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Effect of CO₂ on the processing of Y–Ba–Cu–O superconductors

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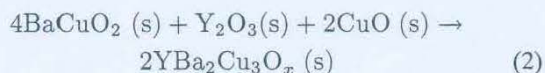
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The superconducting properties of YBa₂Cu₃O_{6+x} reacted with various known ratios of O₂/CO₂ gas mixtures during sintering at different temperatures were studied. J_c was found to decrease drastically upon reaction with CO₂, becoming zero at certain CO₂ activities. The stability region for the 123 superconductor, as a function of CO₂ activity and temperature, was empirically formulated as follows: $\log p_{\text{CO}_2} < (-45,000)/T + 33.4$. The grain boundaries in sintered samples with $J_c = 0$ were investigated with HRTEM in conjunction with EDS. Two distinct types of grain boundaries were observed. Approximately 10% of the grain boundaries were wet by a thin layer of a second phase, deduced to be BaCuO₂. The remaining boundaries were sharp grain boundaries. The grain structure near the sharp grain boundaries was tetragonal. These two types of grain boundaries are thought to be responsible for J_c being zero.

I. INTRODUCTION

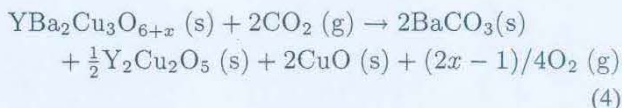
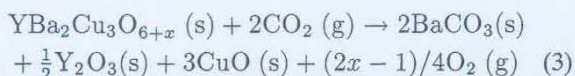
There are two potential sources of CO₂ when YBa₂Cu₃O_{6+x} (123) superconductors are processed by solid-state sintering. One source is the CO₂ contained in the oxygen gas used during sintering and/or annealing. Another source is the CO₂ derived from the decomposition of BaCO₃ during the calcination step. Each source affects the quality of the final product in different ways and can lead to a drop in the critical current density, J_c .

During calcination, the Y₂O₃, BaCO₃, and CuO powders ideally react according to reactions (1) and (2), to form 123.



When BaCO₃ decomposes, according to reaction (1), CO₂ is released. The localized concentration of CO₂ can quickly reach its equilibrium value, and stagnant regions of CO₂ can form, even in systems with flowing gases. This localized CO₂ pressure, depending on the temperature and other thermodynamic conditions, can cause other decomposition reactions, thereby forming undesired phases, which in turn contribute to reduce the critical current density of the final product.

Fjellvåg¹ studied the interaction between CO₂ and YBa₂Cu₃O_{6+x} at a total pressure of 1 atm, with 0.999 atm of O₂ and 0.001 atm of CO₂, and reported two reaction mechanisms:



Reaction (3) was reported to occur at temperatures below 730 ± 10 °C, and reaction (4) at temperatures above 730 ± 10 °C. Both of these reactions lead to the formation of nonsuperconducting phases. As can be seen from these two reactions, the partial pressure of CO₂ will determine the extent to which the nonsuperconducting reaction products are formed. The effect of CO₂ partial pressure on the oxide-carbonate equilibrium, as a function of temperature, was also derived by Fjellvåg, and is shown in Fig. 1. Analytically, the equilibrium partial pressure of CO₂ can be represented by the following expression:

$$\log p_{\text{CO}_2} = \frac{-8900}{T} + 5.7 \quad (5)$$

where p_{CO_2} is in atmospheres and the temperature T is above 730 °C.

The partial pressure of CO₂ can also affect the partial pressure of O₂, which in turn affects the oxygen content of the 123 compound formed, and thus the phase composition of the 123.

