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Fabrication of $YBa_2Cu_3O_{7-x}$ bulk superconductor from the powder without reoxygenation

R. E. ANDERSON
Southwest Texas State University, San Marcos, Texas 78666, USA

M. J. SABLIK, C. I. NICHOLLS, D. PRECIADO
Southwest Research Institute, P.O. Drawer 28510, San Antonio, Texas, 78284 USA

The fabrication of $YBa_2Cu_3O_{7-x}$ sintered ceramic and $YBa_2Cu_3O_{7-x}$ melt product from the powder without additional reoxygenation is reported. The $YBa_2Cu_3O_{7-x}$ is fabricated inside a commercial silicon carbide tube. The SiC tube effectively does not react with the $YBa_2Cu_3O_{7-x}$ and acts to prevent oxygen from diffusing out of the $YBa_2Cu_3O_{7-x}$. The fabrication procedure can, in principle, be used with any tube enclosure which neither reacts with $YBa_2Cu_3O_{7-x}$ nor allows diffusion of oxygen to the outside atmosphere.

1. Introduction

Since the discovery of superconductivity at 92 K in $YBa_2Cu_3O_7$ [1], much work has been expended on fabrication of the bulk superconductor [2–7]. One of the difficulties has been the low critical current densities, J_c [2–5], in the fabricated bulk material.

At present, the material with highest J_c has been produced by melt texturing [2, 3, 8, 9]. Formed via directional solidification through zone-passing, the melt-textured material has a microstructure consisting of densely packed, closely aligned crystal grains. Because the melt-textured material is produced from a bare ceramic column of $YBa_2Cu_3O_{7-x}$ in the open air [8–10], it loses oxygen and must be reoxygenated over a period of many hours and over several days [8–10]. The densification resulting from melt processing increases the time required for this reoxygenation. Our work suggests that this time-consuming reoxygenation may be unnecessary.

In this paper, we report fabrication of bulk $YBa_2Cu_3O_{7-x}$ from the powder without additional reoxygenation. This was achieved by confining the material inside a hollow enclosure which is nonreactive with $YBa_2Cu_3O_{7-x}$ at high fabrication temperatures and which is dense enough to prevent escape of oxygen out of the $YBa_2Cu_3O_{7-x}$. For the enclosure material, we have successfully used commerical silicon carbide. Our best bulk $YBa_2Cu_3O_{7-x}$ has been made inside a tube made of SiC fused with a clay binder.

The discussion below is divided into descriptions of (a) fabrication, (b) test procedures for measuring resisitivity, and (c) results for variously prepared specimens.

2. Fabrication

The first step in fabrication was preparation of the $YBa_2Cu_3O_{7-x}$ powder. Stoichiometric amounts of Y_2O_3, $BaCO_3$, and CuO were ground together in an agate crucible until the colour and texture of the mixture was homogeneous. The grinding process usually lasted about 15 min. Next, the powder mixture was heated for 18 h at 900° C in an oxygen atmosphere. The material was then quenched from 900° C to room temperature by removing it from the furnace. The cooled mixture was then re-ground in the crucible until a smooth, homogeneous, greyish powder was obtained. Pellets of 1 in. diameter and $\frac{1}{8}$ in. thick were made in a press under a pressure of ~ 5000 p.s.i. ($\sim 34{,}5\,\mathrm{N\,mm^{-2}}$). These pellets were heated in oxygen for 6 h at 925° C, quenched to room temperature, and placed in a low-temperature furnace with an oxygen atmosphere at 550° C for 4 h, then slowly cooled to 350° C at a rate of $1°\,\mathrm{C\,min^{-1}}$. The pellets were left at 350° C for an additional 12 h and then slowly cooled to room temperature at $1°\,\mathrm{C\,min^{-1}}$. The pellets were re-ground, new pellets made and reheated at 940° C for 6 h in oxygen, and the previous slow cooling process repeated. This reprocessing procedure was repeated a second and even third time. It was found that reprocessing the pellets resulted in an increase in density of the material. After the final firing at 940° C, the pellets were reground to produce fine $YBa_2Cu_3O_{7-x}$ powder. In powder form, the material takes on water rapidly, so care was taken to keep moisture away from the powder.

