JOURNAL OF MATERIALS SCIENCE 15 (1980) 1449–1455

# Preparation of Cu-Nb alloys for multifilamentary *in situ* superconducting wire

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A study has been made of two techniques, chill casting and consumable arc melting, for preparing ingots of Cu–Nb alloy for production of multifilamentary $Nb_3Sn$ superconducting wire. It was found that $Y_2O_3$, $ThO_2$ and graphite all make excellent crucible materials for melting Cu–Nb alloys at 1850° C. Some difficulty was found with Nb segregation in chill-cast 5 cm diameter ingots. The consumable arc casting technique was shown to produce a uniform Nb dendrite distribution with little macrosegregation in 5 cm diameter castings and is regarded as having excellent potential for scale-up production of uniform Cu–Nb ingots of 25 to 30 cm diameter.

## 1. Introduction

Ductile multifilamentary superconductor wire containing $Nb_3Sn$ in a bronze matrix is available commercially. This wire is produced by the bronze process [1] which was proposed in 1971 [2] and developed shortly thereafter. More recently an alternate technique similar to that first proposed by Tseui [3] has developed and come to be called the *in situ* process. Recent results [4–7] have shown that wires prepared by the *in situ* process have critical currents as high as, and perhaps slightly higher than, the bronze processed wires in the 0 to 12 T range. The first step of the *in situ* process is to prepare a Cu–Nb casting of around 20 to 30 wt % Nb in which Nb dendrites are uniformly dispersed throughout the casting. The cast alloy is then mechanically reduced to wire and the Nb converted to $Nb_3Sn$ by diffusing Sn into the wires.

We have developed two methods for the casting step in this process, a chill casting method and an arc casting method. In this paper we present the details of these methods and data which characterize the microstructure, chemical composition and homogeneity of the cast alloy.

## 2. Chill casting technique

Alloys were prepared by simply melting pure Cu and Nb metals in a crucible and then casting them directly into a water-cooled copper chill mould. The initial chill mould has a 1.4 cm diameter which was later increased to 5 cm diameter in order to evaluate the scale-up potential of the process. Because the scale-up required some significant design changes both designs will be described.

### 2.1. Small-diameter chill castings

A schematic diagram of the small chill casting apparatus is shown in Fig. 1. The crucible is heated from a Ta susceptor which receives power from a 450 kH induction coil through a water-cooled copper concentrator. A central hole in the bottom of the crucible is plugged by a tube of the same material as the crucible. The tube contains a W–5Re/W–26Re thermocouple for temperature measurement. After the alloy has been held for 5 min under 1 atm argon at 1850° C the tube is raised and the molten alloy pours into the chill mould. The crucibles are approximately 26 mm diameter by 36 mm height and the weight of alloy used was either 75 or 130 g. The copper chill mould is tapered slightly to facilitate ingot removal and has an average diameter of just over 1.4 cm.

Alloys cast directly into the copper chill mould exhibited some cavity porosity in the upper third of the casting, which was detrimental to subsequent cold drawing. This problem was overcome in a second mould which contained a 1.4 cm i.d.

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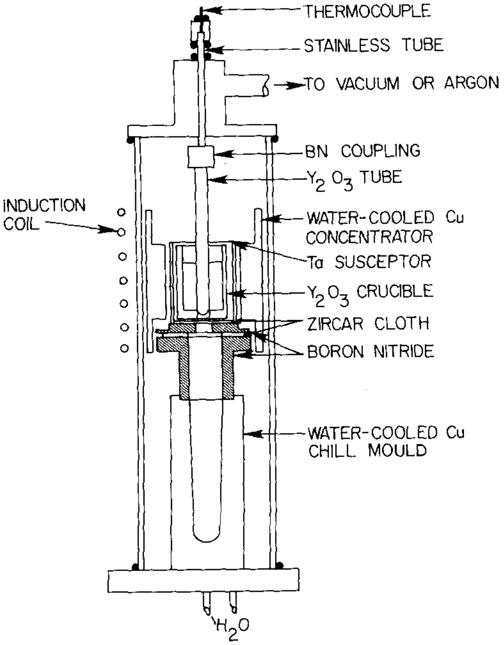

*Figure 1* Schematic diagram of experimental design used to produce 1.4 cm diameter Cu–Nb chill castings.

graphite cylinder standing on the bottom of the copper chill mould. The molten metal then made direct contact with the copper chill only at the bottom. Hence, freezing was more directional from the bottom upward, thereby eliminating the cavity porosity.