The superconducting properties of 123 compounds, as a function of oxygen content, have been studied by other investigators.²⁻⁴ For $x \approx 1$, YBa₂Cu₃O_{6+x} is in the orthorhombic phase and exhibits superconductivity at 90 K. As the oxygen content, which is dependent on both temperature and oxygen partial pressure, decreases, the transition temperature of the orthorhombic phase

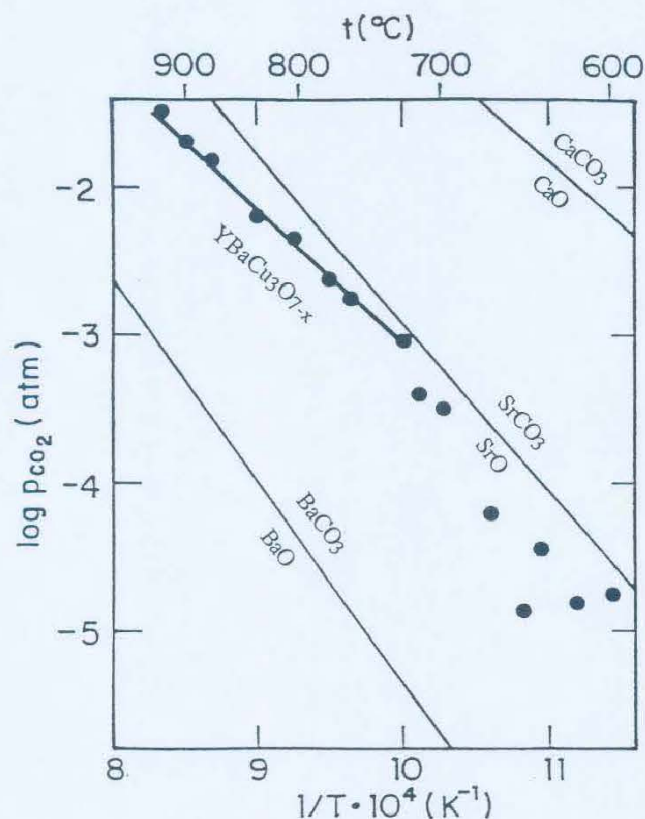


FIG. 1. Stability of $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ with respect to carbonate formation ($p_{\text{CO}_2} + 1 \text{ atm}$).¹

decreases to 60 K, at $0.6 < x < 0.7$. At $x \approx 0.4$, the material becomes tetragonal, and superconductivity is destroyed. The transition of the orthorhombic phase to the tetragonal phase occurs at an oxygen content of $x \approx 0.5$. The equilibrium constant for reactions (3) and (4) is given by:

$$K = \left\{ [p_{\text{O}_2}]^{(2x-1)/4} \right\} / \left\{ [p_{\text{CO}_2}]^2 \right\} \quad (6)$$

Equation (6) shows the effect of partial pressure of CO₂ on the partial pressure of O₂, and thus on the structure of the 123 compound synthesized.

This investigation was undertaken to determine the effect of the presence of CO₂ in atmospheres used for processing 123 compounds. The specific aims of the investigation included (a) determining process conditions necessary for avoiding the formation of undesirable phases, and (b) establishing processing-structure-properties relationships.

II. EXPERIMENTAL PROCEDURE

Appropriate amounts of Y₂O₃, BaCO₃, and CuO were mixed as a 400 gm batch and wet milled for 15 h in methanol in polyethylene jars containing ZrO₂ grinding media. The resultant slurry was pan dried and screened

through a 30 mesh sieve. The screened powder was calcined for 4 h in flowing O₂ with a pressure of $\approx 2 \text{ mm Hg}$ at a temperature of $\approx 850 \text{ }^\circ\text{C}$. During cooling, the vacuum was discontinued, and ambient pressure O₂ was passed through. A 3 h hold at 450 $^\circ\text{C}$ was incorporated into the cooling schedule to promote oxygenation of the powder. The calcined powders were ground, milled, and checked for phase purity by x-ray diffraction (XRD) and differential thermal analysis (DTA). The calcination procedure used in this work gives essentially phase-pure orthorhombic 123 powder.⁵ The calcined powder was cold-pressed into $\approx 1 \text{ cm}$ diameter pellets at $\approx 140 \text{ MPa}$, subdivided into groups, and sintered for 5 h.

Four groups, each made up of four samples, were sintered at temperatures of 910, 940, 970, and 1000 $^\circ\text{C}$, respectively, with oxygen gas at ambient pressure passed through the furnace during the entire process. Sixteen groups, each made up of four samples, were also sintered at the same temperatures, but with CO₂/O₂ gas mixtures, at ambient pressure. The CO₂ concentration in the mixtures ranged from $\approx 50 \text{ ppm}$ to 5%.

