this kind of direct measurement is impossible since the YBCO melt reacts with any known thermocouple bead. Therefore, the following experimental technique was used in this study to measure the solidification interface temperature of 123 single crystal.

§6.3 Experiment

Figure 6.1 shows the both the sample and the furnace employed. Details of the furnace can be found in Chapter 3. The sample was glued to a ceramic tube with inside diameter about 1000 \( \mu \)m using Ceramabond (#569, Aremco Products, Inc.). The ceramic tube was then placed on the sample holder. The sample holder was attached on the motion system. When the sample holder moved upward, the solidification interface grows downward. At steady state, the growth rate of the solidification interface was equal to the pulling rate of the sample holder. After having
moved for a pre-determined distance, the sample holder stopped moving and the sample was taken out of the furnace very quickly. A thermocouple with very small diameter was then placed on the sample holder (figure 6.1(b)). The diameter of the thermocouple shield (Ω Company®) is same as the sample diameter (250 μm). Temperature versus distance inside the furnace was measured by moving down the thermocouple (figure 6.1(c)). Knowing the distance L1, L2 and L3 as shown in figure 6.1, the temperature of the solidification interface was determined from the relation of temperature versus distance.

In order to check the disturbances to the temperature field caused by moving the sample out of the furnace and putting the thermocouple into the furnace, the tiny thermocouple was kept inside this furnace for about 1 hours and then measured the temperature field. After that, the thermocouple was taken out of the furnace and kept in air for about 1 minute. Then the thermocouple was put back inside the furnace and measured the temperature field again. It was found that the temperature profiles obtained from those two measurement were identical. Therefore, it was concluded that the disturbances to the temperature field caused by moving the sample out of the furnace and putting the thermocouple into the furnace were negligible since the diameters of both the sample and the thermocouple were only about 250 μm.

Since the measured temperature at a given position was the average temperature of the thermocouple bead, an error was introduced to each measured temperature. The amount of error in each measurement was estimated by the thermal gradient. Since the diameter of the thermocouple bead was about 250 μm and the temperature gradient was about 100 °C/cm, the temperature difference in 250 μm is about 2.5 °C. Therefore, the measured temperature at a given point was assumed to have plus and minus error of 1.5 °C.

Bi-fiber (or bi-sample) growth was also used to investigate the effect of excess 211 content on the growth interface kinetics. Green samples with different amounts of excess 211 were made by conventional sintering similar to the method reported in Chapter 3. However, the sintering time was less than the time used to sinter high density samples. After the first sintering stage, those green samples were taken out of the furnace. Two samples with different amounts of
excess 211 were put together and put back into the furnace for long time sintering. After the second stage sintering, those two samples with different amount of excess 211 were sintered together and ready for directional solidification. By quenching the solidification interface during directional solidification, both the solidification interface morphology and temperature were obtained. Figure 6.2 shows the sketch of the configuration of the bi-fiber growth inside the furnace. It can be seen that the position of the solidification interface of each fiber indicated the interface temperature at a given temperature field.

§6.4 Experimental Results and Discussion

§6.4.1 Solidification Interface Temperature Measurement

The measured solidification interface temperatures for samples with different amounts of excess 211 and at different growth rates were reported in table 4.1, and are plotted in figure 6.3(a) as solidification interface temperature depression $\Delta T_p$, calculated according to $\Delta T_p = 1000 \degree C - T_{\text{interface}}$, where $T_{\text{interface}}$ is the measured solidification interface temperature. Figure 6.3(a) also plots the solidification interface temperatures measured by Mori et al.[8]. It can be seen that these two sets of data are closely comparable.

It can be seen from figure 6.3(a) that $\Delta T_p$ increased with the increase of the growth rate for all samples. At a given growth rate, however, $\Delta T_p$ was smallest for samples with 20% (wt) excess 211 and largest for samples with 40% (wt) excess 211. At a given $\Delta T_p$, samples with 20% (wt) excess 211 had the highest growth rate and samples with 40% (wt) 211 had the lowest growth rate. Figure 6.3(b) plots the extracted growth rate $R$ from figure 6.3(a) at $\Delta T_p = 17 \degree C$ versus the composition. Also plotted are the measured growth rates versus the composition at $\Delta T_p = 17\degree C$ by Shirohara et al. in a seeded growth experiment (isothermal growth)[10]. It can be seen from both measurements that the growth rates initially increase and then decrease with increasing the 211 weight percent at a given $\Delta T_p$. Further more, they are close to each other despite that one is for thermal gradient growth and the other is for isothermal growth.
According to the solidification model proposed by Cima et al. \cite{9}, the total interface temperature depression $\Delta T_p$ can be expressed as following:

$$
\Delta T_p = \left[ \frac{Rl}{D_L} (C_{S\gamma} - C_{LP}) - \frac{Gl}{m_{L\alpha}} \right] \frac{m_{L\gamma} m_{L\alpha}}{m_{L\alpha} - m_{L\gamma}} 
$$

(6.1)

Where $R$ is the growth rate, $D_L$ is the yttrium diffusivity, $l$ is half of the 211 particle spacing, $C_{S\gamma}$ is the yttrium concentration in $\gamma$ phase, $C_{LP}$ is the yttrium concentration in the liquid at peritectic temperature, $G$ is the temperature gradient, $m_{L\alpha}$ and $m_{L\gamma}$ are the liquidus slopes of $\alpha$ phase and $\gamma$ phase respectively. It can be seen that the effect of thermal gradient on $\Delta T_p$ is the second term in equation (6.1): $(Gl) \times m_{L\gamma}/(m_{L\alpha} - m_{L\gamma})$. Since $(Gl)$ is on the order of $10^{-2} \degree C$ and $m_{L\gamma}/(m_{L\alpha} - m_{L\gamma})$ is less than $10^2$, the effect of thermal gradient on $\Delta T_p$ is very small. Therefore, solidification interface temperature depression $\Delta T_p$ is not a strong function of the growth methods (isothermal growth or thermal gradient growth), as shown in figure 6.3(b).

\section*{§6.4.2 Bi-fiber Growth Experiment}

Figure 6.4 shows the solidification interface of a bi-fiber sample grown at a rate of 1 $\mu m/s$. This bi-fiber sample consisted of one fiber with 20\% (wt) excess 211 and another fiber with 10\% (wt) excess 211. It can be seen that there was a clear boundary in the solidified portion between two fibers (figure 6.3(b)). The solidification interface of the fiber with 20\% (wt) 211 was slightly ahead of the fiber with 10\% (wt) 211. Therefore, its interface temperature was higher. This result was in agreement with the measured result shown in figure 3: the interface temperature increased with the increase of excess 211 at a given growth rate. Since some portion of the fiber with 10\% (wt) excess 211 had the same orientation as the fiber with 20\% (wt) 211, it can be concluded that the fiber with 20\% (wt) was acting as a seed crystal for the other fiber. It can also be noticed that the interface temperature difference in this bi-fiber sample was about 1 $\degree C$, which is smaller than measured result which was about 2 - 4 $\degree C$ shown in figure 6.3(a).
is probably because the combination of solute diffusion between those two fibers and the effect of seed growth.

Figure 6.5 is the bi-fiber growth interface for two fibers with 0%211 and 20%211 respectively at a growth rate of 1 μm/s. It can be seen that the growth morphology is different for each fiber even though they have grown together. For the fiber with 20%211, it was faceted plane front growth; for the stoichiometric 123, it was dendrite growth. It can be seen that the growth interface temperature for the fiber with 20%(wt) 211 was slightly higher than that for the stoichiometric 123 fiber. The difference was about 2°C, based on the temperature gradient of 180 °C/cm. This is less than the measured difference in interface temperature for separately solidified samples of 0% and 20% 211 respectively, which, as can be seen in figure 6.3(a), was about 5 - 8 °C. It can also be seen clearly that the fiber with 20%(wt) excess 211 was acting as a seed crystal for the growth of stoichiometric 123 fiber.

Figure 6.6 is the bi-fiber growth interface for two fibers with 10%(wt) excess 211 and 40%(wt) excess 211, respectively. The growth interface temperature of the fiber with 10%(wt) 211 is much higher than that of the fiber with 40%(wt) excess 211. The difference is about 15 °C, compared with about 20 °C in figure 6.3a for separately solidified samples of 10% and 40% respectively. Even though the fiber with 10%211 was acting as a seed crystal for the fiber with 40%211, the interface of remaining part of the fiber with 40%(wt) excess 211 was still far behind. Figure 6.6 confirms again the experimental measurements shown in figure 6.3 and shows how difficult it is for the interface to grow in the fiber with 40%(wt) excess 211.

