

Semisolid solidification of high temperature superconducting oxides

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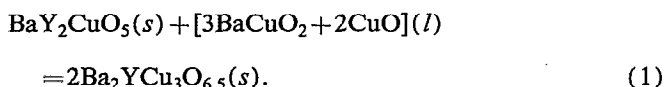
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Experiments are reported on two techniques for melt-texture processing $\text{Ba}_2\text{YCu}_3\text{O}_{6.5}$ by directional solidification from a semisolid melt containing particles of BaY_2CuO_5 and a copper-rich liquid. One of these employs an electric resistance furnace with ambient or oxygen enriched atmosphere; the other is a laser-heated furnace operating at 1.3 atm oxygen. Solidification interface morphologies and other structural features were examined in quenched specimens. Depending on growth rate and temperature gradient, three different types of growth morphologies of the growing 123 phase were observed: "faceted plane front," "cellular dendritic" or "equiaxed blocky." The interface temperature decreased markedly with increasing growth rate for the faceted plane front specimens. In the remaining specimens, solidification took place over a range of temperatures. The temperature of the "root" of the solidification front dropped, but temperature of the solidification front "tip" did not. A solidification model is developed and employed to interpret experimental observations. The model assumes limited diffusion of solute in the liquid during the growth of the superconducting phase. The model shows, in agreement with experiment, that growth rate of the low temperature solid phase has a strong effect on ability to obtain the desirable faceted plane front, and that thermal gradient has only a small effect. Interparticle spacing of the high temperature phase, BaY_2CuO_5 , is also predicted to have a strong effect.

INTRODUCTION

Solidification processing of high temperature superconductors (HTSC) has been the subject of many recent studies. Directional solidification produces HTSC materials with microstructures containing large grains with a preferred orientation.¹⁻⁴ Weak-link electrical behavior is associated primarily with high-angle grain boundaries which greatly reduce the critical current density of bulk HTSC materials. Thus, single crystal microstructures or microstructures with oriented and continuous grains are desirable for applications requiring large amounts of current. Little is known, however, about the kinetic limitations for growth of HTSC materials from melts or semisolid mixtures.

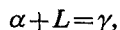
Solidification processing of HTSC materials is complicated by the tendency of ceramic materials to facet during solidification and by incongruent melting of the superconducting compounds. The peritectic reaction which occurs at the $\text{Ba}_2\text{YCu}_3\text{O}_{6.5}$ (BYCO) solidification interface can be described approximately by the following reaction:



Thus, solidification of BYCO occurs by reaction of a liquid (that is rich in copper) with the solid compound, BaY_2CuO_5 . Plane front solidification of BYCO must occur

under conditions where the liquid composition at the growing BYCO interface is greatly different from the solidified crystal. In addition, a change in copper oxidation state occurs on solidification.⁵ The solidification interface must, therefore, be supplied with sufficient oxygen to maintain thermodynamic stability of the phase. The nature of ternary equilibria in the Ba-Y-Cu-O freezing range is not completely known but is the topic of several recent studies, as will be discussed below.

The solidification of binary alloys having a peritectic reaction has been discussed by many authors. No studies report the implications of peritectic solidification theory on BYCO crystal growth. Figure 1 is a schematic pseudo-binary diagram of the type that is often used to describe phase equilibria for the B-Y-Cu-O system in the melting range. The peritectic reaction considered is that at approximately 1283 K



where approximate compositions of the three terms in Eq. (1) are given by α , c_{Lp} , and γ . In dendritic solidification, peritectic reactions such as this usually proceed by the γ phase "surrounding" the primary α phase. Subsequent reaction can then only occur by diffusion through the solid. As a result, the reaction rarely goes to completion.⁶⁻⁸ An exception is the iron carbon system where the high diffusivity of carbon in the solid results in complete transformation during (or after) solidification. Dendritic solidification of ternary alloys involving a peritectic system has also been studied, for example in the Fe-C-X system where one element (carbon) diffuses rapidly and the other

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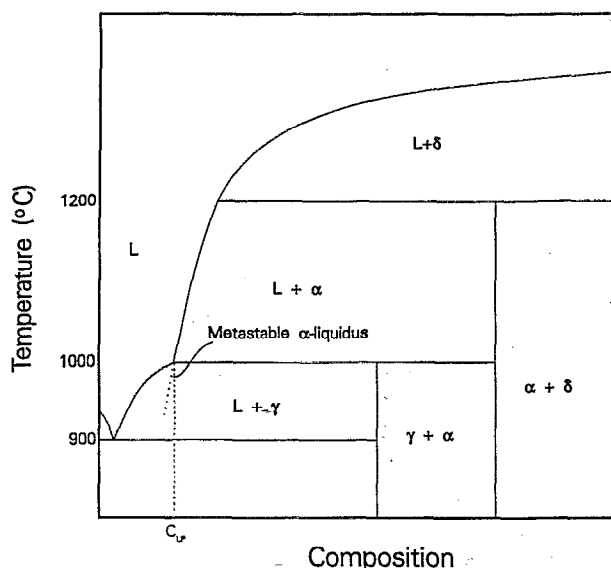


FIG. 1. A binary phase diagram containing a peritectic reaction $L + \alpha \rightarrow \gamma$ used in the peritectic solidification model.

slowly,^{9,10} and in the Ti-Al-B system where little solid diffusion occurs.¹⁰

In recent years, a number of studies have been conducted on directional solidification of peritectic alloys with controlled temperature gradient, G , and growth rate, R .⁷⁻¹¹ Microstructures obtained at high G/R are of particular interest in alloys that would be two phase, $\alpha + \gamma$, at equilibrium. Several investigators have proposed that at sufficiently high G/R and absence of convection, it should be possible to solidify a hypoperitectic alloy with a plane front directly from a liquid of the same composition. The solid forming would consist of a composite of $\alpha + \gamma$ with the amount of the high temperature solid phase, α , becoming vanishingly small as initial composition, approaches the peritectic composition.^{7,12,13} The two phases would form directly from the liquid at approximately the peritectic temperature. Recently, Boettinger¹¹ adapted the Jackson-Hunt analysis¹⁴ of eutectic growth to peritectics and concluded that "coupled growth" of the α and γ phases is inherently unstable. Boettinger *et al.* and Oliver and Kamad¹⁵ have found banded microstructures in directionally solidified Ti-Al alloys. Their results apparently support Boettinger's conclusion.

Incongruently melting phases (such as γ in Fig. 1) can be grown directly from melts which are very different from the composition of γ in the presence of convection. Thus, for example, γ of composition approximately $c_{s\gamma}$ can be grown from liquid of composition c_{Lp} . This is a simple binary representation of the "flux growth" mechanism successfully used to grow crystals of BYCO.¹⁶

In the absence of convection it is found that BYCO (γ of Fig. 1) can be grown from a semisolid two phase material consisting of α [$\text{BaY}_2\text{CuO}_5(s)$] and liquid.¹ It will be shown herein that the mechanism for accomplishing this is quite different from the "surrounding" and solid diffusion mechanism that is commonly observed in metals.

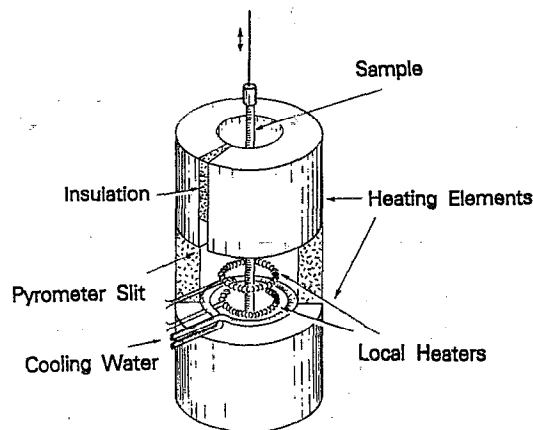


FIG. 2. Sketch of the EHFZ furnace.