The powder was used to pack silicon carbide tubes, obtained commercially. Three types of SiC tubes were used: (a) a hollow furnace electrode (Lindberg Furnace Co); (b) a greyish SiC tube with a clay binder fused in with the SiC (Bolt Technical Ceramics, Watertown Conroe, Texas); and (c) a "recrystallized" silicon carbide tube obtained (I^2R Element Co., Akron, New York). The SiC tubes used were $\frac{1}{4}$ in. i.d. and $\frac{1}{2}$ in o.d. The first two types of SiC tubes were closed at one end. A steel plug was used to seal one end of the third type. $YBa_2Cu_3O_{7-x}$ powder was added to the open end of the SiC tube and compacted as it was added.

To produce sintered material, the powder-filled tubes were refired in a horizontal position at 950° C for 30 to 45 min and quenched to room temperature.

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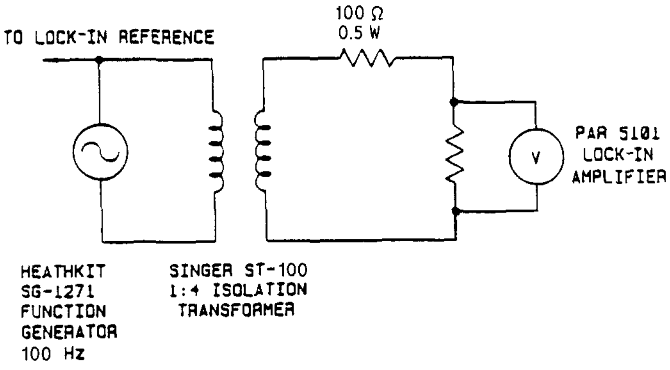


Figure 1 Circuit for measuring resistivity.

If a steel plug was used in packing the powder, it was removed prior to firing.

For melt processing, a vertical, powder-filled SiC tube was locally heated using a hand-held oxyhydrogen torch at temperatures well above the onset temperature of the incongruent melting of $YBa_2Cu_3O_{7-x}$. The torching involved two or three painstakingly slow descending passes over a period of a couple of hours. This procedure was similar to the zone-passing and directional solidification approach used by Jin *et al.* [2, 8, 9]. Also, for the melt-processing experiments, commercial $YBa_2Cu_3O_{7-x}$ powder (Aldrich Chemical Co., Milwaukee, WI.) was used to fill the SiC tube.

3. Electrical resistivity measurements

Electrical resistivity as a function of temperature down to 77 K was measured for each fabricated sample. A standard four-lead arrangement was used with the current leads at the ends. Contacts to the sample were made with 0.1 mm gold wires attached with silver paint. Measurements were carried out using low-frequency (100 Hz to 5 kHz) alternating current. The four-terminal method reduces problems with contact resistance, and use of an a.c. technique reduces errors from small d.c. voltages which may be induced if all leads are not thermally well-anchored. A lock-in amplifier utilized phase-sensitive detection to enhance the signal-to-noise ratio. The measuring circuit is depicted in Fig. 1.

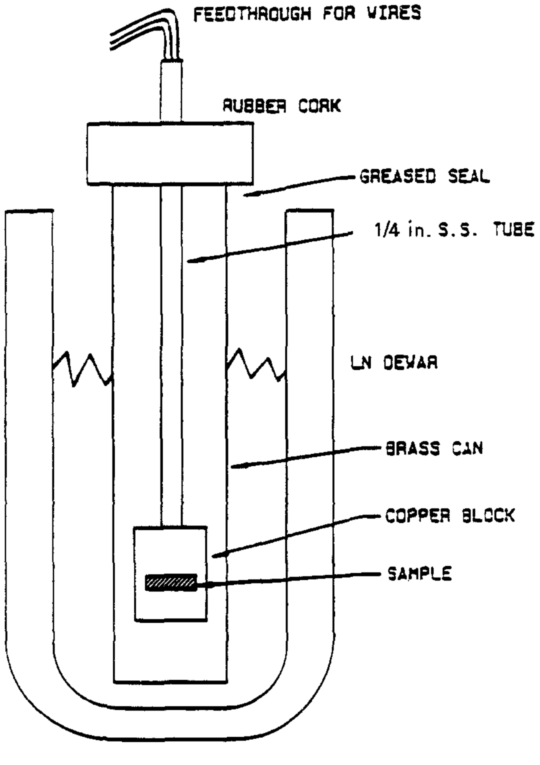


Figure 2 Schematic diagram of cryostat.