§6.4.3 Interface Temperature Depression at Low Excess 211 Content

The relation between the interface temperature depression ΔTp and the amount of excess 211 can be interpreted based on the growth model, equation (6.1), proposed by Cima et al. [9]. According to this model, ΔTp is proportional to \( l \) at a given growth rate. The relationship between \( l \) and 211 volume fraction can be obtained as following.
Figure 6.7(a) shows the peritectic growth model proposed by Cima et al \cite{9}, where $\alpha$ phase represents 211 particles and $\gamma$ phase represents 123 phase and solute diffuses a distance $l$ as $\gamma$ phase grows. Assuming $\alpha$ particles are arranged in closely packed configuration, as shown in figure 6.7 (b), the volume fraction of $\alpha$ phase is:

$$\phi = \frac{4\left(\frac{4}{3} \pi r^3\right)}{a^3} = \frac{16 \pi r^3}{(2l + 2r)^3} = \left(\frac{2}{3}\right)\left(\frac{r}{l + r}\right)^3$$

(6.2)

where $a$ is the distance between $\alpha$ particles, $r$ is the radius of 211 particles. Rearranging equation (6.2) gives:

$$\frac{l}{r} = \left(\frac{2\pi}{3\phi}\right)^{\frac{1}{3}} - 1$$

(6.3)

Where $r$ can be considered as relatively constant for samples with the same amount of excess 211, assuming that particle radius is determined primarily by coarsening.

Table 6.1 shows both calculated 211 particle spacing ($r = 3 \, \mu$m) and interface temperature depression $\Delta T_p$ at $R = 0.5 \, \mu$m/s for samples with different amount of excess 211.

<table>
<thead>
<tr>
<th>211 volume fraction</th>
<th>Half of the 211 particle spacing ((\mu)m)</th>
<th>Calculated $\Delta T_p$ (K) at $R = 0.5 , \mu$m/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>17%</td>
<td>3.9</td>
<td>39</td>
</tr>
<tr>
<td>26%</td>
<td>3.01</td>
<td>30</td>
</tr>
<tr>
<td>35%</td>
<td>2.44</td>
<td>24</td>
</tr>
<tr>
<td>53%</td>
<td>1.74</td>
<td>17</td>
</tr>
</tbody>
</table>

In calculating the interface temperature depression $\Delta T_p$ by equation (6.1), the following data were assumed: $D = 6 \times 10^{-7} \, \text{cm}^2/\text{s}$, $C_{S_f} = 9.6 \times 10^{-3} \, \text{mole/cm}^3$, $C_{L_p} = 1.0 \times 10^{-3} \, \text{mole/cm}^3$, $G = 100$.
K/cm, \( m_{\text{L}_{\alpha}} = 4.5 \times 10^4 \text{ cm}^3/\text{mole} \), \( m_{\text{L}_{\gamma}} = 3.4 \times 10^4 \text{ cm}^3/\text{mole} \). Figure 6.8 plots both measured \( \Delta T_p \) and calculated \( \Delta T_p \) in table 6.1 as a function of 211 volume fraction in the semi-solid melt. It can be seen that both calculated \( \Delta T_p \) and measured \( \Delta T_p \) decrease with increasing 211 volume fraction up to 35% volume fraction of 211. The agreement between calculated \( \Delta T_p \) and measured \( \Delta T_p \) at low 211 volume fraction indicates that the decrease of \( \Delta T_p \) was mainly due to the decrease of 211 particle spacing.

### §6.4.4 Interface Temperature Depression at High Excess 211 Content

When excess 211 is low, \( l \) is the limiting diffusion distance (figure 6.9a) as discussed earlier, and as in the model of Cima et al. \([9]\) and others\([2]\). At high excess 211 content, diffusion distance, \( l \), for solute transports between 211 and 123 continues to decrease. However, solute balance can only be achieved by additional solute transport between the liquid in the vicinity of the interface and the growing 123 interface (notably transport of additional copper from the 123 growing interface to the liquid).

When \( l < r \), the additional solute has to diffuse a distance not less than \( r \), and we may expect it to be considerably greater than \( r \) at high volume fraction of 211, due to particle

Table 6.2 Calculated interface temperature depression (\( \Delta T_p \)) at high excess 211 content

<table>
<thead>
<tr>
<th>211 volume fraction in the semi-solid melt</th>
<th>( l \ (f &lt; r) ) or ( l_{\text{eff}} \ (r &gt; r) ) (( \mu \text{m} ))</th>
<th>Calculated ( \Delta T_p ) (K) at ( R = 0.5 \mu \text{m/s} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>17%</td>
<td>3.9</td>
<td>39</td>
</tr>
<tr>
<td>26%</td>
<td>3.01</td>
<td>30</td>
</tr>
<tr>
<td>35%</td>
<td>3 (( \tau = 1 ))</td>
<td>29</td>
</tr>
<tr>
<td>53%</td>
<td>6 (( \tau = 2 ))</td>
<td>60</td>
</tr>
</tbody>
</table>
agglomeration, as shown in figure 6.10 and schematically in figure 6.9b. Thus, for \( l < r \) (e.g. at volume fraction \( \Phi > 26.4\% \)), the diffusion distance is taken as

\[
\ell_{\text{eff}} = \tau r
\]  

(6.4)

where \( \tau \) is an arbitrary tortuosity factor. Taking \( \tau \) as 2, table 6.2 is the calculated \( \Delta T_p \).

The newly calculated \( \Delta T_p \) is plotted in figure 6.11. It can be seen that \( \Delta T_p \) increases with increasing the amount of excess 211 at high excess 211 content. Therefore, the increase of \( \Delta T_p \) at high excess 211 content is caused by the lengthened copper diffusion path.

§6.5 Summary

Temperature measurements of the growth interface of the superconducting phase 123 were made on samples with different amounts of excess 211 phase and solidified at different growth rates. Both interface temperature measurements and bi-fiber growth experiments showed that the growth interface temperature depression decreased with increasing the amount of excess 211 up to about 20\%(wt) and then increased in samples of 40\% excess 211.

Based on the peritectic reaction model, it is concluded that when the excess 211 content is low, yttrium is the controlling diffusion process and interface temperature is mainly controlled by the 211 particle spacing. When the excess 211 is high, however, copper is the controlling diffusion process and interface temperature is mainly controlled by the 211 particle radius. Because 211 particles at high volume fraction aggregate to each other and make the copper diffusion distance much longer, interface temperature depression increased sharply when the excess 211 increased to 40\%(wt).

§6.6 Reference


Figure 6.1 (a) Configuration of both the sample and the furnace before the sample was taken out of the furnace. (b) Configuration of the thermocouple and the furnace before measuring the temperature versus the distance. (c) The measured relation of temperature versus distance. The temperature of the solidification interface is decided by the distance \((L1 + L2) - L3\).
Figure 6.2 Two fibers with different amount of excess 211 grown together at a constant pulling rate. The growth interface temperature for each fiber was different.
Figure 6.3(a) Interface temperature depression as a function of growth rate for samples with different amount of excess 211. It is assumed in this figure that the interface temperature depression is zero at zero growth rate.
The amount of excess 211 (weight %)

Figure 6.3(b) Growth rate $R$ from figure 6.3(a) at $\Delta T_p = 17^\circ C$ versus composition. Also plotted are the measured growth rates versus the composition at $\Delta T_p = 17^\circ C$ by Shirohara et al. in a seeded growth experiment \cite{10}. It can be seen from both measurements that the growth rate initially increased and then decreased with the increase of the 211 weight percent at a given $\Delta T_p$. 
Figure 6.4 Bi-fiber growth. (a) Top: Two fibers with 10% (wt) excess 211 (right) and 20% (wt) excess 211 (left) grown together. Interface temperature of the fiber with 20% (wt) excess 211 was higher than that with 10% (wt) excess 211. (b) Bottom: Higher magnification of the growth interface and the boundary between those two fibers.
Figure 6.5 Bi-fiber growth. Two fibers with 0% (wt) excess 211 (left) and 20% (wt) excess 211 (right) grown together. It can be seen that some parts of the left fiber grow at the same orientation as the right fiber, indicating that the right fiber grow ahead of the left fiber and acted as a seeding crystal for the left fiber. It can also be seen that the right fiber with 20% (wt) 211 has a faceted plane front but the left fiber with 0% (wt) 211 has a faceted dendrite growth morphology. The growth interface temperature for the fiber with 20% (wt) 211 was higher than that for the fiber with 0% (wt) 211.
Figure 6.6 Bi-fiber growth. Two fibers with 10% (wt) excess 211 (right) and 40% (wt) excess 211 (left) grown together. It can be seen that the growth interface temperature of the fiber with 40% (wt) excess 211 was much higher than that with 40% (wt) excess 211 even though some parts of the left fiber grown with the right fiber as its seeding crystal.
Figure 6.7 (a) Peritectic reaction model. (b) The model to calculate 211 particle spacing, assuming 211 particles are arranged in closely packed configuration.
Figure 6.8 The interface temperature depression $\Delta T_p$ at a growth rate of 0.5 $\mu$m/s for samples with different amount of excess 211. It can be seen that both calculated and measured $\Delta T_p$ decreases with increasing the 211 volume fraction in the semi-solid melt at low 211 content. However, measured $\Delta T_p$ increases at high 211 volume fraction.
Figure 6.9(a) At low 211 volume fraction, \( l \) is much larger than \( r \). Therefore, yttrium diffusion is the controlling process for the growth of 123 interface. Dashed arrows represent copper diffusion away from the 123 interface, non-dashed arrows represent yttrium diffusion from 211 particles to the 123 interface. The controlling diffusion distance is \( l \).