TABLE I Chemical analysis of chill cast 20 wt % Nb alloys (all analyses are ppm atomic except H which is ppm weight)

| Element | Crucible | | | Starting metals§ |
|---|---|---|---|---|
| | $Y_2O_3$* | $ThO_2$† | Graphite‡ | |
| Ta | 30 | 6 | 170 | 18 |
| W | < 2 | < 2 | 2 | < 2 |
| Fe | 9 | 3 | 8 | < 0.1 |
| Si | 11 | < 50 | < 7 | 49 |
| B | 20 | 2 | 3 | 0.6 |
| Na | 3 | 10 | < 0.5 | < 0.6 |
| Zr | 1 | 5 | < 0.7 | < 0.4 |
| Ca | 10 | 1 | 20 | < 1 |
| Al | 10 | 10 | 0.3 | < 0.3 |
| Mg | 2 | 2 | 0.5 | < 0.02 |
| Y | 500 | < 0.2 | < 0.4 | < 0.2 |
| Th | < 1 | 10 | < 0.9 | < 0.9 |
| O | 680¶ | 640 | 470 | 87 |
| H | 0.5 | 3 | 5 | 1 |
| N | 34 | 15 | 15 | 24 |
| C | 62 | – | 2000¶ | 37 |

*Slip-cast from high purity $Y_2O_3$ powder supplied by H. Burkholder, Ames Lab, DOE.

†Purchased from Zircoa Corp., slip cast-composition 0914.

‡Purchased from Union Carbide, Grade AGSX.

§Purchased from Materials Research Corp., Marz grade.

¶Average over three experiments.

### *2.1.1. Impurity pick-up*

Several different materials were examined for potential crucible containers, $Al_2O_3$, $ZrO_2$ (CaO-stabilized), $ZrO_2$ ($Y_2O_3$-stabilized), $Y_2O_3$, BN, $ThO_2$ and graphite. Results on impurity contamination with the first four materials have been previously reported [8], where it was shown that $Y_2O_3$ produced the minimum impurity pick-up. The results on $Y_2O_3$ are reproduced in Table I for reference. Analyses for O, N and H were done by vacuum fusion, for C by combustion and for all remaining elements by spark source mass spectroscopy (SSMS). Only elements whose SSMS analysis was greater than 1 part per million atomic (ppma) are included in Table I. All analyses were performed on samples cut from the cast metal with a SiC cut-off wheel, filed with a steel file to produce a smooth surface, and then cleaned in methanol.

The results in Table I show that $ThO_2$ is an even better crucible material than $Y_2O_3$. However, $ThO_2$ has very poor thermal shock characteristics and a significant radioactive decay problem. The data for graphite crucibles show very little impurity pick-up, with O being lower than with any of the ceramic materials. A thin layer of what appeared to be a niobium carbide remained on the graphite crucible wall after pouring. However, metallographic analysis of several castings revealed no carbide particles in the castings. The measured carbon analysis of Table I is an average over three experiments and indicates an average C pick-up of 2000 ppma for the 5 min hold at 1850° C in graphite crucibles.

The variation of oxygen pick-up with increased Nb content was studied in $Y_2O_3$ crucibles. Increasing the Nb content of the melt from 20 to 60 wt % increased the O pick-up only slightly, from 680 to 1040 ppma.