In this study, BYCO crystals are grown from a semi-solid melt using two methods: electrically heated zone and laser-heated solidification. The interface temperature and morphology are reported as a function of process variables. It will be shown that the solidification mechanism is quite different from the surrounding and solid diffusion mechanism commonly observed in solidification of peritectic alloys.

EXPERIMENT

Figure 2 is a schematic diagram of the electrically heated resistance furnace used to prepare samples by the electrically heated floating zone method (EHFZ). Details can be found elsewhere.¹⁷ Briefly, two conventional electrical heating elements with length 0.051 m and diameter 0.019 m were arranged end-to-end and insulated. Located between the upper and lower heating elements were two smaller devices used to control the shape of the temperature profile. The upper device consisted of a coiled filament wire loop. The lower device consisted of a copper tubing loop which carried a constant flow of water. Inside this tubing loop and separated from the copper with insulation was another filament wire loop. The adjustable current through this filament wire permitted control of the cooling effect of the water flow. Furnace temperature and temperature profile was measured as described below by combination of thermocouple and optical pyrometry. The maximum temperature was controlled to be in the range 1315 to 1386 K and the thermal gradient in the freezing range was between 2.5×10^3 K/m and 1.1×10^4 K/m.

Presintered rods of BYCO were prepared from BaCO_3 , Y_2O_3 , and CuO by repeated calcination at 1223 K followed by isopressing in a rubber tube and sintering at 1258 K. The final diameter of the rods was 0.002 m, and they were nominally 0.07 m long. In making a run, one of the rods was suspended in the furnace using platinum wire and rapidly lowered into the hot furnace until the top of the rod was approximately 0.025 m below the top of the furnace. It was then pulled up through the furnace at a rate from 0.08 to $3.6 \mu\text{m/s}$ and quenched in oil after solidifying typically 0.015 m of material. A total of 51 runs were made; these

TABLE I. Temperature gradient, interface type, and interface temperature for samples grown in the EHFZ furnace.

Sample	Growth rate ($\mu\text{m/s}$)	Temperature gradient (10^4 K/m)	Interface type	Interface temperature	
				Tip ($^{\circ}\text{C}$)	Root ($^{\circ}\text{C}$)
1R	0.08	1	a3		
2R	0.14	1.08	a3	1010	1006
3R	0.22	0.98	a3	1001	1000
4R	0.28	0.27	a3		
5R	0.28	0.52	a3		
6R	0.28	0.6	a3		
7R	0.29	0.86	a3		
8R	0.31	0.58	a3		
9R	0.31	0.91	a3		
10R	0.31	1	a3		
11R	0.31	1.22	a3	992	986
12R	0.33	0.31	a3		
13R	0.39	0.84	a3		
14R	0.42	0.9	a3		
15R	0.46	0.98	a3	976	967
16R	0.48	0.44	a3		
17R	0.55	0.31	a3		
18R	0.56	0.92	a3		
19R	0.56	1	a3		
20R	0.61	0.9	a3		
21R	0.72	0.31	a3		
22R	0.75	1.02	b2	972	972
23R	0.76	0.78	a3		
24R	0.78	1	a3		
25R	0.83	1.14	a3		
26R	0.91	0.25	a3		
27R	1.1	0.91	b2		
28R	1.11	1	b2	971	967
29R	1.28	1	b2		
30R	1.57	0.58	b2		
31R	1.58	0.9	b2		
32R	1.61	1	b2		
33R	1.77	0.58	b2		
34R	1.82	0.9	b2		
35R	1.86	0.58	b3		
36R	1.86	0.78	b2		
37R	1.86	0.9	b2		
38R	2.03	0.78	b2		
39R	2.08	1	b3		
40R	2.17	0.75	b3		
41R	2.22	0.31	c		
42R	2.23	1	b3	977	947
43R	2.42	0.78	b2		
44R	2.63	0.26	c		
45R	2.78	0.68	b2		
46R	2.83	0.92	b3		
47R	2.95	1	b3		
48R	3.03	0.75	b3		
49R	3.22	0.78	b2		
50R	3.28	0.9	b2		
51R	3.61	1	b3		

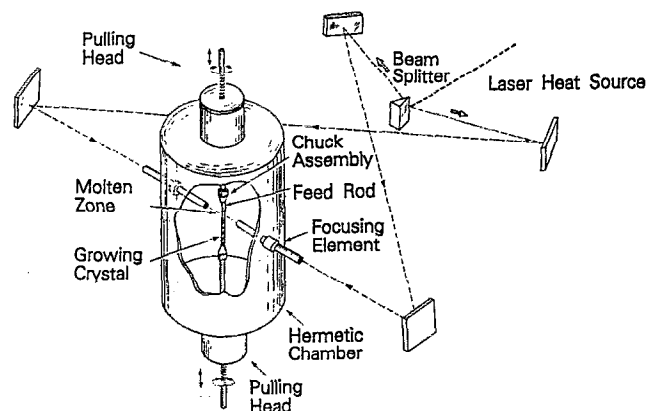


FIG. 3. Sketch of laser heated float zone (LHFZ) furnace.

Commercial 300 μm diameter sintered fibers (CPS Superconductor Co., Milford, MA) were used as feed materials for the LHFZ process. The fibers were composed of BYCO plus 22.8 wt. % BaY_2CuO_5 and their fabrication is described by the manufacturer.¹⁹ As-received fibers were cut into pieces several centimeters long and gripped by chucks with two axes of rotation and two axes of triangulation to allow precise vertical alignment. Two opposing beams were focused onto the fiber to produce a spot size of 900 or 1500 μm . Typical molten zone lengths of 1 or 2 fiber diameters were established in this way. The fibers were pulled through the hot zone using three different methods. In method 1, the fiber was gripped only from above and passed through the hot zone in a downward direction by a motor drive attached to the chuck. In method 2, the fiber was gripped from above and below. Two fiber segments were moved in opposite directions towards the hot spot where they were fused. The lower chuck was immediately reversed and the connected segments were then moved in a downward direction. This method had the advantage that the fiber diameter could be controlled by varying the relative translational velocity of the upper and lower chucks. Method 3 is similar to method 2 except that the pulling direction was upwards. Fibers were grown at nominal rates from 1 to 7 $\mu\text{m/s}$. After the desired length was obtained, the growth was interrupted by closing the beam shutter. This essentially quenched the partially molten zone for subsequent metallographic observation.

The maximum temperature in the zone was above the peritectic temperature but low enough that the zone contained substantial amounts of solid BaY_2CuO_5 . The maximum temperature of the zone in the LHFZ apparatus was measured during growth by optical pyrometry. Measurements were uncorrected for emissivity. The maximum temperature was set in the range 1370 to 1433 K by adjustments of the laser power. Estimates of the temperature gradient were made by measuring the zone length in metallographic sections of quenched fibers. The gradient in the liquid was taken to be the temperature difference between the maximum measured temperature and the peritectic temperature (1273 K) divided by half the zone length. These calculations typically gave gradients that were of the

runs are reported in Table I, along with growth rates (sample pull rates) and the measured temperature gradient.

The laser-heated floating zone technique (LHFZ) used in this study is shown in Fig. 3 and described elsewhere.¹⁸ It consists of a 100-W CO_2 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.

TABLE II. Types of interface and number of grains observed on longitudinal sections of LHFZ samples.