Figure 6.9(b) At high 211 volume fraction, \( l \) is much smaller than \( r \). Therefore, copper diffusion is the controlling process for the growth of 123 interface. The arrows represent copper diffusion. The controlling diffusion distance is \( r \) since 211 particles are aggregated to each other at high volume fraction, the actual diffusion distance is larger than \( r \).
Figure 6.10 (a) The solidification interface and the semi-solid melt for samples with 40% (wt) excess 211. (b) High magnification of (a). It can be seen that 211 particles in the semi-solid melt was aggregated to each other and liquid was separated by those aggregated 211 particles. EDAX composition measurement found that the liquid composition in the area marked "A" was 98% CuO.
Figure 6.11 Calculated interface temperature depression $\Delta T_p$ from table 6.2. It can be seen that both calculated and measured $\Delta T_p$ decrease at low 211 content and increase at high 211 content with increasing 211 volume fraction.
Chapter 7
Solute Distributions in the Semi-Solid Melt during the Growth of YBa$_2$Cu$_3$O$_{6+\delta}$ Single Crystal in the Ternary System of Y-Ba-Cu-O

§7.1 Abstract

Solute distributions in the semi-solid melt and the relation between growth rate and solidification temperature have been obtained for isothermal growth of 123 single crystals in the ternary system of Y-B-Cu-O. This was done by solving the full solute transport problem, both in the boundary layer near the growing crystal, and in the outer semi-solid region. Unlike the binary system, solute concentrations in the semi-solid region are not uniform. The copper concentration decreases and yttrium concentration increases with increasing distance from the 123 growth interface. The 211 volume fraction in the semi-solid melt is approximately constant. Those conclusions agree well with the experimental measurements. The non-uniform solute distributions in the semi-solid region provide a theoretical understanding of the 211 particle segregation phenomena observed in the melt-growth experiments.

§7.2 Introduction

There are two processing methods used to grow 123 single crystal from a semi-solid melt: isothermal growth and growth under a positive thermal gradient. Single crystals are grown at a given constant temperature or a given cooling rate in the isothermal growth method. In this case, the growth rate depends on temperature. In the thermal gradient growth method, constant growth
rates are obtained by moving either the thermal field or the sample at a given constant rate. Temperature at the growth interface depends on growth rate and thermal gradient. For a binary system solidifying at equilibrium at the liquid-solid interface, the liquid concentration at the solid-liquid planar interface is uniquely determined, knowing either the interface temperature or growth rate, since the binary phase diagram gives a unique liquid concentration at a given temperature\(^1\) \(^2\) \(^3\). Consequently, solute distribution outside the boundary layer is uniform. However, in a ternary system, liquid compositions in the semi-solid melt may not be constant even though the liquid composition at the solid-liquid planar interface is uniquely determined by the interface temperature. Liquid compositions in the semi-solid melt can vary along liquidus lines. Determination of the solute distributions and the relationship of the interface temperature, growth rate and liquid composition for the growth of 123 from a ternary melt requires solutions of full solute transport problem, both in the boundary layer near the growing crystal, and in the outer semi-solid region.

This chapter will report the experimental measurement of the solute distributions in the semi-solid melt ahead of the 123 growth interface for isothermal solidification. The theoretical solute distributions and the relationship of the interface temperature, growth rate and the liquid composition at the 123 growth interface are developed and compared with the experimental results.

\section*{7.3 Experiment}

Figure 7.1 is the optical microscopic picture of a sample with 20\% excess 211 isothermally solidified at \(\Delta T = 15 \, ^\circ\text{C}\). The upper region consists of quenched semi-solid melt. This region comprises a high concentration of 211 particles in the quenched liquid matrix. The bottom region is single crystal 123 with small amount of 211 inclusions. EDAX composition measurements were performed in the quenched semi-solid melt ahead of the growth interface. The measured area at each measurement was approximately at \(30 \times 25 \, \mu\text{m}^2\). Therefore, the measured composition was an average composition of 211 particles and quenched liquid phase. Figure 7.2 shows the measured results. It can be seen that the weight percent of CuO in the semi-solid melt decreases
with increasing the distance from the 123 growth interface. Since 211 volume fraction is approximately constant in the semi-solid melt except the boundary layer, as shown in figure 7.3, the decrease of CuO in the semi-solid melt represents the decrease of CuO in the quenched liquid.

The non-uniform solute distributions outside the boundary layer suggest that the solute transport in the semi-solid melt has to be considered in order to obtain the theoretical solute distributions in the semi-solid melt and the relationship among the interface temperature, growth rate and the liquid composition at the 123 growth interface.

§7.4 Theory

Figure 7.4 is a schematic illustration of the solute distributions in the liquid in front of the growing 123 crystals. We assume isothermal growth, and equilibrium at all liquid-solid interfaces so the liquid composition at the 211 interface is given by the metastable extension of the 211 liquidus surface, and liquid composition at the growing interface of the 123 crystal is given by the equilibrium liquid composition between 123, liquid, and 211 on the isothermal section of the ternary phase diagram (point A, B and C in figure 7.5(a) respectively). Assuming the metastable extension of the 211 liquidus surface in the area of interest is planar, as shown in figure 7.5(b), it is determined by an equation of the form:

\[ dT_{L\alpha} = m_{L\alpha}^Y dC_L^Y + m_{L\alpha}^{Cu} dC_L^{Cu} \]  

(7.1)

where \( T_{L\alpha} \) represents the liquidus surfaces of 211, \( C_L^Y \) and \( C_L^{Cu} \) represent yttrium and copper concentrations in the liquid respectively, \( m_{L\alpha}^Y \) and \( m_{L\alpha}^{Cu} \) represent the slopes of the 211 liquidus surface with respect to yttrium and copper respectively:
As in the previous model [1] for 123 solidification from a binary melt, we assume a narrow region of thickness \( l \) (figure 7.4), region I or boundary layer, adjacent to the growing crystal which is devoid of 211 phase. The outer region, Region II, contains both 211 phase and liquid. Solute distributions in both regions and the relation between growth rate and solidification temperature are determined by considering the solute conservation in a small semi-solid element.

\[ \begin{aligned}
 m_{fA}^Y &= \left( \frac{\partial T_{lA}}{\partial C_L^Y} \right)_{C_L^Y} \\
 m_{fA}^{Cu} &= \left( \frac{\partial T_{lA}}{\partial C_L^{Cu}} \right)_{C_L^Y}
\end{aligned} \]

(7.2)

§7.4.1 Solute Distribution in Region II

As shown in figure 7.6, a small volume element is taken in Region II. This element is small enough to be treated as a differential element but large enough to contain a representative amount of liquid plus solid. This element is at a distance \( x \) from the boundary between Region I and Region II \( (x = 0 \) is placed at the Region boundary between Region I and Region II) and moves at the same velocity \( R \) as the solid-liquid interface. Therefore the distance between the solid-liquid interface and the element is always equal to \( x \). Solute is entering and leaving the element in the \( x \) direction by diffusion. The element is moving from left to right at a velocity \( R \) so solute (in both the liquid and solid) enters and leaves the element in the negative \( x \) direction. The equation of solute concentration is written (assuming equal densities of liquid and solid and mass transport by diffusion in the liquid):

\[
\begin{aligned}
\Delta x \Delta y \Delta z \frac{\partial C}{\partial t} &= \Delta y \Delta z \left[ - D f_L \left( \frac{\partial C_L}{\partial x} \right)_x + D f_L \left. \frac{\partial C_L}{\partial x} \right|_{x+\Delta x} \right] \\
&+ \Delta Y \Delta Z \left[ - R C_L^x + R C_L^{x+\Delta x} \right]
\end{aligned}
\]

(7.3)
where $\Delta x$, $\Delta y$ and $\Delta z$ are dimensions of the volume element as shown in figure 7.6, $\overline{C}$ is the average solute concentration in the semi-solid melt, $D$ is diffusion coefficient, $f_L$ is volume fraction of liquid and $C_L$ is solute concentration in the liquid.