Boron nitride (BN) is an extremely desirable crucible material because of its outstanding thermal shock characteristics and its machinability. Experiments were done on a high-purity BN and on ultrahigh-purity pyrolytic BN free from $B_2O_3$. In both cases the metal did not wet the crucible, but a significant B pick-up was found, 20 000 and 3000 ppma, respectively.

### *2.1.2. Macrosegregation*

The longitudinal and radial segregation of Nb was measured in two experiments. In the first experiment a 120 g charge of a 20 wt % Nb alloy was melted in a $Y_2O_3$ crucible and cast into the graphite lined chill mould. Cylindrical samples were cut from the ingots on a lathe, producing samples at radial positions of 0 to 50%, 50 to 70% and 70 to 86% of the full radius of the ingot. Compositions at these three radial positions are shown on Fig. 2 at several positions along the ingot length. It is apparent from these results that a small, but significant amount of Nb segregation was present in the 1.4 cm diameter chill castings.

In the second experiment a 75 g charge of 20 wt % alloy was melted in a $Y_2O_3$ crucible and cast directly into the copper chill mould. Analysis revealed a small longitudinal segregation quite similar to Fig. 2, but a smaller radial segregation. Repeating the experiment with a $ThO_2$ crucible produced a similar result.

### *2.1.3. Microstructure*

The microstructure of all of the alloys studied, 10, 20, 30, 40 and 60 wt % Nb, consisted of a uniform distribution of fine Nb dendrites in a Cu matrix. However, a distinct change in the dendrite morphology was found to occur when graphite crucibles rather than ceramic crucibles were employed. This change in morphology is illustrated by comparing Fig. 3, thoria crucible, to Fig. 4, graphite crucible. The surfaces of both samples were prepared by standard metallographic polishing through Linde A powder followed by a 3 min etch with a solution of 55% phosphoric acid, 25% acetic acid, 20% nitric acid, which preferentially removed the Cu phase. Apparently, the dissolved carbon from the graphite crucibles caused the Nb dendrites to become shorter and fatter. This change in dendrite morphology probably results from the carbon redistribution which occurs upon solidification of the Nb dendrites.

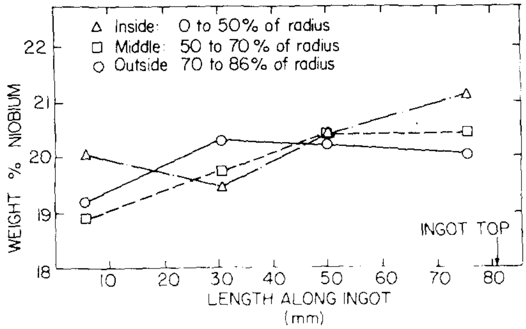

*Figure 2* Plot of composition profile measured on a chill-cast 1.4 cm diameter ingot of Cu–20 wt % Nb. Cast from a $Y_2O_3$ crucible after a 5 min hold at 1850° C.

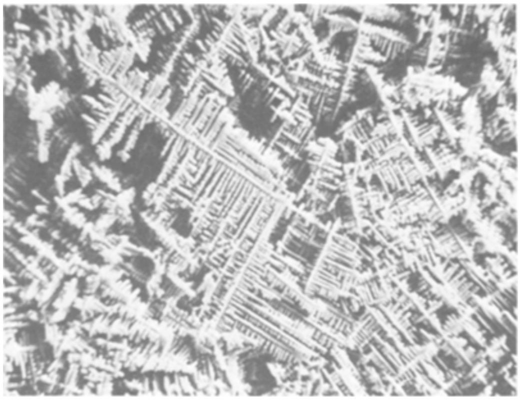

*Figure 3* Cu–20 wt % Nb alloy cast from a $ThO_2$ crucible and etched for 3 min, × 364.