Sample	Growth method ^a	Growth rate ($\mu\text{m/s}$)	Temperature gradient (10^6 K/m)	Interface type ^b	Beam diam. (μm)	Zone length (μm)	Diameter		Number of grains
							Feed (μm)	Fiber (μm)	
1L	1	1.4	0.90	a3	900	330	300	325	2
2L	1	1.4	1.10	a3	900	210	300	~300	3 to 5
3L	1	1.4	1.30	a3	900	210	300	300	3 to 5
4L	1	1.7	2.30	a3	900	120	300	290	2
5L	1	2.2	1.00	a2	900	310	300	290	1
6L	2	2.2	2.30	a1	900	120	300	290	1
7L	2	2.8	0.50	a1	1500	410	250	200	1
8L	1	2.8	0.60	a3	1500	550	250	220	$> 10^c$
9L	2	2.8	0.60	a3	1500	550	250	220	10^c
10L	1	2.8	0.80	a3	900	350	300	240	6^c
11L	1	2.8	1.30	a2	900	220	300	280	1
12L	2	2.8	1.30	a2	900	220	300	260	1
13L	2	2.8	1.90	a2	900	160	300	280	1
14L	3	3.3	1.90	a3	900	160	300	230	8^c
15L	1	3.3	0.90	a3	900	350	300	300	polycrystalline
16L	3	3.3	1.40	b1	900	210	250	180	polycrystalline
17L	2	4.2	0.60	b1	1500	550	250	220	polycrystalline
18L	1	4.2	1.10	b1	900	260	300	300	polycrystalline
19L	1	4.2	1.10	b1	900	270	300	280	polycrystalline
20L	3	5	1.20	b1	900	250	300	225	polycrystalline
21L	3	5.6	0.90	b1	900	330	300	225	polycrystalline
22L	1	5.6	1.00	b1	900	290	300	300	polycrystalline
23L	3	6.9	1.00	b1	900	300	300	230	polycrystalline

^aGrowth method: See text for explanation.^bSee Fig. 5 for explanation.^cNon-steady state (short fiber).

order of 10^6 K/m . A total of 23 runs was successfully carried out by laser growth; these runs are summarized in Table II. The atmospheres used in the two processes were slightly different; the LHFZ experiments were performed under oxygen (1.27 atm) while the EHFZ experimental atmosphere consisted of either ambient conditions or flowing oxygen.

GENERAL OBSERVATIONS OF QUENCHED INTERFACES

Figure 4 summarizes the interface morphologies observed in all EHFZ and LHFZ samples. Three different growth regimes are revealed when the interface morphologies are plotted on a graph of temperature gradient, G , versus growth rate, R . The three types of interfaces are termed, "faceted/plane front," "cellular/dendritic," and "equiaxed blocky."¹⁰ Note that the temperature gradient axis spans two orders of magnitude while the growth rate has a linear axis. A one hundred-fold increase in temperature gradient, from 10^4 K/m to 10^6 K/m , increases the critical growth rate for large faceted crystals by only a factor of two.

The three terms describing interface morphology are explained by the schematic illustration of the BYCO interface in the quenched specimens shown in Fig. 5. Note there are several different types of structures grouped in the first and second categories; these are termed a1, a2, a3, and b1, b2, b3, respectively, and these designations correspond to

the experiment observations reported in Tables I and II. Polished sections of representative quenched interfaces are shown in Figs. 6 and 7 for the EHFZ and LHFZ, respectively. Figure 6 illustrates structures a3, b2, b3, and c. Figure 7 illustrates four types of structures; a1, a2, a3, and b1.

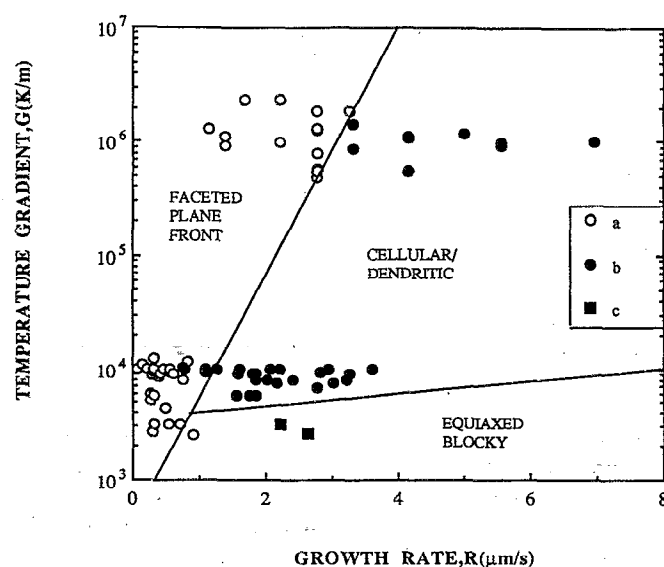


FIG. 4. Effects of temperature gradient and growth rate on the morphology of the solidification interface.

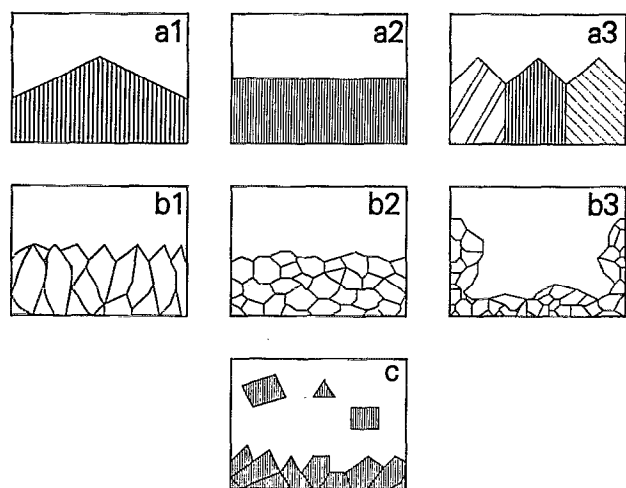


FIG. 5. Sketches of interface morphology.

RESISTANCE FURNACE GROWN SAMPLES

Examination of the directionally solidified material grown in the resistance furnace, using electron microscopy and optical microscopy indicates it is multiphase and consists of a matrix of BYCO with BaY_2CuO_5 inclusions that are approximately 5 to 15 μm in diameter. The identification of phases was made by energy dispersive x-ray analysis. These microstructural features are commonly found in BYCO samples prepared by solidification processing.²⁻⁴ The multiphase nature of solidified stoichiometric samples is the result of incomplete peritectic reaction, which entraps grains of the high temperature phase, BaY_2CuO_5 , within the BYCO grains.

The solidification interface changes from highly faceted, to a cellular/dendritic or equiaxed microstructure with increasing growth rate. Samples prepared with relatively low temperature gradients of approximately 3×10^3 K/m and growth rates greater than 1 $\mu\text{m/s}$ show an equiaxed blocky microstructure. Large faceted grains of BYCO are observed growing within the partially molten zone. Regions that are rich in barium and copper are found in the solidified material and are apparently formed from residual melt. These regions are rather large but relatively infrequent in samples produced at growth rates less than 1 $\mu\text{m/s}$.

The most prominent features in Fig. 6 are the highly faceted interfaces between the solidified material and the quenched zone for samples produced at low growth rates. The facets are often oriented at approximately 45° with respect to the rod axis. The exact facet orientation is, of course, difficult to establish from a two-dimensional random section like those shown in Fig. 6. A maximum growth rate for highly faceted interfaces is observed to be between 1.3 and 1.6 $\mu\text{m/s}$. The material produced by quenching the molten zone is hydrolytically unstable. We commonly observe etching of the barium- and copper-rich portions of these samples from ambient humidity. This reaction is specific and can be used to etch away much of the quenched zone. The resulting surface can be viewed by

scanning electron microscopy, which shows that the facets form ridges that are long in the direction perpendicular to the short faces.