Bars of 1 mm² cross section and 10 mm long were cut from each pellet for critical current density (J_c) measurements. A criterion of 1 $\mu\text{V}/\text{cm}$ was applied to J_c measurements. Representative samples were used for measuring the critical transition temperature (T_c) by resistivity and low field RF SQUID magnetometer.

Samples were also mounted and polished, using a diamond paste, down to 1 μm , for optical and scanning electron microscopy. The mean grain size of each sample was measured using the line intercept method. High resolution transmission electron microscopy (HRTEM) was used for studying the microstructure and composition of the grains and grain boundaries. Phase composition of the sintered samples was studied by XRD.

Finally, the samples that had been sintered in 50 ppm, 500 ppm, and 0.5% CO₂ containing atmospheres were reannealed in pure oxygen flow, at 450 $^\circ\text{C}$ for 15 h, to check the reversibility of the second phases formed. Samples that had been sintered in pure oxygen flow were reannealed in oxygen flow, with 5% CO₂ for 10 h, to check for formation of second phases.

III. RESULTS

A. Sintering temperature and atmosphere

The effects of sintering temperature and atmosphere on the density and the critical current density of the samples tested are shown in Figs. 2 and 3, respectively. Figure 2 shows that the sintering temperature has a major effect on the density of the sample, as can be expected. However, the sintering atmosphere, within the range investigated in this work, does not appear to affect the density. The critical current density, on the other hand,

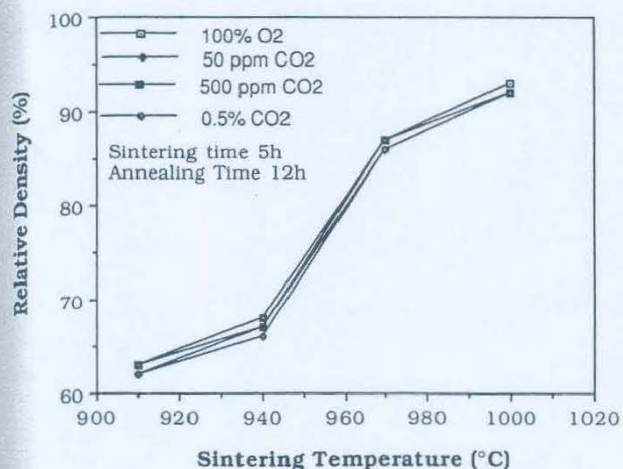


FIG. 2. The effect of sintering temperature on density.

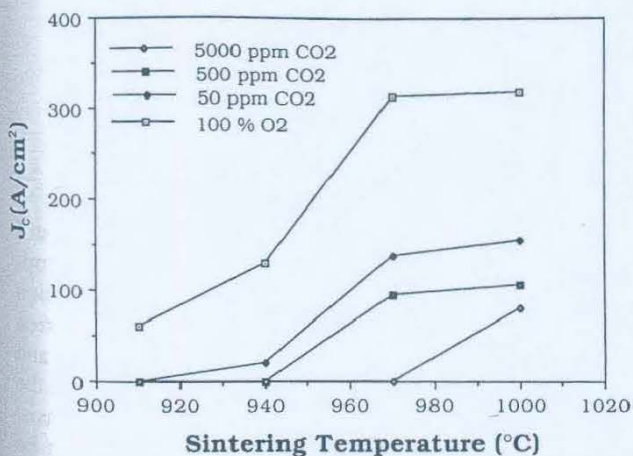
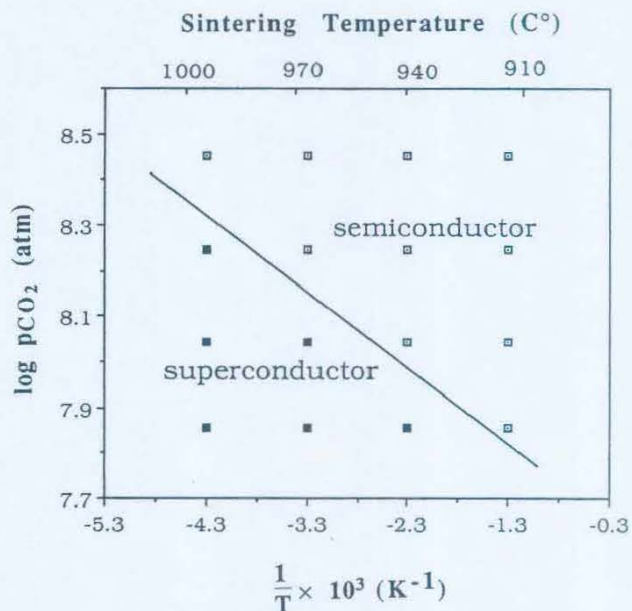
was found to be affected by both sintering temperature and CO₂ content in the sintering atmosphere, as shown in Fig. 3. J_c values decreased with decreasing sintering temperature and increasing CO₂ content. Figure 4 summarizes these results and presents them in terms of processing conditions, namely p_{CO_2} and T , necessary for production of superconductors. The solid line separates the stability regions of superconductors and semiconductors. An experimental relationship between p_{CO_2} and T was derived from this diagram, and found to be as follows:

$$\log p_{\text{CO}_2} = C/T + D \quad (7)$$

where $C = -45,000 \text{ K}$ and $D = 33.4$.

B. Microstructure and atmosphere

The microstructures of two typical samples are shown in Figs. 5 and 6. In Fig. 5 the microstructures of samples sintered at 910, 940, 970, and 1000 °C, and 100% O₂ are shown. The grain size as determined by

FIG. 3. The effect of sintering temperature on J_c .FIG. 4. Stability of 123 compounds as a function of p_{CO_2} and temperature.

the line intercept method is plotted in Fig. 7. Large grain growth is observed at 970 °C, and the grain size data are in good agreement with the density and J_c data reported earlier in Figs. 2 and 3. The denser samples have larger grain sizes, and the J_c increase is thought to result from the increase in connectivity between the grains. From Fig. 6 it can also be seen that the crystals of the samples sintered in lower CO₂ atmospheres are twinned, whereas those sintered in 5% CO₂ do not show any twinning. The twin structure in 123 determines its orthorhombic superconducting properties,⁶ and it can be concluded that the samples sintered in 5% CO₂ are not orthorhombic. Close examination of the microstructure also shows that the extent to which the orthorhombic structure is present decreases with increasing CO₂ presence in the sintering atmosphere.

C. Relationship between T_c and atmosphere

The critical temperature, T_c , of the samples was measured by both resistivity and magnetization techniques, and are shown in Figs. 8 and 9, respectively. The data in Fig. 8(a), for a sample sintered at 940 °C and 100% O₂, exhibits onset of transition at 90 K and zero resistance at 82 K. A linear temperature dependence of resistivity (R), with $\delta R/\delta T > 0$ before the onset of superconductivity, indicates that this sample is a good superconductor. Figure 8(b) shows the data for a sample sintered in an atmosphere containing 50 ppm CO₂. Two transition temperatures, one at 90 K and one at 80 K, are observed, indicating the presence of a second superconducting transition (or phase), and zero resistance is observed at 78 K. For samples sintered in an atmosphere containing 0.5%