## 2.2. Large-diameter chill castings

Initial efforts to increase the casting diameter from 1.4 to 5 cm involved simply scaling-up the design of Fig. 1 to the larger size, and increasing the r.f. power generator from 30 to 50 kW. However, at the larger size the power losses in the concentrator became too large and an alternate design shown in Fig. 5 was developed. A 3 kg charge of Cu–Nb was melted in a 10 cm diameter by 10 cm high graphite crucible with the crucible acting as the susceptor for the r.f. coil. Because the molten alloy wets the graphite and forms a layer of carbide on its surface it was found necessary to use a ceramic pouring spout and a ceramic pouring tube as shown in Fig. 5. The Cu chill mould was split along its length for purposes

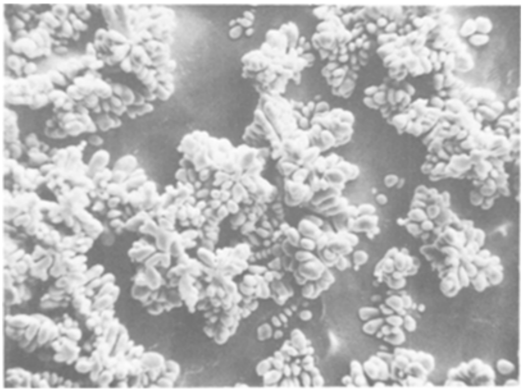

*Figure 4* Cu–20 wt % Nb alloy cast from a graphite crucible under conditions identical to the sample of Fig. 3. Etched for 3 min, × 812.

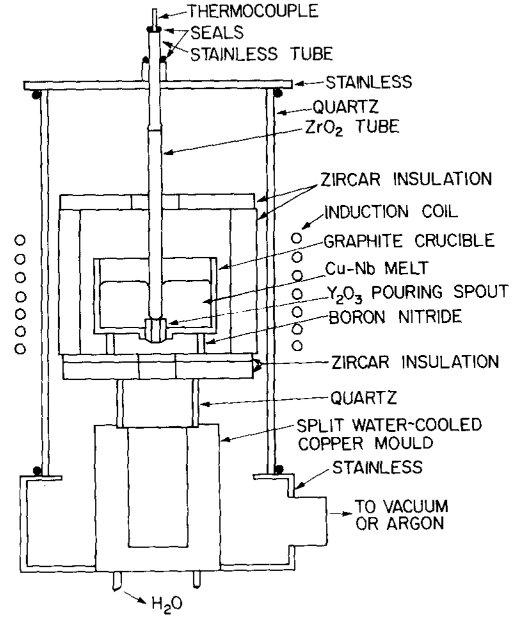

*Figure 5* Schematic diagram of experimental design used to produce 5 cm diameter Cu–Nb chill castings.

of removing the solidified ingot. The alloys were held at 1850° C under 1 atm argon for periods of 5 to 15 min prior to casting. Pouring spout diameters of 5.3 mm and 3.6 mm produced casting times of 30 and 80 sec, respectively. Pouring directly into the Cu mould produced a sound casting with no cavity porosity.

### 2.2.1. Impurity pick-up

The larger diameter castings were developed to indicate the feasibility of scaling-up the chill casting process and, consequently, the starting metals used were the same as those employed in the production of commercial superconducting wire. The Cu metal is commonly referred to as OFHC or 101 Cu and it meets ASTM Designation B 170, Grade 1. The Nb is specified as metallurgical grade with a 99.85% minimum impurity level. These starting metals were analysed and the impurity level, weighted for a Cu–25 wt % Nb alloy, are listed in Table II.

The impurity level of both 20 and 30 wt % Nb chill castings are also shown in Table II. There seems to be very little impurity pick-up from the graphite crucible other than carbon. The significant variation of carbon impurity level between the bottom and top of the ingot is the result of Nb macrosegregation as explained below. There