Divide both sides of equation (7.3) by $\Delta x\Delta y\Delta z$ and take the limit and assume $D$ is constant:

$$\frac{\partial \overline{C}}{\partial t} = D \frac{\partial}{\partial x} \left( f_L \frac{\partial C_L}{\partial x} \right) + R \left( \frac{\partial \overline{C}}{\partial x} \right)$$

(7.4)

At steady state:

$$\frac{d\overline{C}}{dx} = - \frac{D}{R} \frac{d}{dx} \left( f_L \frac{dC_L}{dx} \right)$$

(7.5)

where

$$\overline{C} = f_\alpha C_\alpha + f_L C_L$$

(7.6)

$$f_\alpha + f_L = 1$$

(7.7)

$C_\alpha$ and $C_L$ are concentration of the $\alpha$ phase (211) and of the liquid respectively; $f_\alpha$ and $f_L$ are the volume fractions of $\alpha$ phase and liquid respectively in the semi-solid element. Boundary conditions for equation (7.4) are:

$$\begin{cases}
C_L^Y = C_L^{\infty Y} \\
C_L^{\infty} = C_L^{\infty Cu} \\
f_L = f_L^{\infty}
\end{cases} \text{ at } x = \infty$$

(7.8)
\begin{align*}
\begin{cases}
C_{\alpha}^{Y} = C_{L_{\alpha}}^{Y} \\
C_{\alpha}^{Cu} = C_{L_{\alpha}}^{Cu} \\
f_{L_{\alpha}} = f_{L_{\alpha}}^{0+}
\end{cases}
\text{ at } x = 0
\end{align*} \tag{7.9}

Where \(C_{L_{\alpha}}^{Y}\) and \(C_{L_{\alpha}}^{Cu}\) are the yttrium and copper concentration in the liquid at the region boundary between Region I and Region II respectively, as shown in figure 7.4; \(f_{L_{\alpha}}^{0+}\) is the corresponding liquid volume fraction at the region boundary on the Region II side; the liquid volume fraction at the region boundary on the Region I side (boundary layer side) is equal to zero for stoichiometric 123 samples; \(C_{L_{\alpha}}^{\infty Y}\) and \(C_{L_{\alpha}}^{\infty Cu}\) are the yttrium and copper concentration in the liquid far away from the growth interface at a given temperature, respectively; \(f_{L_{\alpha}}^{\infty}\) is the corresponding liquid volume fraction. \(C_{L_{\alpha}}^{\infty Y}\), \(C_{L_{\alpha}}^{\infty Cu}\) and \(f_{L_{\alpha}}^{\infty}\) are obtained from the phase diagram.

Integrating both sides in equation (7.1) from point \(m_{1}\) \((C_{LP}^{Y}, C_{LP}^{Cu}, T_{P})\) to point \(m_{2}\) \((C_{L_{\alpha}}, C_{L_{\alpha}}, T_{0})\) (\(m_{1}\) and \(m_{2}\) are defined in both figure 7.5 and 7.7\(^{[4]}\)) gives:

\[
T_{0} - T_{P} = \int_{C_{LP}^{Y}}^{C_{\alpha}^{Y}} m_{\alpha}^{Y} dC_{L}^{Y} + \int_{C_{LP}^{Cu}}^{C_{\alpha}^{Cu}} m_{\alpha}^{Cu} dC_{L}^{Cu}
\tag{7.10}
\]

Where \(m_{1}\) can be chosen from any point along the peritectic liquid line BE in figure 7.5b and \(P_{1}P_{2}\) in figure 7.7 since its role in above integration is only a benchmark. For convenience, \(m_{1}\) is chosen as the point of the equilibrium peritectic reaction liquidus point\(^{[1]}\) in the 123-211 pseudo-binary system. Therefore, \(T_{P}\) is the corresponding temperature at \(m_{1}\) and \((C_{LP}^{Y}, C_{LP}^{Cu})\) are corresponding liquidus composition at \(m_{1}\), and \(m_{2}\) is the liquid composition at temperature \(T_{0}\) on the extended 211 liquidus surface. Since the surface is assumed planar surface, \(m_{\alpha}^{Y}\) and \(m_{\alpha}^{Cu}\) are constants. Equation (7.10) becomes:

\[
T_{0} = T_{P} + m_{\alpha}^{Y} (C_{\alpha}^{Y} - C_{LP}^{Y}) + m_{\alpha}^{Cu} (C_{\alpha}^{Cu} - C_{LP}^{Cu})
\tag{7.11a}
\]

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Equation (7.12a) can be arranged into:

\[ m^Y_{L\alpha} C^Y_{L\alpha} + m^{Cu}_{L\alpha} C^{Cu}_{L\alpha} - T_0 = m^Y_{L\alpha} C^Y_{LP} + m^{Cu}_{L\alpha} C^{Cu}_{LP} - T_P \]

or

\[ a C^Y_{L\alpha} + b C^{Cu}_{L\alpha} + c T_0 = d \]

(7.11b)

where

\[
\begin{align*}
    a &= m^Y_{L\alpha} \\
    b &= m^{Cu}_{L\alpha} \\
    c &= -1 \\
    d &= m^Y_{L\alpha} C^Y_{LP} + m^{Cu}_{L\alpha} C^{Cu}_{LP} - T_P
\end{align*}
\]

Therefore, a, b, c and d are constants which are independent of temperature and liquid composition. It can be seen that equation (7.11b) actually describes the 211 liquidus line at a given temperature \( T_0 \) (line BD in figure 7.5(b)).

Arranging equation (7.5) into:

\[
\frac{d}{dx}\left( \bar{C} + \frac{D f_L}{R} \frac{dC_L}{dx} \right) = 0 \quad (7.12)
\]

Therefore:

\[
\bar{C} + \frac{D f_L}{R} \frac{dC_L}{dx} = a_1 \quad (7.13)
\]

where \( a_1 \) is a constant. Substitution of equation (7.6) and (7.7) into above equation gives:

\[
(1-f_L)C_\alpha + f_L C_L + \frac{D f_L}{R} \frac{dC_L}{dx} = a_1 \quad (7.14)
\]

Rearranging the above equation gives:
\[
\frac{dC_L}{dx} + \frac{RC_L}{D} = \frac{R(a_1 - C_\alpha)}{D} \frac{1}{f_L} + \frac{RC_\alpha}{D}
\quad (7.15)
\]

Since there are two concentration variables in the liquid (yttrium and copper), two equations are obtained from equation (7.15) as following:

\[
\frac{dC^Y_L}{dx} + \frac{RC^Y_L}{D^Y} = \frac{R(a_1 - C^\alpha_\alpha)}{D^Y} \frac{1}{f_L} + \frac{RC^Y_\alpha}{D^Y}
\quad (7.16a)
\]

\[
\frac{dC^\text{Cu}_L}{dx} + \frac{RC^\text{Cu}_L}{D^\text{Cu}} = \frac{R(a_2 - C^\alpha_{\text{Cu}})}{D^\text{Cu}} \frac{1}{f_L} + \frac{RC^\alpha_{\text{Cu}}}{D^\text{Cu}}
\quad (7.16b)
\]

Where \(C^\alpha_\alpha\) and \(C^\text{Cu}_{\text{Cu}}\) are yttrium and copper concentration in the \(\alpha\) phase (211 particles) respectively and they are both constant; \(D^Y\) and \(D^\text{Cu}\) are the diffusion coefficients of yttrium and copper in the liquid respectively and both are considered as constant; \(f_L\) is the liquid volume fraction in the semi-solid region and is a function of distance \(x\) from the region boundary between Region I and Region II.

Solving equations (7.11b), (7.16a) and (7.16b) with boundary conditions (7.8) and (7.9) (as shown in appendix A) gives:

\[
C^Y_L = C^\infty_L + (C^\infty_\alpha - C^\infty_L) \exp(-\frac{R}{D^*}x)
\quad (7.17a)
\]

\[
C^\text{Cu}_L = C^\infty_{\text{Cu}} + (C^\infty_{\alpha\text{Cu}} - C^\infty_L) \exp(-\frac{R}{D^*}x)
\quad (7.17b)
\]

where

\[
D^* = \frac{m^\text{Cu}_{\alpha} D^Y (C^\infty_{\alpha\text{Cu}} - C^\infty_{\text{Cu}}) + m^Y_{\alpha} D^\text{Cu} (C^\infty_L - C^\infty_\alpha)}{(m^Y_{\alpha} C^Y_L + m^\text{Cu}_{\alpha} C^\text{Cu}_{\text{Cu}} - T_p + T_0) - (m^Y_{\alpha} C^\alpha_L + m^\text{Cu}_{\alpha} C^\text{Cu}_{\alpha})}
\]
and
\[ f_L = R \left( \frac{1}{D_Y} - \frac{1}{D_{Cu}} \right) C_L^Y \cdot \frac{B}{A} \]  \hspace{1cm} (7.18)

where
\[ A = \frac{R f_L^{\infty}}{D_Y} \left( C_L^Y - C_{Cu}^Y \right) + \frac{m_{L\alpha} R f_L^{\infty}}{m_{L\alpha} D_{Cu}} \left( C_L^{\infty_{Cu}} - C_{Cu}^{\infty} \right) \]  \hspace{1cm} (7.19)
\[ B = \frac{R C_{Cu}^Y}{D_Y} \frac{(-T_0 - m_{L\alpha} C_{LP}^Y - m_{L\alpha} C_{LP}^{Cu} + T_p) + \frac{m_{L\alpha} R C_{Cu}^Y}{m_{L\alpha} D_{Cu}}}{m_Y} \]  \hspace{1cm} (7.20)

It can be seen that equation (7.17) describes the solute (both yttrium and copper) distributions and equation (7.18) describes the 211 particle distribution (or the liquid volume fraction distribution) in Region II, respectively. \( D^* \) only depends on temperature \( T_0 \) and initial composition.