X-ray pole figure analysis of transverse cross sections indicates preferential orientation of the crystals such that the {103} plane is perpendicular to the growth direction. The orientation, however, is often not perfect and infrequently deviates by as much as 25°. This observation contrasts with many reports that find preferred *a*-axis orientation when BYCO is solidified in a temperature gradient.^{3,20,21} Several low index crystal planes are consistent with the 45° orientation of the facets with respect to the {103} plane: {001}, {100}, and {110}. Pole figure x-ray analysis, however, shows that only the {001} and {200} planes are 45° to the {103} and that the {110} reflection cannot be detected in the hemisphere formed from transverse section. This suggests that the facets are formed along the {001} and {100} planes. These planes are also the most commonly observed facets for flux grown crystals, indicating the {001} and {100} planes are slow growth surfaces.

Temperature versus position in the furnace, as indicated earlier, was known from thermocouple profiles of the furnace prior to inserting the sample rod. These measurements were confirmed for temperatures in the region of the interface (1223–1323 K) by optical pyrometry which agreed with the thermocouple profile within about 5 K. Knowing the temperature distribution and specimen location, it was then possible to determine temperature of the growing BYCO interface after determining location of the interface metallographically. Results of experiments on a series of seven runs are plotted in Fig. 8. Note that interface temperature drops rapidly from about 1283 to 1243 K at low growth rates. At higher growth rates, solidification takes place over a range of temperatures. Here, the temperature of the “tip” of the solidification front is essentially constant with increasing growth rate while the temperature of the “root” of the solidification front drops.

LHFZ GROWN SAMPLES

The stability of the partially molten zone in LHFZ growth was observed to depend on temperature, growth rate, and growth method. Stable zones were formed when the maximum zone temperature did not exceed 1423 K and growth rates were above 1.4 $\mu\text{m/s}$. Instability of the zone at lower growth rates appeared to be associated with migration of liquid from the zone toward the cooler region of the sample.

Faceted solidification interfaces were also observed in the LHFZ fibers at low growth rates, as shown in Fig. 7. The microstructure again varies in a systematic way with growth rate with a gradual transition from faceted/planar and faceted interfaces to cellular dendritic interfaces with increasing growth rate. The dimensions of the facets are, however, much smaller than those obtained in the resistance furnace. Some of the fiber solidification interfaces appeared flat with single crystal growth of BYCO occurring in the solidified material. The BYCO grains occupy

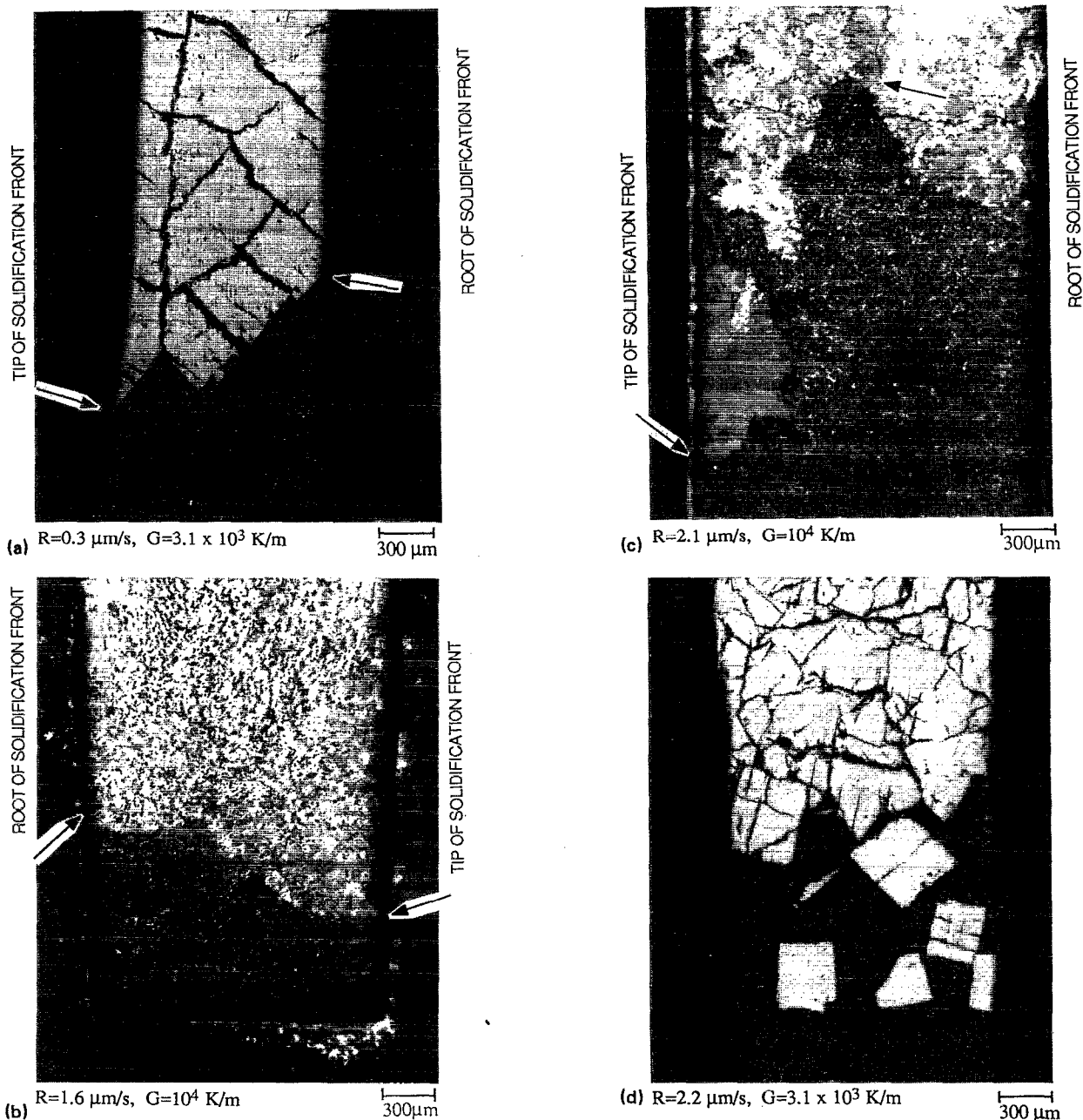


FIG. 6. Microstructures from samples grown in the EHFZ furnace. (a) Faceted plane front, type a3; (b) Cellular/dendritic, type b2; (c) Cellular/dendritic, type b3; (d) Equiaxed blocky, type c.

much of the fiber cross sections for many of the samples as determined by optical microscopy with polarizing filters. These grains are continuous indicating that secondary nucleation is relatively infrequent. Single crystal fibers were produced at intermediate growth rates (Table II). A number of grains (three or four) were observed in fibers prepared at the slower rates. This phenomenon is possibly related to the difficulty in producing stable zones at low growth rates, as described above.

The effect of the peritectic reaction on BaY_2CuO_5 particle size is shown in Fig. 9. The quenched interface of a sample prepared by LHFZ has been sectioned and polished so that the microstructure in both the solidified and partially molten regions can be resolved. The volume fraction

and BaY_2CuO_5 particle size abruptly decreases upon being engulfed in the growing BYCO crystal and remains constant as a function of distance into the crystal. The solidified region contains a higher volume fraction of BaY_2CuO_5 than do samples prepared in the electrically heated furnace, because the fibers are initially rich in BaY_2CuO_5 . Residual liquid phase is difficult to find, presumably because of more complete reaction due to excess BaY_2CuO_5 . The figure clearly illustrates that the peritectic reaction occurs largely or entirely in a volume very close to the solidification interface.