To monitor the sample temperature, a platinum resistance thermometer was mounted in a copper block to provide a high heat capacity isotherm. The sample was bonded to the copper block with vacuum grease as a demountable adhesive. Care was taken both to put sample and thermometer in good thermal contact with the block and to cool the system fairly slowly ($\sim 2\,K\,min^{-1}$). With such a rate of cooling, the system at any time and temperature could be considered to be quasistatic and measurements taken could be considered to represent equilibrium values for that temperature. In cooling, the mounted sample was either suspended in a vacuum space with walls cooled to 77 K, or the sample was cooled with a few torr of dry helium exchange gas introduced into the vacuum space. Warming was accomplished by withdrawing the sample to a region of the cryostat above the level of liquid nitrogen. Fig. 2 shows a schematic diagram of the liquid nitrogen cryostat used in the experiments.

4. Results

Table I identifies the various specimens. We discuss specimens sintered from the powder at 950° C for 30 to 45 min inside various commercial SiC tubes. Experiments with $YBa_2Cu_3O_{7-x}$ melt product formed inside commercial SiC tubes are also discussed.

Fig. 3 shows resistivity plotted against temperature for $YBa_2Cu_3O_{7-x}$ specimens sintered from the powder inside Lindberg furnace element tubes made of SiC. The data represent an average of cooling and warming data for each specimen. Data for two specimens are shown: (a) a reoxygenated specimen and (b) an unreoxygenated specimen.

It is seen that the $YBa_2Cu_3O_{7-x}$ shows evidence of a superconducting transition even when the sample is not reoxygenated overnight. The superconducting transition, however, is not as well defined for the case without reoxygenation. Both specimens 1 and 2 exhibit semiconducting behaviour superimposed on the superconducting behaviour, indicating that the specimens are multi-phase. The furnace element rods had a slight porosity, and it is probable that some oxygen escaped through the pores of the rod during sintering although the rate of escape of oxygen was reduced considerably from what it would be if sintered in the open atmosphere.

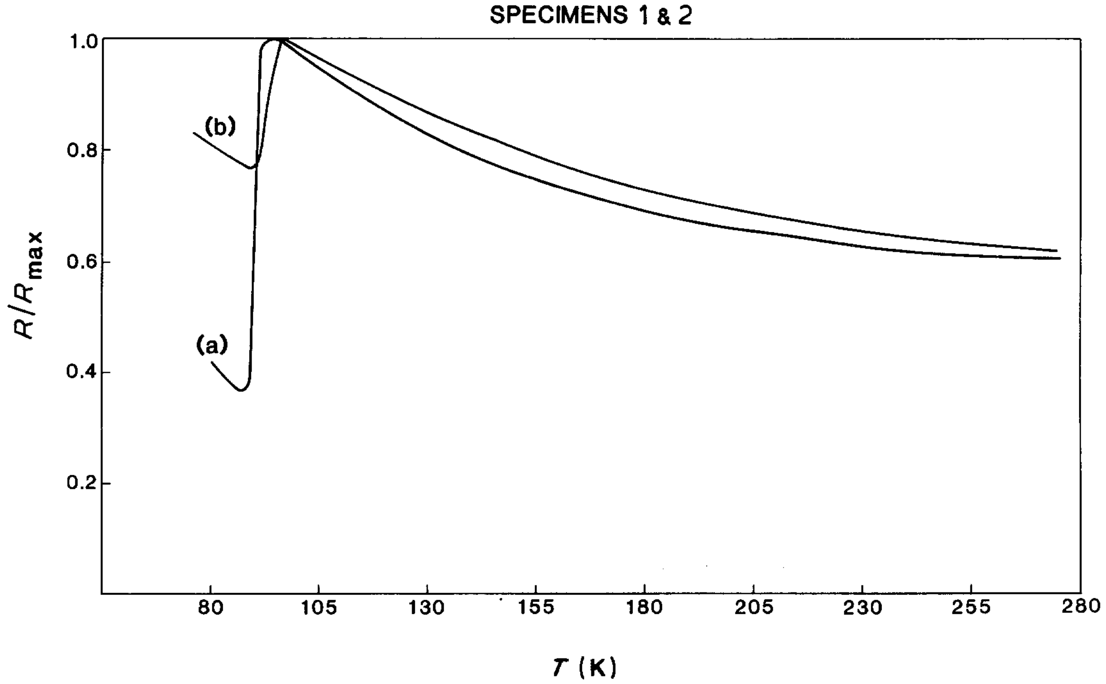


Figure 3 Resistivity–temperature plots for specimens sintered in porous SiC tubes with the specimen (a) reoxygenated and (b) not reoxygenated.