TABLE II Chemical analyses of 5 cm diameter Cu–Nb alloys prepared by both arc casting and chill casting (all analyses are ppma except H which is ppmw)

| Element | Arc casting* | | Chill casting* | | Starting metals |
|---|---|---|---|---|---|
| | 30% Nb 3 melts | 20% Nb 2 melts | 30% Nb | 20% Nb | |
| Ta | 150 | 30 | 70 | 40 | 45 |
| W | 30 | < 3 | 6 | < 4 | 9 |
| Fe | 10 | 20 | 20 | 17 | 24 |
| Si | 9 | 20 | 50 | 10 | 40 |
| B | 9 | 9 | 4 | 2 | 8 |
| Ni | 5 | 5 | 5 | 8 | 9 |
| Ag | 5 | 4 | 3 | 4 | 11 |
| S | 4 | 10 | 10 | 9 | 4 |
| Sn | 1.4 | 10 | < 0.4 | 10 | 0.2 |
| Pb | 2.1 | 5 | 1 | 6 | 2 |
| Na | < 0.6 | 5 | < 3 | 9 | < 0.6 |
| K | < 0.8 | 2 | < 3 | 7 | < 1 |
| Ca | 0.7 | 3 | 2 | 2 | 0.7 |
| Cr | 2 | 2 | 0.8 | 1 | 0.7 |
| Sb | 4 | 1 | 0.7 | 2 | 0.4 |
| Mg | 0.5 | 1 | 3 | 1 | 0.1 |
| Zr | < 0.7 | 4 | 46 | 30 | 1 |
| Y | 0.2 | < 0.3 | 20 | 6 | < 0.2 |
| O | 610 | 470 | 420 | 330 | 270 |
| H | 15 | 8 | 3 | 3 | 3 |
| N | 30 | 34 | 25 | 19 | 144 |
| C (Bot) | 2200 | 2100 | 6600 | 2600 | 70 |
| C (Top) | 2600 | – | 1300 | 550 | – |

*Graphite was grade AGSX, Union Carbide Corp.

TABLE III Chemical analyses for Nb in 5 cm diameter by 16.5 cm length chill castings. Analyses made at 1.9 cm from the bottom and 3.1 cm from the top

| Target composition (wt % Nb) | Hold time at 1830° C (min) | Average compositions | | Radial composition difference at bottom (% Nb) |
|---|---|---|---|---|
| | | Bottom (% Nb) | Top (% Nb) | |
| 20 | 5 | 29.4 | 13.4 | 6.7 |
| 20 | 15 | 26.6 | 15.7 | 6.1 |
| 30 | 5 | 46.4 | 10.0 | 2.0 |
| 30* | 5 | 39.6 | 18.8 | 0.03 |

*Pouring spout diameter decreased from 5.3 to 3.6 mm thereby increasing pour time from 30 to 80 sec.

is also some minor pick-up of Y and Zr from the pouring spout and tube.

### 2.2.2. *Macrosegregation*

The ingots were cut as explained in Table III and sections were machined out at radii of 32% and 82% of the full radius. It is seen from Table III that there is a significant segregation of Nb to the bottom of the ingot which is diminished only slightly by increasing either the holding time at temperature or the pouring time. However, increasing the pouring time from 30 to 80 sec did seem to reduce radial segregation.

The significant segregation found in these larger diameter chill castings must be produced either by inadequate mixing in the crucible or by formation during the solidification process. Observation of the melt revealed that the Nb remained at the bottom of the crucible during the solutioning stage, which thermal arrests indicated was completed at 1680 to 1700° C. If natural convection currents were not adequate to homogenize the liquid composition during the 5 or 15 min hold at 1850° C, one would expect a higher Nb content at the ingot bottom, as observed. To check this possibility several experiments were done where the melt was solidified directly in the crucible by simply turning off the power after a 5 min hold at 1850° C. Metallographic examination indicated strong Nb segregation at the crucible bottom and chemical analyses of a 20 wt % Nb alloy gave a composition of 34% Nb at the ingot bottom. Metallographic analysis showed that the Nb dendrites at the bottom of the crucible formed by nucleation at the bottom wall and growth upward rather than by a settling of the dendrites from the liquid, thus indicating inadequate mixing for homogenization. Similar experiments on solidified crucible metal in the small casting apparatus where segregation was not a problem showed a uniform Nb distribution. Hence, there is strong evidence that the segregation in the larger diameter ingots resulted from inadequate homogenization of the liquid by natural convection currents, whereas the natural convection was adequate to produce homogenization in the smaller diameter design. To produce adequate liquid mixing in the design of Fig. 5 it would be necessary to either introduce some type of mechanical stirring device or perhaps use a lower frequency induction current where the current would penetrate further into the melt to increase liquid mixing.