The average BaY_2CuO_5 particle size in the zone and in the solidified material varies with residence time in the zone as shown in Fig. 10. The average particle sizes were

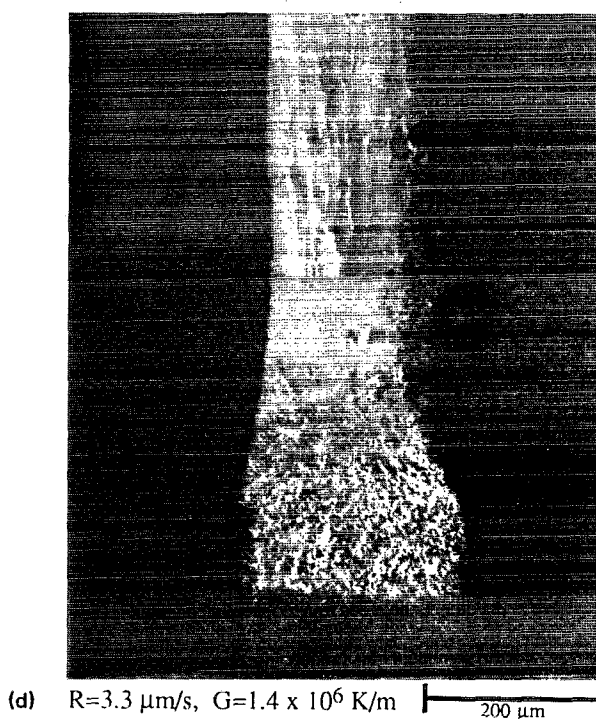
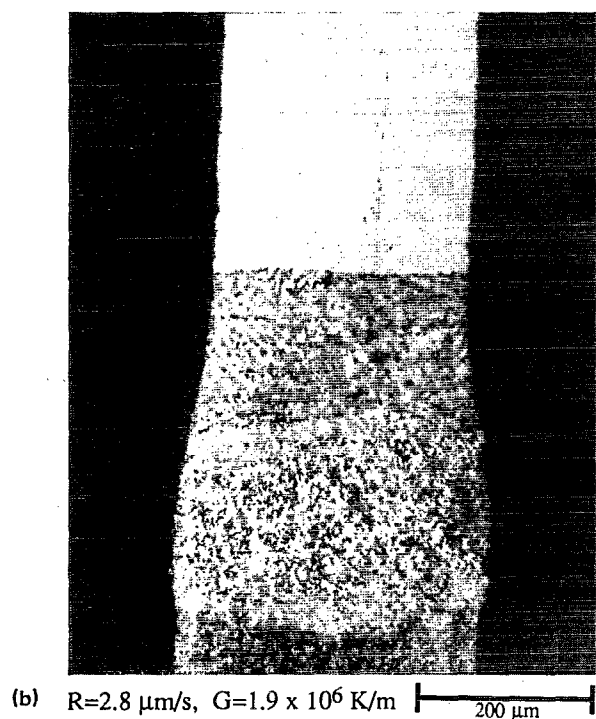
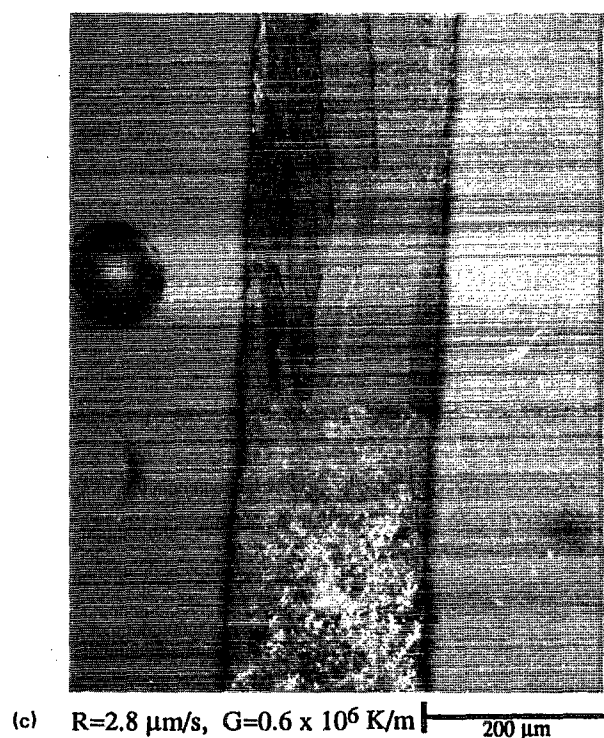
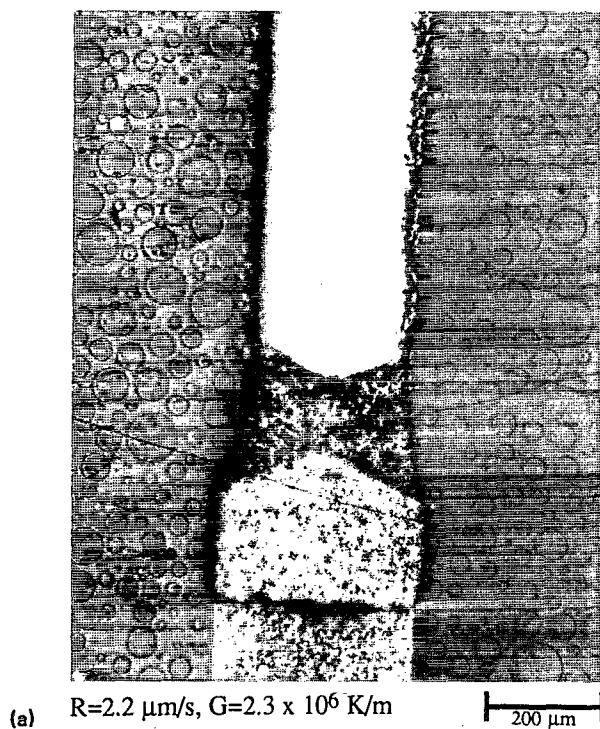


FIG. 7. Microstructures grown in the laser heated float zone furnace. (a) Faceted/plane front, type a1; (b) Faceted/plane front, type a2; (c) Faceted/plane front, type a3; (d) Cellular/dendritic, type b1.

obtained by a line intercept method²² using a series of photomicrographs of the LHFZ samples. Increasing residence time gives increasing BaY_2CuO_5 particle size suggesting that the particles coarsen when in contact with liquid. The particle size in the solidified material does indeed follow a $1/3$ power dependence with residence time. The average particle size in the zone, however, has a 0.8 power dependence. The BaY_2CuO_5 particles within the zone appear to

have a bimodal size distribution. This phenomenon is likely the result of the excess BaY_2CuO_5 which is added to the feed material. The excess BaY_2CuO_5 apparently has a particle size distribution which is distinct from that produced from the melting of BYCO. Finer particles are apparently produced at the melting interface. The fine particles are preferentially consumed as is indicated by the increase in average particle size upon solidification.

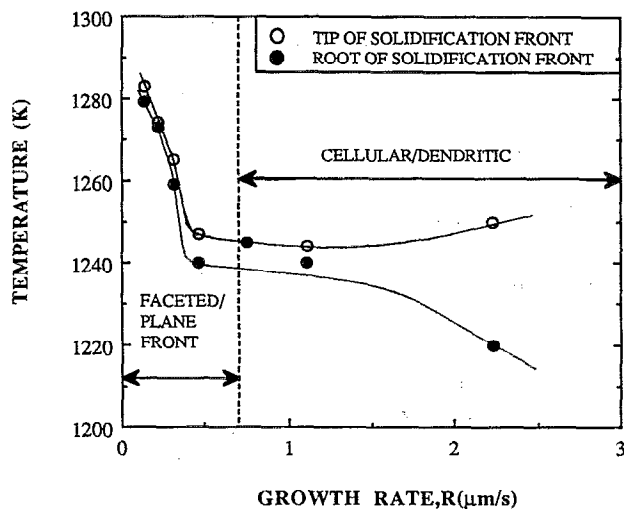


FIG. 8. Undercooling at the solidification front.