The resistivities in the figures are normalized with respect to the largest value of the resistivity measured for a particular sample.

In Fig. 4, resistivity plotted against temperature is shown for $YBa_2Cu_3O_{7-x}$ sintered from the powder inside hollow tubes made of silicon carbide mixed with clay binder. The tubes had a smooth surface and were dense and hard and nonporous. Note that the behaviour was superconducting (R = 0) below T_c and quasimetallic above T_c when the specimen was not reoxygenated. With reoxygenation, a slight degradation was observed, indicated by a semiconducting behaviour above T_c. Note, however, that zero resistance was still achieved at 90 K. These cases suggest that reoxygenation can be eliminated as a step if sintering is done inside dense SiC tubes. Apparently, the clay binder plugs the pores in the SiC material and prevents escape of oxygen from $YBa_2Cu_3O_{7-x}$. The slight degradation of the specimen in the case of overnight reoxygenation may mean that extended heating of the specimen inside the tube might eventually result in a chemical reaction between specimen and the clay binder.

TABLE I Identification of specimens

Specimen 1	$YBa_2Cu_3O_7$ sintered at 950° C for 45 min inside SiC hollow furnace rod; reoxygenated in the tube for 4 h at 550° C and then slowly cooled in oxygen at 1° C min^{-1} to room temperature overnight.
Specimen 2	Same as specimen 1 but not reoxygenated after sintering.
Specimen 3	$YBa_2Cu_3O_7$ sintered at 950° C for 45 min inside hollow rod made of SiC plus a clay binder; reoxygenated by same procedure as specimen 1.
Specimen 4	Same as specimen 3 but not reoxygenated after sintering.
Specimen 5	$YBa_2Cu_3O_7$ sintered at 950° C for 30 min inside hollow rod made of "recrystallized" SiC; reoxygenated by same procedure as specimens 1 and 3.
Specimen 6	Same as specimen 5 but not reoxygenated after sintering.
Specimens 7a, b, c, d	$YBa_2Cu_3O_7$ melt product from a simulated set of three zone passes down a tube made of SiC plus a clay binder over a 3 h period using a hand torch (see text); (a) melt product from the top quarter of the tube; (b) second quarter from top; (c) third quarter from top; (d) bottom quarter.

Fig. 5 shows resistivity–temperature curves for $YBa_2Cu_3O_{7-x}$ sintered from the powder inside "recrystallized" SiC tubes. This form of SiC contains some free silicon. However, the silicon apparently does not poison the transition temperature [11, 12], so the shoulder seen at the transition in curve (a) apparently has another cause. Possibly, there is also free carbon in the "recrystallized" SiC. The tubes were very porous and, hence, we hypothesize that oxygen was lost through the pores during sintering. This accounts for the almost complete lack of a superconducting transition when the sample was not reoxygenated overnight.

Figs 6a to 6d show data for $YBa_2Cu_3O_{7-x}$ melt product taken from inside the top quarter, second quarter, third quarter, and bottom quarter of a containment tube made of SiC plus clay binder. The specimen in the bottom quarter is expected to be degraded because the simulated zone passing with the oxyhydrogen torch was from top to bottom. Impurities and impurity phases, thus, were pushed to the bottom as the melt zone transferred from top to bottom. Resistivity–temperature curves for specimens in the other sections were roughly the same in appearance.