### 2.2.3. *Microstructure*

The microstructures of the Nb dendrites were similar to those obtained with the small diameter ingots. In addition, a macroetch revealed structural features somewhat similar to the well known V segregate pattern of cast ingots, which was a reflection of the radial segregation pattern.

## 3. Consumable arc casting

5 cm diameter castings of 20 and 30 wt % Nb were prepared by a consumable electrode arc technique. A standard consumable arc furnace [9] was modified slightly as shown in Fig. 6. A graphite sleeve, 6.25 cm o.d. by 5.2 cm i.d., was placed inside of the 6.25 cm water-cooled copper cylinder. The initial electrode consisted of a Nb rod within a Cu tube with the relative sizes adjusted to give a Nb wt % of either 20 or 30%. A 6 mm thick Cu–Nb plate was placed upon the bottom of the graphite cylinder and 10 to 15 g Cu–Nb lathe turnings were placed above the plate. The plate served as a strike pad and the arc was initiated by shorting through the turnings. The electrode was then consumably arc-melted into the graphite-lined mould under $\frac{1}{2}$ atm argon at a rate of roughly 500 g min$^{-1}$ using a current of 1000 A at a voltage of around 22 to 26 V. Longitudinal sections of the

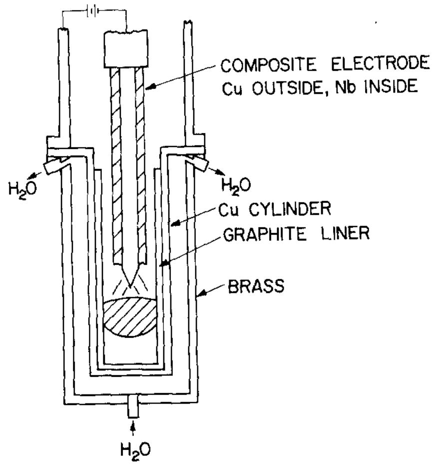

*Figure 6* Schematic diagram of experimental design used to produce 5 cm diameter Cu–Nb castings by the consumable arc technique.

initially melted electrode revealed several particles of Nb-rich metal on the order of 1 mm diameter which had not been well dispersed. However, after a second arc melting, good homogeneity was achieved. The electrode for the second arc melt was fabricated from the first melt ingot by rod-rolling to a diameter of approximately 3 cm.

## 3.1. Impurity pick-up

Two castings were analysed, a 20 wt % Nb casting made using two melts and a 30 wt % Nb casting made using three melts. The results, see Table II, show very similar impurity pick-up as that of the large diameter chill castings, except that there is no Y or Zr pick-up, and the carbon is not segregated along the length.

## 3.2. Macrosegregation

Several ingots were sectioned in a manner similar to the large-diameter chill castings and the results of the chemical analyses are shown in Table IV. It may be seen that both the longitudinal and radial segregation are significantly reduced over the large-diameter chill castings. Both the longitudinal and radial segregation were generally found to be less than 1 wt % Nb.

## 3.3. Microstructures

Metallographic examination revealed a uniform dispersion of dendrites with a morphology intermediate between Figs. 3 and 4, slightly more elongated than Fig. 4, but not as much as in Fig. 3. Macroetching of sectioned ingots did not reveal a macrosegregation pattern as with the large-diameter chill casting. However, a faint set of parallel striations was revealed running across the longitudinal sections. These striations were found to be the result of alternating variations in Nb dendrite size and morphology, from fine long dendrites to shorter fat dendrites. Typical dendrite diameter in 30% alloys varied from roughly 6 to 9 $\mu$m between striations, as revealed by SEM examination of deep etched samples. In the 20% alloys the dendrite sizes were about 20% smaller.