PERITECTIC SOLIDIFICATION FROM A SEMI-SOLID MELT

A simple model for peritectic solidification is described in this section to aid in the interpretation of the experimental observations above. Only the general features of the true Ba-Y-Cu-O phase diagram are known in the melting range.²³ Thus, for simplicity, we consider solidification with peritectic reaction for the case of a binary system. We refer to Fig. 1 in the following as if it were a true binary diagram.

The main assumption of our model is that the peritectic reaction takes place by diffusional transport through the liquid. That is, the α phase particles dissolve in the liquid



FIG. 9. Microstructure of the region containing the solidification interface of a LHF sample. (Top) liquid + 121; (bottom) 213 + 121.

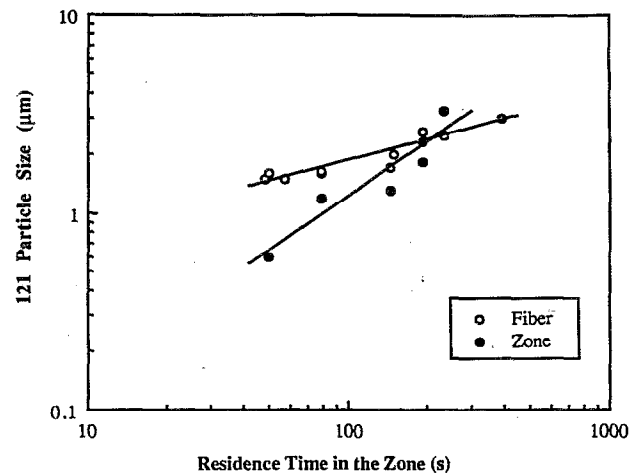


FIG. 10. Dependence of 121 particle size on the residence time in the semisolid zone. The measurements were done close to the solidification interface in the 121 + L and in the 213 + 121 regions.

in the region just ahead of the solidification interface. Solute then diffuses toward the interface where it is consumed by growth of the crystal. This interpretation is based on our microstructural observation of the solidification interface, shown in Fig. 9.

Assume now that α particles are separated by a distance $2l$ and the alloy is slightly hypoperitectic so some α phase is retained in the final structure. The diffusion profile in the growth direction (x) in front of the growing γ interface varies with time and location y perpendicular to the growth direction. Schematically, this profile is shown in Fig. 11(b), along the line AA' of Fig. 11(a). In the following, we will take this curve to represent the time average solute profile in front of the growing interface. The curve is drawn assuming diffusion to the interface over an average distance l , with liquid compositions at $x=0$ and at $x=l$ determined as follows.

First, we assume that the α particles are in interfacial equilibrium with their surrounding liquid and are large enough that the effect of radius of curvature on melting point is negligible. Of course, if the particles are sufficiently small, this radius of curvature effect could be a significant, even a major, driving force for the mass transport leading to γ solidification. Izumi *et al.* have considered the case in detail where radius of curvature the α comprises the driving force for the peritectic reaction.²⁴

The interfaces are faceted in the actual case of solidification of BYCO and so not in equilibrium with the melt. Indeed, this faceting may be essential to achieving the plane front solidification observed in BYCO. Nonetheless, we assume that the undercooling at the faceted interface is small compared with the solutal undercoolings to be described below, and assume the equilibrium partition ratio applied also at the γ interface.

Figure 12 is an expanded portion of the phase diagram of Fig. 1, in the region of the peritectic. The dashed line is the metastable extension of the α liquidus. The temperature of the growing γ interface, T_0 , is undercooled an

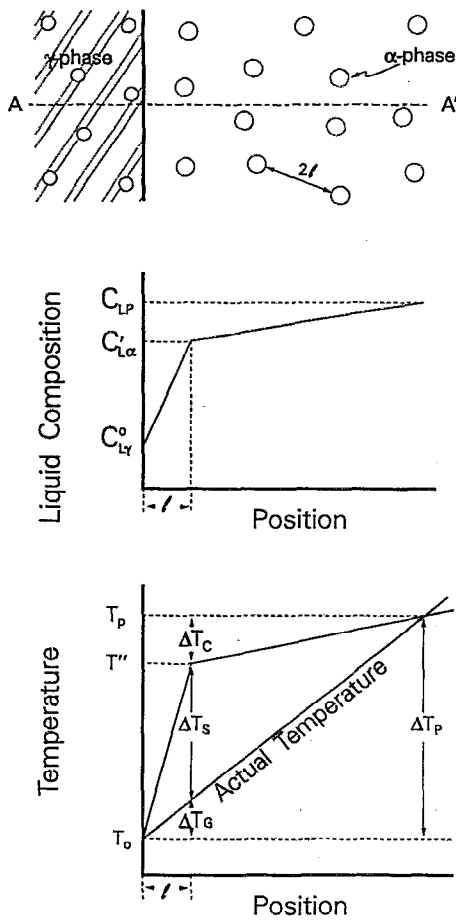


FIG. 11. Peritectic solidification model; (b) Solute diffusion profile in front of the growing γ interface; (c) Temperature distribution in the liquid ahead of the solidification interface.

amount ΔT_p below the peritectic temperature, T_p , where

$$\Delta T_p = \Delta T_G + \Delta T_s + \Delta T_c \quad (2)$$

where ΔT_G is depression of the integrated temperature resulting from the temperature gradient, G . ΔT_s is the maximum "constitutional supercooling" ahead of the interface

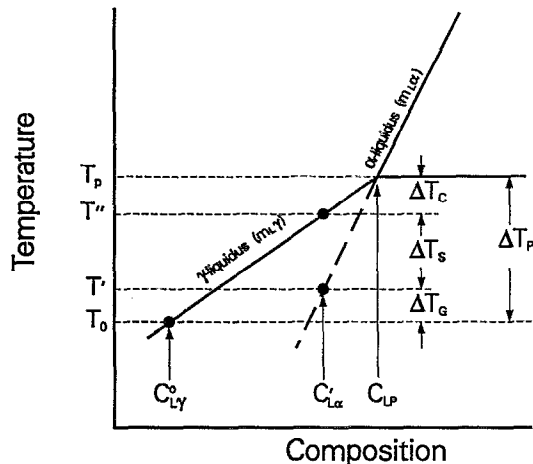


FIG. 12. Enlarged section of the phase diagram.