In the Y-B-C-O system, the diffusion coefficients of yttrium and copper are unknown and expected to be closely similar in this low viscosity liquid. If equal diffusion coefficients of yttrium and copper are assumed, equation (7.17) becomes (see appendix C):
\[ f_L = \frac{-B}{A} = \frac{1}{f_L^{\infty}} \]  \hspace{1cm} (7.21)

Therefore, the volume fraction of 211 particles in the entire Region II is the equal to \( 1 - f_L^{\infty} \) even though the solute concentrations in the liquid (both yttrium and copper) in Region II change according to equation (7.17). Further more, if \( D_Y = D_{Cu} \), then
\[ D^* = D_Y = D_{Cu} = D \]  \hspace{1cm} (7.22)

Let the origin of x axis change from the Region boundary to the 123 growth interface for conveyance, the solute distribution equations (7.17a) and (7.17b) for equal diffusion coefficients become:
§7.4.2 Solute Distribution in Region I

Region I is the boundary layer where no 211 particles exist for a stoichiometric 123 sample. At steady state, equation (7.5) is valid for Region I with the condition that $\overline{C} = C_L$. The solution for this differential equation is:

$$C_L = A^0 + B^0 \exp\left(-\frac{R}{D} x\right)$$ (7.24)

where $R$ is the growth rate; $D$ is the diffusivity for both yttrium and copper (same diffusivity is assumed), and $x$ is the distance from the 123 growth interface. The boundary conditions are:

$$\begin{cases}
C_L = C_{L,\gamma}^0 \\
D \frac{dC_L}{dx} \bigg|_{x=0} = R \left(C_{\gamma} - C_{L,\gamma}^0\right)
\end{cases} \text{ at } x = 0$$ (7.25)

$$\begin{cases}
C_L \bigg|_{x=l} = C_{L,\alpha}^0 \\
-D \frac{dC_L}{dx} \bigg|_{x=l-\varepsilon} = -D f_L \frac{dC_L}{dx} \bigg|_{x=l+\varepsilon} - (1 - f_L) R \{C_{\gamma} - C_L \bigg|_{x=l+\varepsilon}\}
\end{cases} \text{ at } x = l$$ (7.26)

where $C_{L,\gamma}^0$ and $C_{L,\alpha}^0$ are the solute concentrations in the liquid at the 123 growth interface and the region boundary, respectively. Applying boundary condition (7.25) to equation (7.24) gives:

$$C_L = C_{\gamma} + (C_{L,\gamma}^0 - C_{\gamma}) \exp\left(-\frac{R}{D} x\right)$$ (7.27)

Substitution of equation (7.27) into first equation in boundary condition (7.26) gives:
\[ C_L = C_\gamma + (C_{L\gamma}^0 - C_\gamma) \exp\left(-\frac{R_I}{D}\right) \] (7.28)

Therefore, if \( \frac{R_I}{D} \) is small compared to the unit, the solute concentration at the Region boundary is approximately equal to:

\[ C_L = C_\gamma + (C_{L\gamma}^0 - C_\gamma) \left(1 - \frac{R_I}{D}\right) \] (7.29)

Substitution of both equations (7.27) and (7.23) into the second equation of boundary condition (7.26) gives:

\[ D \left( -\frac{R_I}{D} \right) (C_{L\gamma}^0 - C_\gamma) \exp\left(-\frac{R_I}{D}\right) = D f_L \left( -\frac{R_I}{D} \right) (C_{L\alpha}^\alpha - C_{L\gamma}^\gamma) + (C_{\alpha} - C_{L\alpha}) (1 - f_L) R \] (7.30)

If \( \frac{R_I}{D} \) is small compared to the unit, equation (7.30) becomes:

\[ C_L = C_\gamma + (C_{L\gamma}^0 - C_\gamma) \left(1 - \frac{R_I}{D}\right) \] (7.31)

It can be seen that equation (7.31) is exactly the same as equation (7.29). Therefore, both equations in boundary condition (7.26) are satisfied as long as equation (7.29) or (7.31) is satisfied. Equation (7.29) can be written in the following form for both yttrium and copper:

\[ D^Y \frac{C_{L\alpha}^\gamma - C_{L\gamma}^\gamma}{l} = R (C_\gamma^Y - C_{L\gamma}^0) \] (7.32a)

\[ D^{Cu} \frac{C_{L\alpha}^{Cu} - C_{L\gamma}^{Cu}}{l} = R (C_\gamma^{Cu} - C_{L\gamma}^{0Cu}) \] (7.32b)
Equations (7.32) describe the relations between the solute concentrations in the liquid at the 123 growth interface and at the Region boundary. It is interesting to notice that equation (7.32a) and (7.32b) are the same as the boundary condition at the 123 growth interface in the binary model. However, unlike the binary model, the liquid composition at a distance \( l \) from the 123 growth interface in the ternary system \((C_{L\alpha}^\gamma, C_{L\alpha}^{Cu})\) is different from the liquid composition at infinity \((C_{L\alpha}^{\infty\gamma}, C_{L\alpha}^{\infty Cu})\).

In summary, equations (7.32a) and (7.32b) (for Region I) combined with equations (7.22a) and (7.32b) (for Region II) provide a full solution of the solute distribution problem for equal solute diffusion coefficients in the isothermal growth situation.

§7.4.3 The Relation Between Growth Rate and Solidification Temperature

Solute concentrations in the liquid at the 123 growth interface \((C_{L\gamma}^{\delta\gamma}, C_{L\gamma}^{\delta Cu})\) are determined from the isothermal section of YBCO ternary phase diagram, figure 7.5a, assuming that the interface kinetics can be neglected. The relation between growth rate and the solidification temperature can be obtained by solving equations (7.11(b)), (7.32(a)) and (7.32(b)):

\[
R = \frac{D}{l} \frac{m_L^Y \left( C_{LY}^Y - C_{LY}^{\delta Y} \right) + m_{L\alpha}^Cu \left( C_{LY}^{Cu} - C_{LY}^{\delta Cu} \right)}{m_L^Y \left( C_{Ly}^Y - C_{LY}^{\delta Y} \right) + m_{L\alpha}^Cu \left( C_{Ly}^{Cu} - C_{LY}^{\delta Cu} \right)} \Delta T
\]

(7.33)

where \(C_{LY}^{\delta Y}\) and \(C_{LY}^{\delta Cu}\) are function of \(\Delta T\).