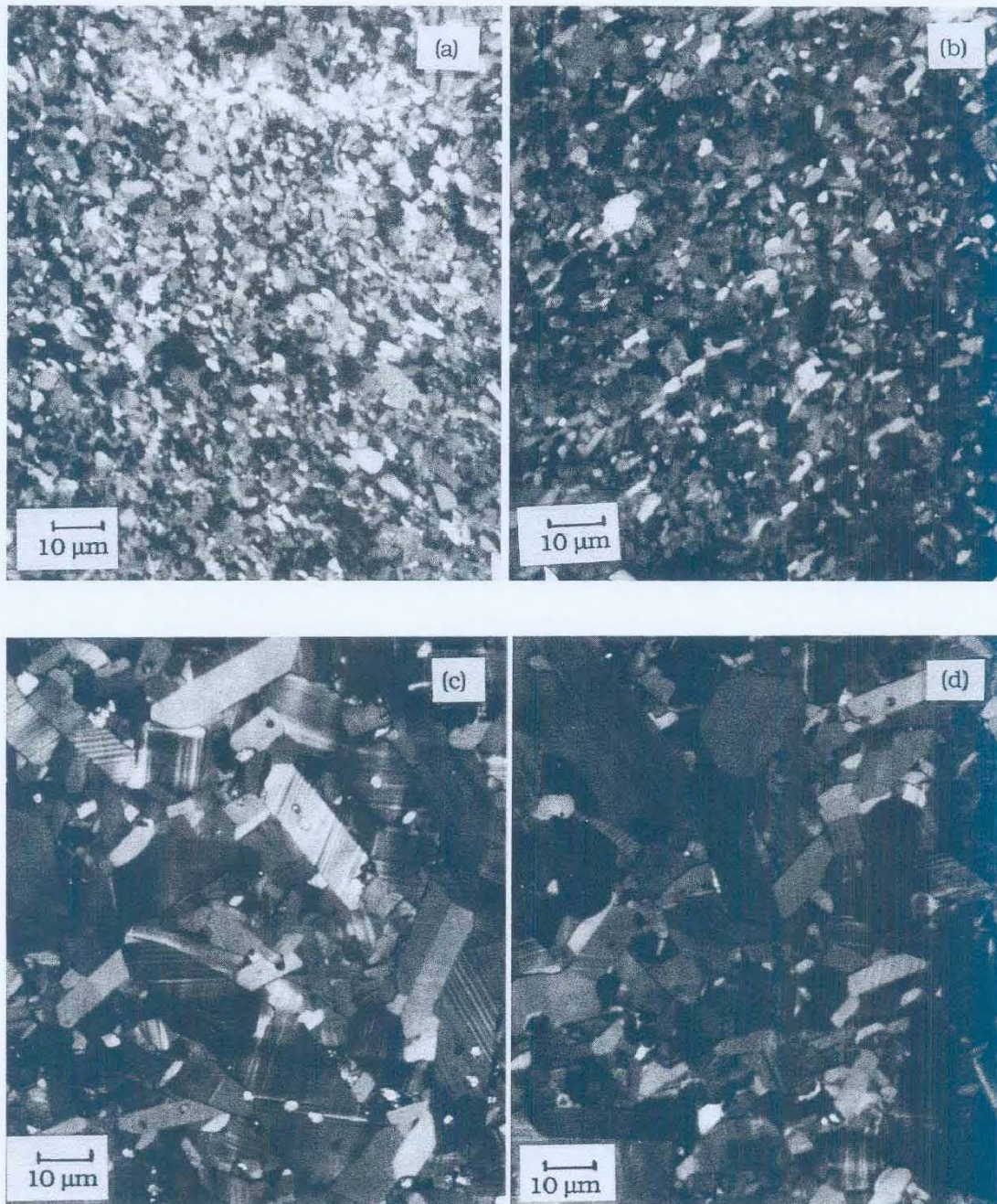


FIG. 5. Optical micrographs for samples sintered under 100% O₂ at (a) 910 °C, (b) 940 °C, (c) 970 °C, and (d) 1000 °C.

CO₂, $\delta R/\delta T < 0$ [Fig. 8(c)], and the sample shows marked semiconducting characteristics. Increasing CO₂ contents in the sintering atmosphere were found to increase the electrical resistivity of the sample. These findings are in good agreement with the findings of Wang *et al.*,⁷ Nakazawa and Ishikawa,⁸ and Kwok *et al.*⁹

The diamagnetism observed in the data reported in Fig. 9 indicates that the major phase of these samples is still superconducting. The presence of CO₂ is found to be

detrimental, despite the fact that the major phases are still superconducting. The decrease in superconducting properties is found to be directly related to the concentration of CO₂ in the sintering atmosphere. It can be inferred that CO₂ leads to partial carbonation of the sample, and that these carbonated phases may accumulate along the grain boundaries. Thus, although these samples consist of superconducting grains, these grains would then be isolated by nonsuperconducting second phases along