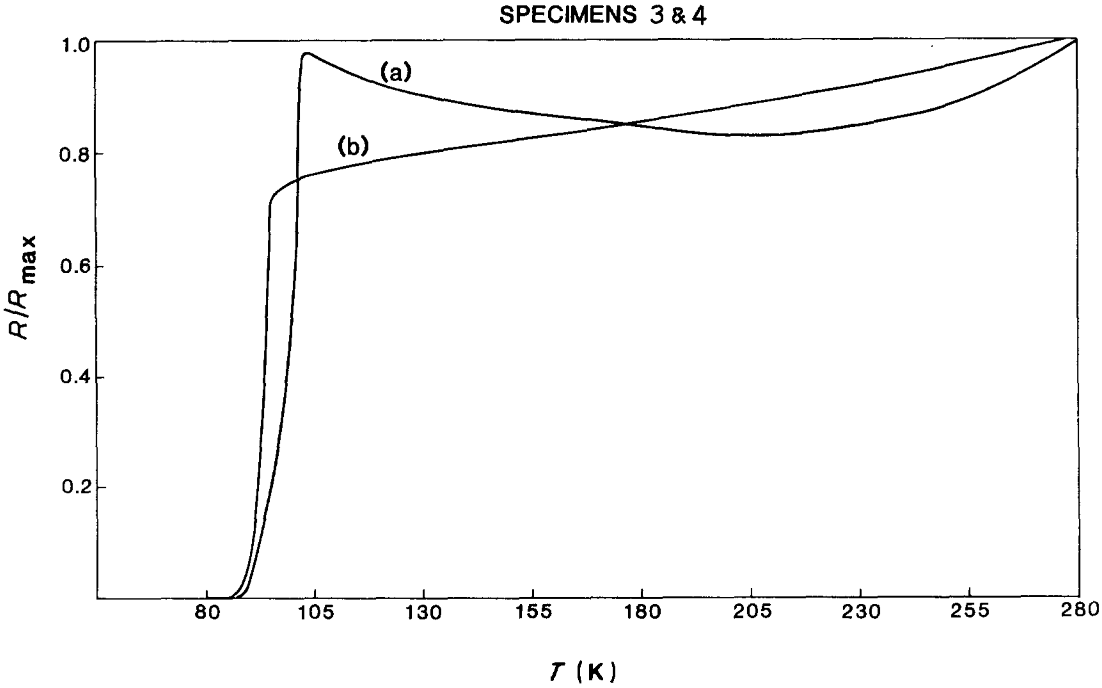


Figure 4 Resistivity–temperature plots for specimens sintered in dense SiC tube made with clay binder with the specimen (a) reoxygenated and (b) not reoxygenated.

The superconducting transition is degraded slightly from the best sintered specimens possibly due to incorporation of impurities from the tube at the elevated temperatures, but more probably due to the fact that the Aldrich $YBa_2Cu_3O_{7-x}$ powder was for $x = 0.5$, for which the superconducting transition has been usually found to be 60 K [13].

The solid curves in Figs 6a to c show resistivity–temperature plots down to 77 K. The dashed curves in Figs 6b and c represent data taken several months later when liquid helium was obtained. Between measurements, the samples were stored in bottles sealed with tape but not in a desiccator. With the passage of time, the samples apparently showed a tendency to degrade to semiconducting behaviour above the transition. The original measurements displayed a broad transition which was interrupted at 77 K. The measurements down to liquid helium temperatures show a shoulder at 60 K and zero resistivity below 45 K, indicating that some of the material was bulk superconducting at 60 K instead of 92 K. It is not clear how much of the specimen was 60 K material at the time of the first measurement, but clearly some of it had to be because zero resistivity was not achieved at 77 K. The fact that some of the material showed the 92 K transition suggests that zone solidification in a confinement tube can actually result in better superconducting material.