(i.e., temperature difference between the equilibrium liquidus and the actual temperature at $x=l$). ΔT_c is the temperature depression resulting from the deviation in solute concentration at the α interface from that of the peritectic liquid composition, c_{Lp} . These quantities are shown diagrammatically in both Figs. 11(c) and 12. From Fig. 11(c),

$$\Delta T_G = (T' - T_0) = Gl. \quad (3)$$

The solute content in equilibrium with the γ interface (at $x=0$, $T=T_0$) is $c_{L\gamma}^0$, and that at $x=l$ and T' in equilibrium in the α particles is $c_{L\alpha}'$. These quantities are shown in Figs. 11(b) and 12. These two points define the solute distribution curve of type 11-(b) for $x < l$. For $x > l$ the curve is given by the equilibrium α liquidus. Equating solvent rejected from the growing γ interface with that diffusing into the liquid gives

$$-R(c_{s\gamma} - c_{L\gamma}^0) = -D_L \left(\frac{c_{L\alpha}' - c_{L\gamma}^0}{l} \right), \quad (4)$$

where R is the growth rate and D_L is the diffusion coefficient of solute in the liquid. The slope of the equilibrium γ liquidus and metastable α liquidus are both assumed to be constant and are denoted $m_{L\gamma}$ and $m_{L\alpha}$, respectively. A relation between interface undercooling (ΔT_p) and growth rate, R , can be derived by assuming $c_{s\gamma} - c_{L\gamma}^0 \approx c_{s\gamma} - c_{Lp}$ and by substituting relationships for $c_{L\gamma}^0$ and $c_{L\alpha}'$ into Eq. (4). Linear liquidus lines, as shown in Fig. 12, result in $c_{L\gamma}^0 = c_{Lp} - \Delta T_p/m_{L\gamma}$ and $c_{L\alpha}' = c_{Lp} - (\Delta T_p - \Delta T_s)/m_{L\alpha}$. Substitution of these expressions into Eq. (4) and making use of Eq. (3) gives

$$\Delta T_p = \left[\frac{Rl}{D_L}(c_{s\gamma} - c_{Lp}) - \frac{Gl}{m_{L\alpha}} \right] \frac{m_{L\gamma}m_{L\alpha}}{m_{L\alpha} - m_{L\gamma}}. \quad (5)$$

Thus, ΔT_p is linearly proportional to R when G is sufficiently small. Similarly, the following relation can be written between R and ΔT_s

$$\Delta T_s = m_{L\gamma} \frac{Rl}{D_L}(c_{s\gamma} - c_{Lp}) - Gl. \quad (6)$$

The quantity ΔT_s is the constitutional supercooling at $x=l$; it is the maximum constitutional supercooling in the semisolid region. In solidification of this type, there must always be finite constitutional supercooling in front of the growing interface in order to create the compositional driving force for diffusion from the particle surface to the crystal interface. Apparently, the surface energy relationships and faceting effect permit interface stability with some finite amount of undercooling ΔT_s (or, alternately stated, with some finite gradient of undercooling) $\Delta T_s/l$. Thus, if some specific maximum constitutional supercooling is assumed, Eq. (6) provides a description of the important variables which influence maximum growth rate, $R_{\max}$, for plane front solidification. The equation may therefore be written:

$$R_{\max} = \frac{D_L}{l(c_{s\gamma} - c_{Lp})} \left[\frac{(\Delta T_s)_{\max} + Gl}{m_{L\gamma}} \right]. \quad (7)$$

The significance of temperature gradient, G , depends on the relative magnitude of Gl and $(\Delta T_s)_{\max}$. Since l is of the order of the particle dimension, Eq. (7) indicates that the maximum growth rate is relatively insensitive to temperature gradient.

An interesting feature of this type of solidification is that the total depression of the interface temperature, ΔT_p , may be much greater than the constitutional supercooling, ΔT_s , when $m_{L\alpha} \rightarrow m_{L\gamma}$. This may be seen by combining Eqs. (6) and (7):

$$\Delta T_p = \left(\frac{m_{L\alpha}}{m_{L\alpha} - m_{L\gamma}} \right) \Delta T_s + Gl. \quad (8)$$

At values of $R > R_{\max}$ we expect cells, dendrites, or new grains to form as was experimentally observed in this study. On the basis of established solidification principles, we expect that at $R > R_{\max}$, where cells or dendrites form, the "tip" of the solidifying front should cease dropping rapidly with increasing R .⁷ The temperature of the "root" of the solidification interface should, however, continue to drop, ultimately reaching (in this case) the eutectic temperature of approximately 1173 K. These expectations are in qualitative agreement with the experimental results shown in Fig. 8.

DISCUSSION

The experimental evidence shown in Fig. 4 indicates that the maximum velocity for continuous growth of BYCO crystals does not vary significantly between the methods used in this study. This occurs despite greater than two orders of magnitude difference between the temperature gradients in the EHFZ and LHFZ methods. Also, the growth velocities required in this study to produce large grains of BYCO in a temperature gradient are also similar to that observed by others. It is, however, often difficult to compare the results of other studies because of the variety of experimental configurations and the difficulty in measuring temperature gradients. Experimental methods involve either motion of the sample in a static temperature gradient or a time varying temperature profile. Wang *et al.*²⁰ obtained oriented BYCO by halogen lamp heated floating zone at growth rates of 1.8 $\mu\text{m/s}$ in a gradient of 1.4×10^4 K/m. Shi *et al.*²¹ prepared oriented BYCO by cooling a partially molten sample at 5.6×10^{-3} K/s in a zirconia crucible in a temperature gradient of 2×10^3 K/m. Combination of their cooling rate and temperature gradient suggests an effective growth rate of 0.14 $\mu\text{m/s}$.

The theoretical analysis, above, suggests the fundamental importance of growth rate for semisolid solidification of BYCO crystals. The model assumes that the composition gradient between the crystal interface and BaY_2CuO_5 particle surfaces is responsible for a significant portion of the interfacial undercooling. The magnitude of the total temperature depression of the interface is intimately related to phase equilibria in the region of the peritectic, as described in Eq. (5). Reference to the simple binary phase diagram in Fig. 1 shows that the liquidus slopes must be large for small c_{Lp} . That is, for a given

eutectic and peritectic temperature, $m_{L\gamma}$ and $m_{L\alpha}$ increase as c_{Lp} decreases. Thus, Eq. (5) predicts ΔT_p to be large for systems in which the solute is sparingly soluble. Studies of high temperature phase equilibria in the Ba-Y-Cu-O system indicate that the amount of dissolved yttrium at the peritectic temperature is very small. Oka *et al.*²⁶ report that the maximum solubility of $\text{Ba}_2\text{YCu}_3\text{O}_{6.5}$ in $\text{Ba}_3\text{Cu}_7\text{O}_{10}$ liquid is 15% on an atom basis at the peritectic temperature which is equivalent to a yttrium content of less than 2.3 mole %. Fischer *et al.*²⁷ report that the maximum solubility of yttrium in the melt is only 2 mol%. Other studies also report that the ternary eutectic between $\text{Ba}_2\text{YCu}_3\text{O}_{6.5}$, CuO, and BaCuO_2 has very little yttrium and that the primary phase field for $\text{Ba}_2\text{YCu}_3\text{O}_{6.5}$ is very small.^{25,28} A comprehensive study by Maeda *et al.*²⁸ reports that the yttrium solubility is 2 mol% as Y_2O_3 and that the slope of the BaY_2CuO_5 liquidus is large compared with that for BYCO near the peritectic temperature.

Consideration of the rate at which yttrium can be transported to the growing interface is also helpful to understand the importance of yttrium solubility. Growth of a BYCO crystal at a freezing interface requires that yttrium be supplied at sufficient rate to the growth interface. Equation (4) describes this mass balance restriction. The supply of yttrium solute is provided by dissolution of BaY_2CuO_5 in the liquid ahead of the growth interface. Since yttrium is only sparingly soluble in the liquid, it seems likely that its transport to the interface would be the rate limiting step at sufficiently high growth rates.