Table 7.1 shows the related parameters used to calculate the growth rate and the solute distributions in the liquid during the growth of 123 single crystal. Table 7.2 shows the solute concentrations at the 123 growth interface at different solidification temperature taken from the ternary phase diagram \([4]\). Figure 7.8 plots the calculated growth rates at different solidification temperatures, using equation (7.33), and the measured growth rates by Endo et al.\([5]\) for a sample with 20% excess 211. It can be seen that they are comparable. Also plotted is the measured \(\Delta T_p\) (17 °C) at 0.25 \(\mu m/s\) for thermal gradient growth from figure 6.3(a). It can be seen that \(\Delta T_p\) is not
a strong function of the growth methods (isothermal growth or thermal gradient growth), as discussed in Chapter 6.4.1,

### Table 7.1 Parameters for calculating the growth rate and solute distributions in the semi-solid melt

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_Y^\alpha$ yttrium concentration in 211 particles</td>
<td>$2.7 \times 10^{-2}$ (mole/cm$^3$)</td>
</tr>
<tr>
<td>$C_{Cu}^\alpha$ copper concentration in 211 particles</td>
<td>$2.18 \times 10^{-2}$ (mole/cm$^3$)</td>
</tr>
<tr>
<td>$C_Y^\gamma$ yttrium concentration in 123 phase</td>
<td>$9.6 \times 10^{-3}$ (mole/cm$^3$)</td>
</tr>
<tr>
<td>$C_{Cu}^\gamma$ copper concentration in 123 phase</td>
<td>$2.78 \times 10^{-2}$ (mole/cm$^3$)</td>
</tr>
<tr>
<td>$C_Y^P$ yttrium concentration in the liquid at equilibrium peritectic temperature</td>
<td>$1.0 \times 10^{-3}$ (mole/cm$^3$)</td>
</tr>
<tr>
<td>$C_{Cu}^P$ copper concentration in the liquid at the equilibrium peritectic temperature</td>
<td>$3.5 \times 10^{-2}$ (mole/cm$^3$)</td>
</tr>
<tr>
<td>$T_p$ equilibrium peritectic temperature</td>
<td>1273 (K)</td>
</tr>
<tr>
<td>$l$ the length of the boundary layer</td>
<td>$5.0 \times 10^{-4}$ (cm)</td>
</tr>
<tr>
<td>$C_{L\alpha}$ yttrium concentration in the liquid in infinity at temperature T0</td>
<td>$9.8 \times 10^{-4}$ (mole/cm$^3$)</td>
</tr>
<tr>
<td>$D$ diffusivity for both yttrium and copper</td>
<td>$6 \times 10^{-7}$ (cm$^2$/s)</td>
</tr>
<tr>
<td>$m_Y^{L\alpha}$ the slope of 211 liquidus surface with respect to yttrium</td>
<td>$4.5 \times 10^4$ (cm$^3$/mole)</td>
</tr>
<tr>
<td>$m_{Cu}^{L\alpha}$ the slope of 211 liquidus surface with respect to copper</td>
<td>$-0.5 \times 10^2$ (cm$^3$/mole)</td>
</tr>
</tbody>
</table>

### Table 7.2 Solute concentrations at the growth interface of 123

<table>
<thead>
<tr>
<th>$\Delta T$ (°C)</th>
<th>Yttrium (mole/cm$^3$)</th>
<th>Copper (mole/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>$7.5 \times 10^{-4}$</td>
<td>$3.2 \times 10^{-2}$</td>
</tr>
<tr>
<td>10</td>
<td>$7.0 \times 10^{-4}$</td>
<td>$3.4 \times 10^{-2}$</td>
</tr>
<tr>
<td>15</td>
<td>$6.4 \times 10^{-4}$</td>
<td>$3.6 \times 10^{-2}$</td>
</tr>
<tr>
<td>20</td>
<td>$5.7 \times 10^{-4}$</td>
<td>$3.8 \times 10^{-2}$</td>
</tr>
<tr>
<td>25</td>
<td>$4.7 \times 10^{-4}$</td>
<td>$4.1 \times 10^{-2}$</td>
</tr>
</tbody>
</table>

§7.4.4 Calculated Solute Distributions in the Semi-solid Melt

Figure 7.9 shows calculated yttrium and copper concentration distributions in the semi-solid melt isothermally solidified at $\Delta T = 15$ °C versus the distance from the 123 growth interface
using equations 7.23 and 7.32. It can be seen that both copper and yttrium concentrations in the liquid change with the distance from the 123 growth interface. However, the copper concentration changes much more than yttrium on an absolute scale: \( \Delta C_{\text{Cu}} = 0.2 \times 10^{-2} \) mole/cm\(^3\) and \( \Delta C_{\text{Y}} = 0.5 \times 10^{-4} \) mole/cm\(^3\). The yttrium concentration gradient in the boundary layer is much larger than that in the region II and is not continuous at the Region boundary. However, the copper concentration gradient in the boundary layer is close to the Region II and are approximately continuous at the Region boundary.

Figure 7.10 shows the calculated weight percentage of CuO in the semi-solid melt by taking into account of both the 211 volume fraction and the solute concentrations in the liquid from figure 7.9 as following:

\[
W_1 + W_2 + W_3 = 1 \quad (7.35)
\]

\[
\frac{2W_1}{MW_1} = \frac{f_L C^Y_L + (1 - f_L) C^Y_\alpha}{\rho_1 + \rho_2 + \rho_3} = \text{Mo1} \quad (7.36)
\]

\[
\frac{W_2}{MW_2} = \frac{f_L C^\text{Cu}_L + (1 - f_L) C^\text{Cu}_\alpha}{\rho_1 + \rho_2 + \rho_3} = \text{Mo2} \quad (7.37)
\]

where \( W_1, W_2 \) and \( W_3 \) are the weight percent of \( \text{Y}_2\text{O}_3 \), CuO and BaO in the semi-solid melt respectively, \( MW_1 \) and \( MW_2 \) are the mole weight of \( \text{Y}_2\text{O}_3 \) and CuO respectively, \( \rho_1, \rho_2, \) and \( \rho_3 \) are the density of \( \text{Y}_2\text{O}_3 \), CuO, and BaO respectively, \( f_L \) is the liquid volume fraction, \( C^Y_\alpha \) and \( C^\text{Cu}_\alpha \) are the calculated yttrium and copper concentration in the 211 phase respectively, \( C^Y_L \) and \( C^\text{Cu}_L \) are the calculated yttrium and copper concentration in the liquid phase respectively. Solving equations (7.35), (7.36) and (7.37) together gives the weight percent of CuO:

\[
W_2 = \frac{\Delta C_{\text{CuO}}}{\Delta} \quad (7.38)
\]
where

\[
\Delta \text{CuO} = \begin{vmatrix}
\text{Mo}^1 & 2\text{W}^1 & \text{Mo}^1 \\
\rho_1 & \text{MW}^1 & \rho_3 \\
\text{Mo}^2 & \text{W}^2 & \text{Mo}^2 \\
\rho_1 & \text{MW}^2 & \rho_3 \\
1 & 1 & 1
\end{vmatrix}
\quad \text{and} \quad
\Delta = \begin{vmatrix}
\text{Mo}^1 & \text{Mo}^1 & \text{Mo}^1 \\
\rho_1 & \rho_2 & \rho_3 \\
\text{Mo}^2 & \text{Mo}^2 & \text{Mo}^2 \\
\rho_1 & \rho_2 & \rho_3 \\
1 & 1 & 1
\end{vmatrix}
\]

Also plotted in figure 7.10 are measured results in figure 7.2. It can be seen that the calculated CuO weight percentage is comparable to the measured result and both of them decrease with increasing the distance from the 123 growth interface.

§7.4.5 Solidification Path

Solidification path is the locus of solute compositions in the liquid ahead of a planar interface\(^7\). The relation between the two solutes (yttrium and copper) in Region II can be obtained by combination of the two equations in equation (7.32):

\[
\frac{C^Y_{L} - C^\infty_{L}^Y}{C^Y_{La} - C^\infty_{L}^Y} = \frac{C^Cu_{L} - C^\infty_{L}^Cu}{C^Cu_{La} - C^\infty_{L}^Cu}
\]

Figure 7.11 plots the calculated solidification path for a sample solidified at \(\Delta T = 15^\circ\text{C}\). The liquid composition at infinity (point A) is obtained from the pseudo-binary phase diagram. The liquid composition at the 123 growth interface (point B) is the equilibrium liquid composition among 123, 211 and liquid at \(\Delta T = 15^\circ\text{C}\). With decreasing the distance from the 123 growth interface, the liquid composition moves from point A to point B. The average composition of the semi-solid melt ahead of the 123 growth interface is deviated from the overall composition of the sample.

Since the liquid in the semi-solid region is in equilibrium with 211 particles, the solidification path is the same as the metastable 211 liquidus line at the solidification temperature.
§7.5 Discussion

§7.5.1 211 Particle Distribution in Region II

It can be seen from equation (7.18) that the 211 particle distribution in Region II depends on the diffusion coefficients of both yttrium and copper in the liquid. The 211 volume fraction in Region II is constant if both diffusion coefficients are the same. However, if the diffusion coefficients of yttrium and copper are not the same, we can do a rough estimation of the liquid volume fraction in the region II. If assuming \( m_{L_{\alpha}}^{Cu} = 0 \), equation (7.18) becomes:

\[
\frac{1}{f_L} = \frac{1}{f_L^\infty} \left[ \frac{D^Y \left( \frac{1}{D^Y} - \frac{1}{D^{Cu}} \right)}{C_{L}^{\infty Y} - C_{L}^{Y}} \right] \cdot \frac{B}{A}
\]

Since \( D^Y \) and \( D^{Cu} \) are in the order of \( 10^{-6} \) cm\(^2\)/s, \( C_{L}^{Y} \) and \( C_{L}^{\infty Y} \) are in the order of \( 10^{-4} \) mole/cm\(^3\) and \( C_{L}^{Y} \) is in the order of \( 10^{-2} \) mole/cm\(^3\), the first term in equation (7.40) is in the order of \( (1/f_L^\infty) 10^{-2} \) and is much smaller than the second term. The second term is approximately equal to \( (1/f_L^\infty) \). Therefore, the 211 volume fraction in Region II only has a very small change from infinite to the region boundary. In other words, even if the diffusivities of yttrium and copper are not the same, the liquid volume fraction \( f_L^\infty \) at infinite and \( f_L \) on the Region boundary are approximately the same. Therefore, the assumption of the equal diffusion coefficients for both yttrium and copper is appropriate.