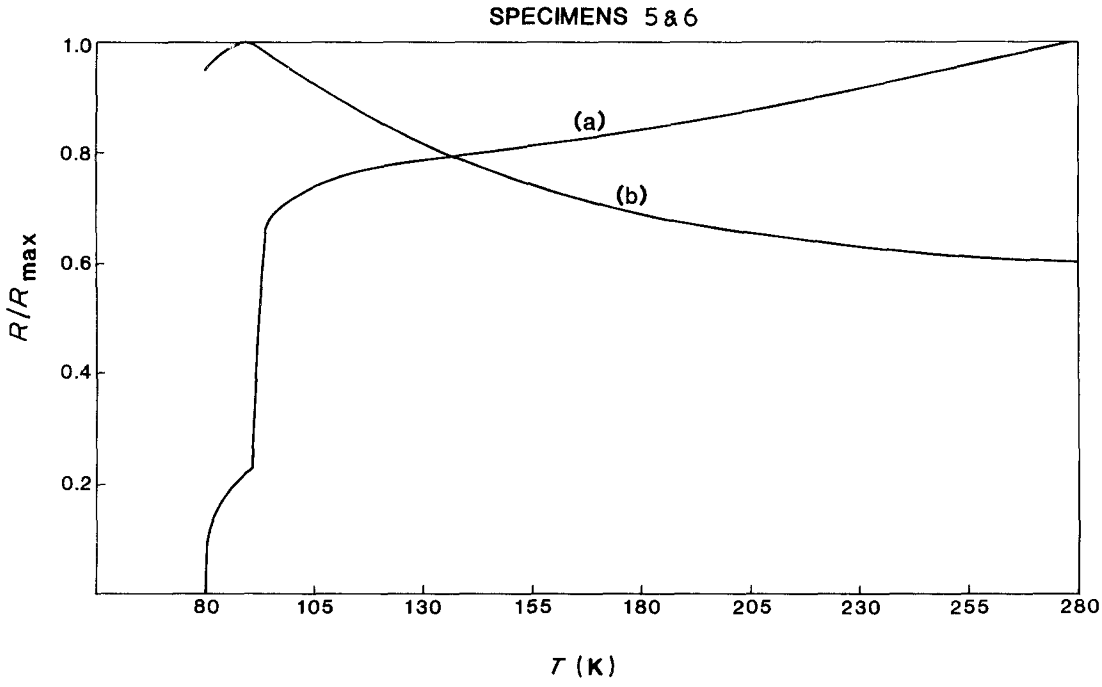


Figure 5 Resistivity–temperature plots for specimens sintered in "recrystallized" SiC tube, with the specimen (a) reoxygenated and (b) not reoxygenated.