## 3.4. Solidification front

In the consumable arc process the electrode drips into the molten pool at a relatively constant rate. However, one would expect the freezing rate at the solid–liquid interface to fluctuate in response to changes in heat transfer conditions produced when the molten drops hit and mix into the molten pool. It seems most probable that the observed striations result from such fluctuations in growth rate.

Therefore, the striations reveal the shape of the Nb dendrite/liquid growth front. The shape is qualitatively shown in Fig. 6. Examination of the top of ingots to locate the point where striations stop when the power is shut off, indicates that the molten pool depth is probably less than 15 mm. Examination of the Cu–Nb phase diagram [8] reveals that when the temperature drops from 1700° C to 1500° C in alloys of 20 and 30 wt % Nb

TABLE IV Chemical analyses for Nb in 5 cm diameter by 38 cm length consumable arc castings. Analyses made at 13 cm from the bottom and 7 cm from top

| Target composition (wt % Nb) | Number of arc casts | Average Compositions | | Radial composition difference | |
|---|---|---|---|---|---|
| | | Bottom (% Nb) | Top (% Nb) | Bottom (% Nb) | Top (% Nb) |
| 20 | 2 | 20.6 | 19.9 | 0.17 | 0.51 |
| 20 | 2 | 20.3 | 20.3 | 0.06 | 0.74 |
| 30 | 3 | 29.1 | 30.5 | 0.74 | 2.3 |
| 30 | 2 | 29.7 | 29.8 | 1.9 | 0.54 |

most of the Nb dendrites will have already formed, approximately 80 and 90%, respectively. Therefore, since the liquid Cu solution does not freeze until approximately 1080° C, one expects the Cu solidification growth front to lie below that shown on Fig. 6, at some distance determined primarily by the longitudinal temperature gradient in the system. Because of their relatively uniform distribution it appears that the Nb dendrites must form a fairly stable structural network in the two-phase zone as solidification occurs. Suitable macroetching revealed the Cu grain boundaries running nearly parallel to the growth axis, thus indicating the Cu growth front is probably flatter than the Nb dendrite front shown on Fig. 6.

## 4. Conclusions

Experiments on 1.4 cm diameter chill castings of Cu–Nb alloys have shown that both $Y_2O_3$ and $ThO_2$ provide satisfactorily inert crucible materials. Resistance to impurity pick-up from graphite crucibles was as good as or better than these ceramic crucibles with respect to all elements except carbon, and the carbon pick-up was only around 2000 ppma. The carbon pick-up was observed to change the dendrite morphology from long thin dendrites to shorter fat dendrites.

Attempts were made to scale-up the process to 5 cm diameter castings using both chill casting and consumable arc casting techniques. A significant macrosegregation of Nb was found in the chill casting technique and evidence indicates that it resulted from inadequate homogenization of the melt. The consumable arc technique required two melts to produce a uniform Nb dispersion. Ingots as large as 10 kg were produced having a very uniform dendrite distribution with radial and longitudinal segregation less than 1 wt % Nb.

Commercial consumable arc processes are routinely carried out with ingots of the order of 25 to 30 cm diameter. Based on this study, we conclude that the consumable arc technique offers excellent potential for scale-up to these sizes, which would allow large scale production of homogeneous Cu–Nb ingots by the *in situ* process of producing ductile multifilamentary $Nb_3Sn$ wire.

## Acknowledgements

This work was supported by the US Department of Energy, contract no. W-7405-Eng-82, Division of Materials Science (budget code AK-01-02). The authors were assisted by Mr T. Myers and Mr E. Ritland in the casting processes. The chemical analyses were carried out under the direction of Mr R. Bachman, Mr R. Conzemius and Dr R. Kniseley. The $Y_2O_3$ crucibles, pouring spouts and tubes were produced for us by Mr W. Calderwood.

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Received 28 September and accepted 19 October 1979.