§7.5.2 Liquid Composition at the 123 Growth Interface

EDAX measurement shown in figure 7.2 suggests that the liquid composition at the 123 growth interface is different from that at infinity obtained by pseudo-binary phase diagram. Therefore, the average composition of the semi-solid melt ahead of the 123 growth interface is deviated from the overall composition of the sample. If assuming that the 123 growth interface is in
equilibrium with the liquid and 211 phase, the liquid composition at the 123 growth interface is
given by the equilibrium composition, as shown in figure 7.5a and used in the derivation of
equation (7.33). Consequently, the liquid compositions at the 123 growth interface are different
from that at infinity, which is in agreement with the EDAX measurement.

On the other hand, if the 123 growth interface is not in equilibrium with the liquid and 211
phase, the EDAX measurement shown in figure 7.2 may be explained by the formation of another
phase, $\text{BaCuO}_2$, ahead of the 123 growth interface since the formation of $\text{BaCuO}_2$ form the semi-
solid melt (211 + liquid) will increase the copper concentration in the liquid.

Since $\text{BaCuO}_2$ has not been found by both EDAX and microprobe measurement in the
semi-solid melt ahead of the 123 growth interface, it is concluded that the 123 growth interface is
in equilibrium with the 211 phase and liquid. Therefore the liquid composition at the 123 growth
interface is determined by the equilibrium liquid composition at a given solidification temperature,
as shown in figure 7.5a.

§7.5.3 The Effect of Interface Kinetics on the Solute Distribution in the Semi-
Solid Melt

As discussed above, the solute concentrations in the liquid at the 123 growth interface
calculated by equation (7.33) is not valid if interface kinetics can not be neglected. However, the
equations (7.23) and (7.32) are still valid since the derivation of both equations did not use any
assumption on the interface kinetics. If the interface kinetics has to be considered, the solute
concentrations in the liquid at different 123 growth interface (ab plane and c plane) are different
since the surface energies at a-b plane and c plane of 123 single crystal are different. Therefore, the
solute concentration distributions in the semi-solid melt along a-b direction and c direction are
different according to equation (7.23) and (7.32). As the result, it is possible to have solute
transport in the semi-solid melt from a-b direction to c direction or vise versa[^6].

§7.5 Summary
The solute distributions in the semi-solid melt and the relation between growth rate and solidification temperature has been obtained during the isothermal growth of 123 single crystal in the ternary system of Y-B-Cu-O. Unlike the binary system, it shows that solute concentrations in the semi-solid are not constant. The copper concentration decreases and yttrium concentration increases with increasing the distance from the 123 growth interface. It also shows that the 211 volume fraction in semi-solid melt are approximately constant.

§7.6 Reference


§7.7 Appendix

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A: Derivation of equations (7.17) and (7.18)

In Region II, $C_{Lx}^Y = C_L^Y$ and $C_{Lz}^{Cu} = C_L^{Cu}$. Therefore, equation (7.11b) can be arranged as:

$$C_L^{Cu} = -\frac{a}{b} C_L^Y - \frac{1}{b} (cT_0 - d)$$  \hspace{1cm} (A-1)

Differentiating both sides of equation (A-1) gives:

$$\frac{dC_L^{Cu}}{dx} = -\frac{a}{b} \frac{dC_L^Y}{dx}$$  \hspace{1cm} (A-2)

Combination of equations (A-1) and (A-2) gives:

$$\frac{dC_L^{Cu}}{dx} + \frac{R}{D_L^{Cu}} C_L^{Cu} = -\frac{a}{b} \left[ \frac{dC_L^Y}{dx} + \frac{R}{D_L^{Cu}} C_L^Y \right] - \frac{R}{hD_L^{Cu}} (cT_0 - d)$$  \hspace{1cm} (A-3)

Equating the right sides of equation (A-3) and (7.16b) gives:

$$\frac{dC_L^Y}{dx} + \frac{R}{D_L^{Cu}} C_L^Y = -\frac{R}{aD_L^{Cu}} (cT_0 - d) - \frac{br(a_2 - C_{Lz}^{Cu})}{aD_L^{Cu}} \frac{1}{f_L} \left( bRC_L^{Cu} \right)$$  \hspace{1cm} (A-4)

Subtraction of equation (A-4) from equation (7.16a) gives:

$$\left( \frac{R}{D_L^{Y}} - \frac{R}{D_L^{Cu}} \right) C_L^Y = A \frac{1}{f_L} + B$$  \hspace{1cm} (A-5)

where $A$ and $B$ are

$$A = \frac{R}{D_L^{Y}} (a_1 - C_L^Y) + \frac{br}{aD_L^{Cu}} (a_2 - C_{Lz}^{Cu})$$  \hspace{1cm} (A-6)
\[
B = \frac{RC_y}{DY} + \frac{R}{aD_{Cu}}(cT_0 - d) + \frac{b}{d} \frac{RC_{Cu}}{D_{Cu}}
\]

(A-7)

Therefore, the liquid fraction in the melt can be expressed as

\[
\frac{1}{f_L} = \frac{R}{A} \left( \frac{1}{DY} - \frac{1}{D_{Cu}} \right) C_y^L \cdot \frac{B}{A}
\]

(A-8)

Equation (A-8) is the relation between the liquid fraction and the yttrium concentration in the melt.

Substitution of equation (A-8) back to equation (7.16a) gives:

\[
\frac{dC_y^L}{dx} + P C_y^L = Q
\]

(A-9)

where \(P\) and \(Q\) are only a function of growth rate \(R\) which is constant at steady state:

\[
P = \frac{R}{DY} \left[ 1 - \frac{R(a_1 - C_{\alpha})}{A} \left( \frac{1}{DY} - \frac{1}{D_{Cu}} \right) \right]
\]

(A-10)

\[
Q = \frac{R}{DY} \left[ C_y^L \cdot B(a_1 - C_{\alpha}) \right]
\]

(A-11)

Equation (A-9) is a linear ordinary differential equation and the solution is

\[
C_y^L = \frac{Q}{P} + \eta_1 \exp(-Px)
\]

(A-12)
where \( \eta_1 \) is an integration constant. It is noticed that \( P \) has to be positive since otherwise the solution is diverged when \( x \) approaches infinity. Substitution of equation (A-12) into equation (7.11b) gives:

\[
C_{Lu}^C = - \left[ \frac{a}{b} \frac{Q}{P} + \frac{1}{b} (cT_0 - d) \right] + (- \frac{a}{b} \eta_1) \exp(-Px) \quad (A-13)
\]

Applying boundary conditions (7.8) to (A-12) and (A-13) gives,

\[
C_{Ly}^C = \frac{Q}{P} \quad (A-14)
\]

\[
C_{Lu}^C = - \left[ \frac{a}{b} \frac{Q}{P} + \frac{1}{b} (cT_0 - d) \right] \quad (A-15)
\]

Therefore, constants \( a_1 \) and \( a_2 \) can obtained from equation (A-14) and (A-15). However, since those two equations are very tedious, another method to get \( a_1 \) and \( a_2 \) are employed here. It can be seen from equation (A-12) and (A-13) that \( dC/dx = 0 \) when \( x \) approaches \( \infty \). Therefore, \( a_1 \) and \( a_2 \) are determined from equation (7.16) using boundary conditions (7.8) and \( dc/dx = 0 \) at \( x = \infty \):

\[
a_1 = C_{\alpha}^Y + \int_{L}^{\infty} (C_{Lu}^C - C_{\alpha}^Y) \quad (A-16)
\]

\[
a_2 = C_{\alpha}^C + \int_{L}^{\infty} (C_{Lu}^C - C_{\alpha}^C) \quad (A-17)
\]

As can be seen in the appendix B that equations (A-16) and (A-17) satisfy with equations (A-14) and (A-15). Therefore combination of equations (A-9), (A-10), (A-16), (A-17) and boundary conditions (7.8) gives

\[
C_{Ly}^Y = C_{Ly}^{\infty Y} + (C_{\alpha}^Y - C_{\alpha}^{\infty Y}) \exp(- \frac{R}{D^*} x) \quad (A-18)
\]

and
\[ C_L^{Cu} = C_L^{Cu^\infty} + (C_L^{Cu} - C_L^{Cu^\infty}) \exp\left(-\frac{R}{D^*}x\right) \quad (A-19) \]

where

\[
D^* = \frac{b D^Y (C_L^{Cu^\infty} - C_L^{Cu}) + a D^C (C_L^{Cu^\infty} - C_L^{Cu})}{(d - c T_0) - (a C_C + b C_C^{Cu^\infty})} \quad (A-20)
\]