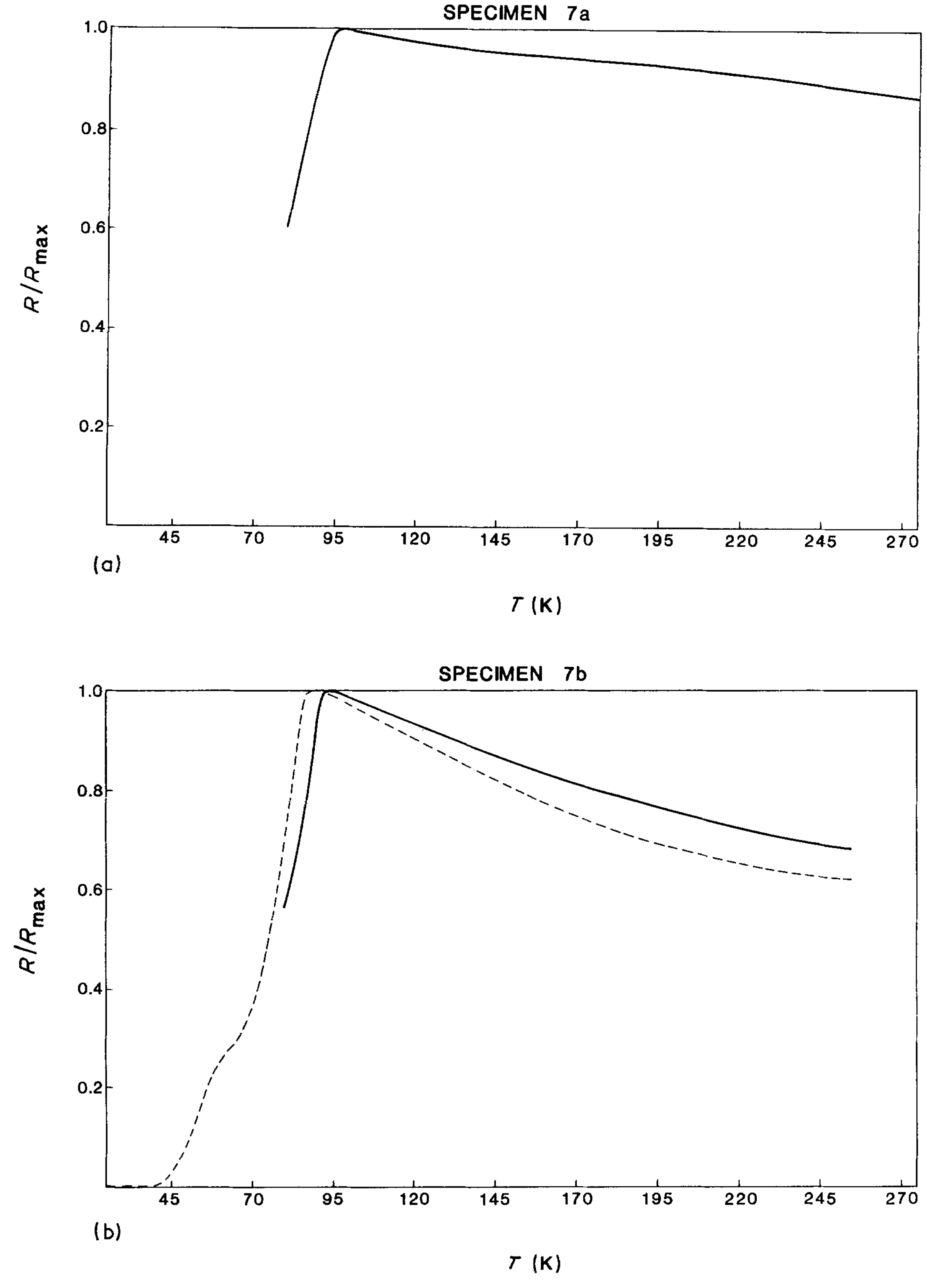
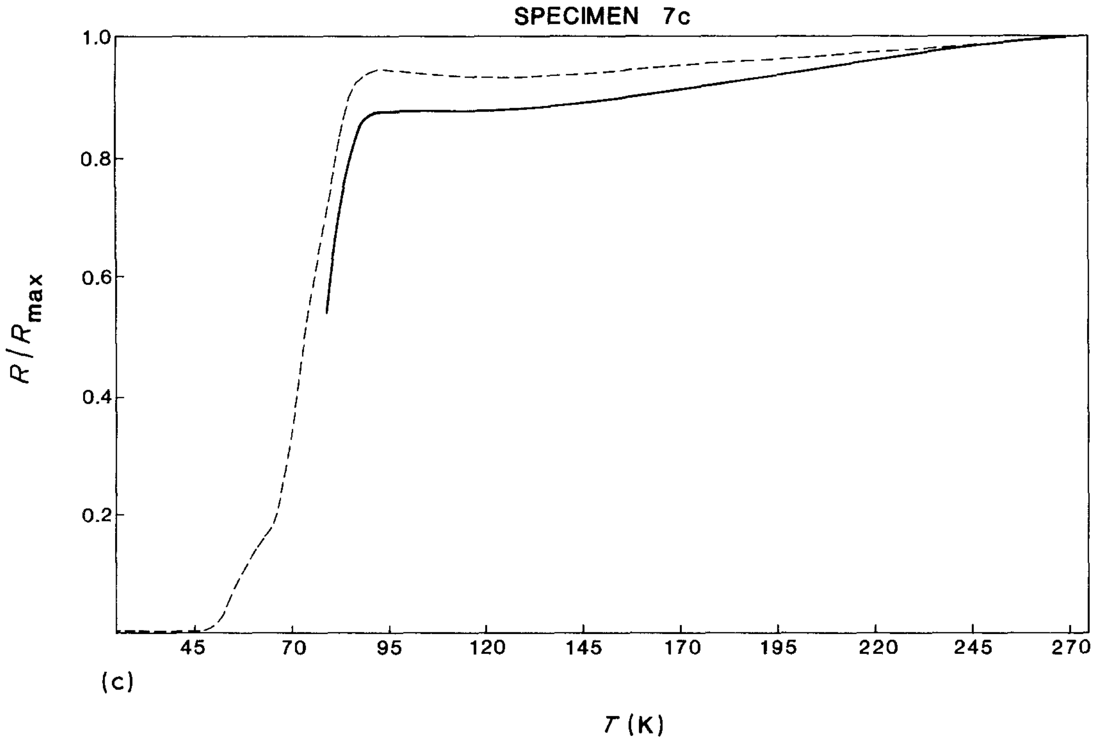


Figure 6 Resistivity–temperature plots for melt-processed $YBa_2Cu_3O_{7-x}$ material from (a) the top quarter; (b) the second quarter (– – –) (c) the third quarter; (d) the bottom quarter of the SiC tube with clay binder. Data taken above and below 77 K several months later on the same sample; Because the melt zone moved from top to bottom, the sample at the bottom end should contain a larger concentration of impurity phases.