The predictive power of Eqs. (5) and (7) can be tested by suitable approximation of the diffusivity and phase equilibria. Data on the diffusivities of cations in cuprate melts are not known to the authors. Estimates for the yttrium diffusivity can, however, be obtained from the coarsening data shown in Fig. 10. Ostwald ripening of ceramic grains in contact with liquids at high temperature has been used to estimate liquid diffusivities. These studies are reviewed by White²⁹ and Fischmeister and Grimvall.³⁰ Classical coarsening models like those developed by Greenwood,³¹ Wagner,³² and Lifschitz *et al.*³³ are found to be applicable even at high concentrations of solid particles. The relationship between grain size and time is often stated as³¹

$$r^3 - r_0^3 = \frac{6DcM^2\gamma}{\rho^2RT}(t - t_0), \quad (9)$$

where M and ρ are the molecular weight and density of the precipitate. The interfacial energy between the particles and the liquid is γ , and R and T are the gas constant and temperature, respectively. The characteristic particle radius, r , is for those particles that are twice the mean particle size. Residence times of 390 s are required for the particles to grow to an average of 3 μm in diameter from an initial size of approximately 1 μm . Substitution shows that the group of constants on the right in Eq. (9) is approximately 8.0×10^{-21} m^3/s . This group of constants can be used to estimate the diffusivity since all other terms are approximately known. The density and molecular weight of BaY_2CuO_5 are 6.2×10^3 kg/m^3 and 0.459 kg/mole, respectively, and the average temperature of the zone is

taken as 1400 K. The interfacial energy is taken as 0.5 J/m², a value considered representative of many ceramic systems in liquid oxides.³⁴ A liquid composition of 2 mole% BaY₂CuO₅ at the peritectic temperature is consistent with the phase equilibria studies, discussed above. The composition is equivalent to 0.8×10^3 mole/m³. The consistent diffusivity has a value of 6×10^{-11} m²/s which is not unlike that expected for diffusivities in metal oxide melts.³⁴

Estimates of the liquidus slopes, $m_{L\alpha}$ and $m_{L\gamma}$, are also required to use Eqs. (5) and (7). The freezing range over which BYCO is in equilibrium with liquid is approximately 100 K (Ref. 27) while the composition varies from c_{Lp} to the eutectic composition, c_{eu} . The eutectic is known to contain only very small amounts of yttrium.²⁷ A rough estimate of $m_{L\gamma}$ is therefore, $100/(0.8 \times 10^3 - 0.00)$ or 0.125 K m³/mole. The liquidus slope of the high temperature phase, BaY₂CuO₅, is more difficult to estimate. Phase equilibria results²⁸ do indicate that the liquidus composition varies significantly from c_{Lp} only when the temperature is much greater than the peritectic temperature. This is consistent with a comparatively large value of $m_{L\alpha}$. The effect of this slope enters Eq. (5) through the term $m_{L\alpha}/(m_{L\alpha} - m_{L\gamma})$ which is close to unity for large values of $m_{L\alpha}$.

Equation (5) indicates that the total interface undercooling is linearly proportional to the growth rate, R , at sufficiently small values of Gl . This is indeed observed in Figure 8 for growth rates where large facets are present at the solidification interface. The observed ratio $\Delta T_p/R$, is approximately 9.3×10^7 K s/m. The approximations above permit comparison between the observed slope and the calculated value of the slope. The average particle size for the EHFZ samples is approximately 10 μm. We assume that the length scale for diffusion is roughly the same magnitude ($l = 10$ μm) and that D_L and $m_{L\gamma}$ are approximately 6×10^{-11} m²/s and 0.125 K m³/mole, respectively. Secondly, the concentrations c_{γ} and c_{sp} are taken as 4.8×10^3 and 0.8×10^3 mole/m³, respectively. Finally, if $m_{L\alpha}/(m_{L\alpha} - m_{L\gamma})$ is close to unity, substitution in Eq. (5) predicts $(\Delta T_p/R)_{calc}$ is 8.3×10^7 Ks/m. The calculated value is remarkably close to that observed.

The data in Fig. 4 indicate a slight temperature gradient dependence of the maximum growth rate for planar growth. This second-order dependence is predicted by Eq. (7). Diffusion length scales of the order of the particle size suggest, however, that the Gl term is insignificant for the temperature gradients used in this study, since $\Delta T_G \approx (3 \times 10^{-6} \text{ m})(10^6 \text{ K/m}) = 3 \text{ K}$ for the LHFZ samples and $(10 \times 10^{-6} \text{ m})(10^4 \text{ K/m}) = 0.01 \text{ K}$ for the EHFZ samples. Thus, the apparent increase in interface stability of LHFZ grown samples over those prepared by EHFZ cannot be completely attributed to the effect of temperature gradient. The fibers for LHFZ were richer in BaY₂CuO₅ than the rods used in the EHFZ experiments and contained much smaller initial BaY₂CuO₅ particle size. Secondly, the fiber zone length during LHFZ was much shorter than that during EHFZ which means that particles had much longer residence times in the later case. Thus, coarsening is much more significant in the EHFZ experiments. These factors

combine to effectively reduce the characteristic diffusion distance in the LHFZ samples which in turn requires a large growth rate to produce the same degree of undercooling, as predicted by Eq. (5) in the limit of small Gl . Equation (5) also suggests that the ratio of maximum growth rates between the LHFZ and the EHFZ samples should be in the inverse ratio of the BaY₂CuO₅ particle sizes for each case or approximately $(10 \times 10^{-6} \text{ m})/(3 \times 10^{-6} \text{ m}) = 3$. The maximum growth rate does indeed differ by a factor of three between the two techniques, as shown in Fig. 4.

The magnitude of the undercooling shown in Fig. 8 is large, given what is known about the phase equilibria in the Ba-Y-Cu-O system. Equation (8) indicates that $\Delta T_s \approx \Delta T_p$ when $m_{L\alpha} \gg m_{L\gamma}$ and Gl is small. Thus, $(\Delta T_s)_{max}$ is of the order of $(\Delta T_p)_{max}$ or nearly 40 K. This is a substantial fraction of the freezing range over which BYCO is in equilibrium with liquid, known to be approximately 100 K.²⁵ The highly faceted morphology of the BYCO crystals is consistent with large interfacial energies which apparently contributes to the large undercooling required to nucleate new BYCO grains ahead of the solidification interface. The data in Figure 8 also indicate that BaY₂CuO₅ particles do not act significantly as nucleation sites for the growth of BYCO crystals. Otherwise, nucleation would occur at temperatures much closer to the peritectic temperature.

CONCLUSIONS

Semisolid solidification of HTSC oxides is accompanied by several phenomena that are not encountered in conventional solidification. First, the peritectic reaction occurs by dissolution of the high temperature phase (BaY₂CuO₅) into the liquid followed by reprecipitation on the BYCO crystal surface. This interpretation is the result of direct microstructural observation of quenched solidification interfaces. The reaction effectively stops once the crystal engulfs the high temperature phase since the contribution of solid-state diffusion is negligible. Thus, the reaction *does not* proceed by the more conventional mechanism in which reaction occurs at the interface between the high temperature phase and the liquid.

Secondly, the high temperature phase particles must become supercooled very close to the crystal interface in order to create the concentration gradient needed to drive mass transport and thereby sustain the reaction. Consideration of the mass transport restrictions and the thermodynamic driving force shows that the largest constitutional undercooling is a small distance ahead of the interface. This condition in classical solidification would normally cause a planar solidification interface to become unstable since small perturbations would grow. The situation with BYCO is, however, much different. Apparently, the highly faceted crystal interface prevents the growth of such perturbations and the growth becomes limited by the undercooling that will cause nucleation of new crystals ahead of the interface.

The concepts above can be expressed quantitatively and be used to show that the maximum growth rate at which a planar interface can be sustained is inversely proportional to the BaY₂CuO₅ particle size. This model quan-

tatively predicts the relationship between interface undercooling and growth rate when reasonable values of the physical parameters are used. The magnitude of the temperature gradient has only a minor effect on the maximum growth rate for planar solidification as was observed experimentally. Analysis indicates that production of single crystal filaments of BYCO using simple planar growth may be limited to growth rates of the order of $3\text{ }\mu\text{m/s}$ using $1\text{ }\mu\text{m}$ particles of BaY_2CuO_5 . Such low growth rates mean that other growth morphologies must be developed that can be produced faster, yet lead to microstructures that are not weak linked.

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