Substitution of \(a, b, c\) and \(d\) into above equation gives:

\[
D^* = \frac{m_L^{Cu} D^Y (C_L^{Cu^\infty} - C_L^{Cu}) + m_L^{Cy} D^C (C_L^{Cu^\infty} - C_L^{Cu})}{(m_L^{Cy} C_L^{Cu^\infty} + m_L^{Cu} C_L^{Cu^\infty}) - (m_L^{Cy} C_L^{Cu^\infty} + m_L^{Cu} C_L^{Cu^\infty})} \quad (A-21)
\]

**B: Verification of boundary condition**

\[ C_L^{Cu^\infty} = \frac{Q}{P} \]

If assuming \(C_L^{Cu^\infty} = \frac{Q}{P}\), substitution of \(P\) and \(Q\) into it gives:

\[
C_L^{Cu^\infty} = \frac{R}{D^Y} \left[ C_C^{Cu^\infty} - \frac{B(a_1 - C_C^{Cu^\infty})}{A} \right] - \frac{R}{D^Y} \left[ 1 - \frac{R(a_1 - C_C^{Cu^\infty})}{A} \left( \frac{1}{D^Y} - \frac{1}{D^C} \right) \right] \quad (B-1)
\]

Through combination of equation (B-1) with equations (A-6), (A-7), (A-16) and (A-17) and tedious algebraic operation, following equation appears:

\[
b C_C^{Cu} (C_L^{Cu^\infty} - C_C^{Cu^\infty}) - (c T_0 - d) (C_L^{Cu^\infty} - C_C^{Cu^\infty}) - b C_C^{Cu} (C_L^{Cu^\infty} - C_C^{Cu^\infty}) = b C_L^{Cu^\infty} (C_L^{Cu^\infty} - C_C^{Cu^\infty}) + a C_L^{Cu^\infty} (C_L^{Cu^\infty} - C_C^{Cu^\infty}) \quad (B-2)
\]

Rearrange equation (B-2) into:
\[ C_{\alpha} \left[ a C_{L}^{\infty Y} + b C_{L}^{\infty Cu} + c T_0 - d \right] = C_{L}^{\infty Y} \left[ a C_{L}^{\infty Y} + b C_{L}^{\infty Cu} + c T_0 - d \right] \quad (B-3) \]

Since both sides are equal to zero, equation (B-3) is correct. Therefore, \( C_{L}^{\infty Y} = \frac{Q}{P} \).

\[ C \]

If \( D_{Y} = D_{Cu} = D \), then
\[
A = \frac{R f_{L}}{D} \left[ (C_{L}^{\infty Y} - C_{\alpha}^{\infty Y}) + \frac{m_{Cu}^{Cu}}{m_{L,\alpha}} (C_{L}^{\infty Cu} - C_{\alpha}^{Cu}) \right]
\]
\[
B = \frac{R}{D} \left[ C_{\alpha}^{\infty Y} + \frac{1}{m_{\gamma}} (T_0 - m_{L,\alpha} C_{L}^{\infty Y} - m_{L,\alpha} C_{Cu}^{Cu} + T_p) + \frac{m_{Cu}^{Cu} C_{Cu}^{Cu}}{m_{L,\alpha}} \right]
\]

Therefore, \( \frac{A}{B} = -f_{L}^{\infty} \).
Figure 7.1 The optical microscopic picture of a sample with 20% (wt) excess 211 isothermally solidified by the melt-growth method at $\Delta T = 15 \, ^{\circ}\text{C}$. The top region is the quenched semi-solid melt. The bottom region is the solidified 123 with 211 inclusions.
Figure 7.2  The measured CuO %(wt) in the semi-solid melt ahead of the 123 growth interface. The measured area at each measurement was approximately 30×25 μm². Therefore, the measured composition was an average composition of 211 particles and quenched liquid phase.
Figure 7.3 The measured 211 volume fraction distribution in the semi-solid melt. It can be seen that the 211 volume fraction is approximately constant in the semi-solid melt except the boundary layer.
Figure 7.4 Solute (yttrium and copper) distributions in the semi-solid melt.
Figure 7.5(a) The isothermal section of the ternary phase diagram at $T_0 = 975$ °C. The liquid composition at the growing interface of 123 crystal is given by the point B, which is the equilibrium liquid composition between 123, 211 and liquid.
Figure 7.5(b) Illustration of the liquidus surfaces. m1 is the equilibrium peritectic reaction liquidus point at Tp as in [1]. Point B is the liquidus point at the 123-liquid interface; the equilibrium liquid composition between 211, 123 and liquid at T0. ABCD is the isothermal plan at T0. BD is the liquidus line of 211 at T0. 211 liquidus surface is assumed as planar.
Figure 7.6 Small element taken from region II (the semi-solid melt region) which contains 211 particles and liquid.
Figure 7.7 Ternary phase diagram of Ba-Y-Cu-O system: P₁-P₂ is the peritectic reaction (L+211 - > 123) liquidus line; m₂-P₄ is the peritectic reaction (L + Y₂O₃ -> 211) liquidus line. It also shows the binary section along 211 and 123. m₁ is the liquidus point of peritectic reaction (L +211 -> 123 ) in the binary system.
Figure 7.8 Calculated and measured growth rate for isothermal growth at different solidification temperatures. It can be seen that they are in agreement. The measured ΔT (17 °C) for thermal gradient growth at 0.25 μm/s is also plotted.
Figure 7.9 Calculated solute concentration distributions in the semi-solid melt solidified at $\Delta T = 15 \, ^{\circ}\text{C}$ as a function of the distance from the 123 growth interface. It can be seen that both copper and yttrium concentrations in the liquid change with the distance. However, the copper concentration changes much more than the yttrium concentration.
Figure 7.10 The measured CuO %(wt) and the calculated CuO %(wt) in the semi-solid melt.
Figure 11 Solidification path A-B at $\Delta T_p = 15$ °C, where A is the liquid composition at infinity and B is the liquid composition at the 123 growth interface. Since the liquid in the semi-solid region is in equilibrium with 211 phase, the solidification path is the same as the metastable 211 liquidus line at this temperature.
Chapter 8
Conclusions

(1) A new quench technique was developed to obtain best quenched 123/liquid interfaces ever published so far for detailed microstructural examination.

(2) Depending on growth rate and composition, three types of growth morphologies of the growing 123 phase were observed: "faceted plane front", "cellular/dendritic" and "equiaxed blocky". Dendrite growth with distinguishable secondary arms occurred in samples with stoichiometric 123.

(3) The maximum growth rate at which a single crystal could be obtained increased from 1 μm/s to 1.5 μm/s as excess 211 content increased from 0 to 20 % (wt). It then decreased to 1 μm/s as excess 211 increased to 40 % (wt). Therefore, the optimized composition to obtain a single crystal is 20 % (wt) excess 211.

(4) The amount of excess 211 has a strong influence on the microscopic growth morphology of single crystal 123. The microscopic 123 growth interface was flat at high excess 211 content, but not flat at low excess 211 content. A highly curved 123 envelope was formed on 211 particles located at the 123 growth interface at zero excess 211 content (stoichiometric 123 samples) due to the large 211 particle spacing, making the interface temperature lower.
(5) Solidification interface temperatures of YBa$_2$Cu$_3$O$_{7-\delta}$ (123) single crystals were measured for samples with different amounts of excess Y$_2$BaCuO$_5$ (211) phase at different growth rates. The experimental results show that the solidification interface temperature depression, $\Delta T_p$, increased with increasing the growth rate for samples with a given amount of excess 211. At a given growth rate, however, $\Delta T_p$ initially decreased and then increased with the increase of the amount of excess 211.

(6) The initial decrease of $\Delta T_p$ with increasing the amount of excess 211 was due to the decrease of the 211 particle spacing. The increase of $\Delta T_p$ at high excess 211 content was due to the lengthened diffusion path required for solute transport through the liquid.

(7) Solute distributions have been obtained in the semi-solid melt during the isothermal growth of 123 single crystal in the ternary system of Y-B-Cu-O. This was done by solving the full solute transport problem, both in the boundary layer near the growing crystal, and in the outer semi-solid region.

(8) Both the composition measurement in the semi-solid melt and the theoretical computation show that solute concentrations in the semi-solid region are not constant. The copper concentration decreases and yttrium concentration increases with increasing the distance from the 123 growth interface.