The results seen in Figs 6a to c nevertheless suggest that if the tube of sample is very slowly passed through a hot zone at a uniform rate in a more carefully performed experiment with better powder ($x < 0.3$), the melt product should be superconducting at 77 K without the need for reoxygenation. The procedure needs to be tested. If degradation of the transition temperature still occurs, it may mean that reaction takes place possibly between the $YBa_2Cu_3O_{7-x}$ and the clay binder, in which case the binder could be changed or an alternate dense material similar to SiC could be used. Because the 60 K phase is usually attributed to oxygen deficiency [13], a carefully controlled directional solidification inside the confinement tube with better powder should limit loss of oxygen and, therefore, limit the formation of the 60 K phase.

5. Conclusion

We have demonstrated that if $YBa_2Cu_3O_{7-x}$ solid is fabricated inside a hollow essentially nonreactive tube such as commercial SiC, it would appear that reoxygenation can be eliminated as part of the fabrication



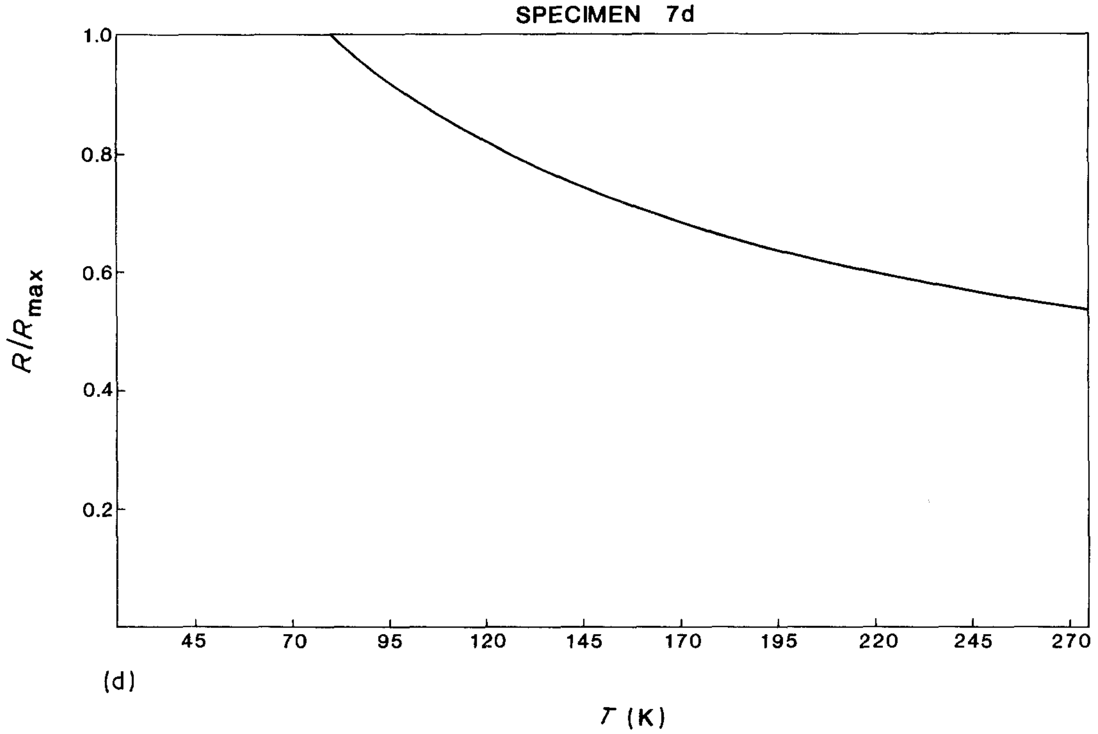


Figure 6 Continued

procedure. Preliminary results indicate that this might be possible, even with $YBa_2Cu_3O_{7-x}$ zone-passed, densified melt product [14].

In the effort to produce material with higher critical current density, J_c, it would be useful not to have to reoxygenate, because reoxygenation results in expansion and strain which tends to introduce microcracking [15], which in turn interferes with efforts to produce higher J_c. It is recommended, therefore, that further "confinement" experiments inside hollow tubes be attempted in order to find the optimal nonreactive enclosure material to confine the $YBa_2Cu_3O_{7-x}$ and prevent loss of oxygen out of the $YBa_2Cu_3O_{7-x}$ as the bulk material forms.

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