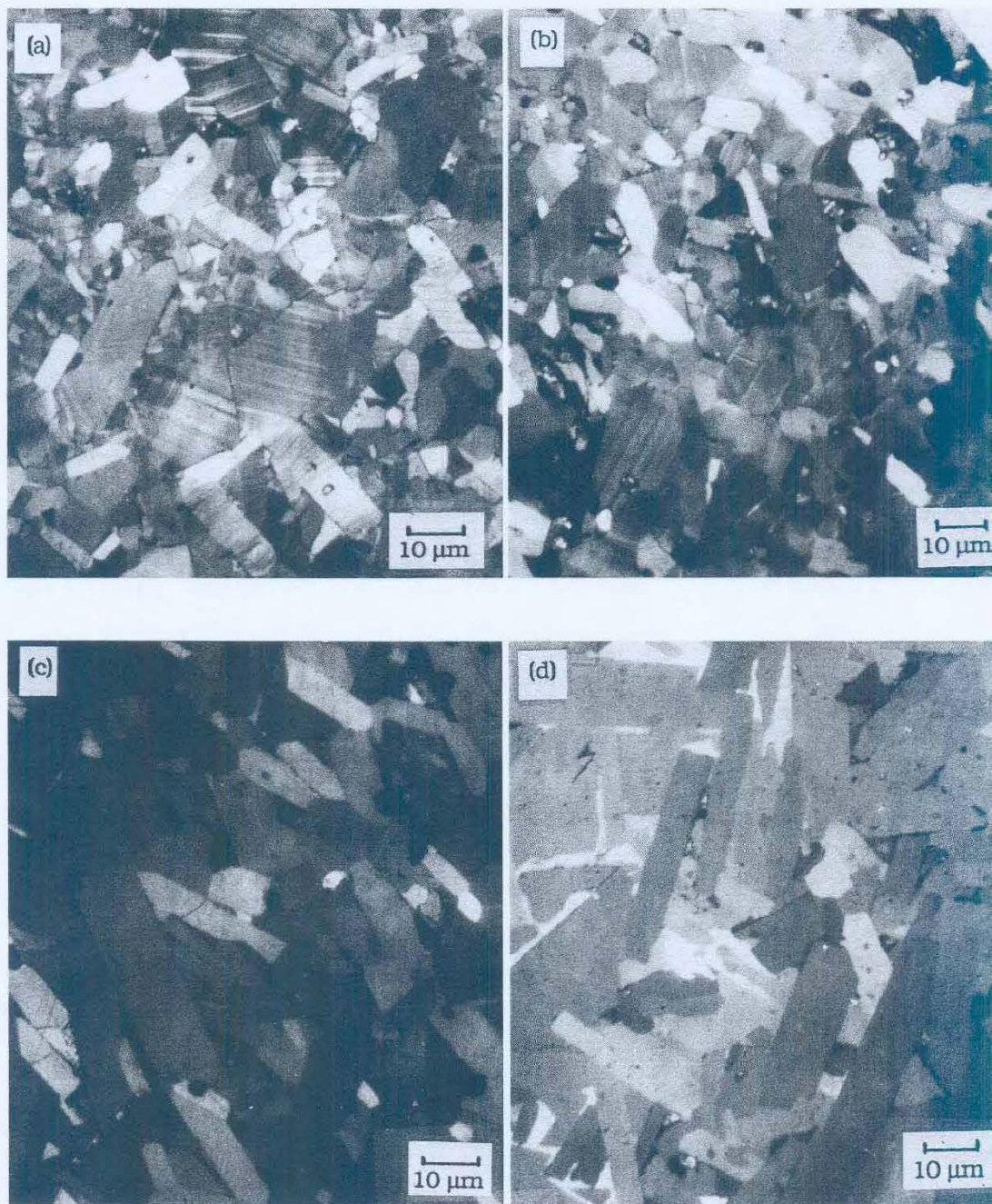


FIG. 6. Optical micrographs for samples sintered at 1000 °C, with (a) pure O₂, (b) O₂ + 50 ppm CO₂, (c) O₂ + 0.5% CO₂, and (d) O₂ + 5% CO₂.

the grain boundaries which would cause the J_c value to decrease strongly. This hypothesis was checked by transmission electron microscopy (TEM).

D. Microstructure and composition determined by TEM

The compositions at and near grain boundaries in typical sintered samples were investigated using TEM in

conjunction with energy dispersive spectroscopy (EDS). No evidence of second phases at grain boundaries was found in samples sintered in a 100% O₂ atmosphere. However, two distinct types of grain boundaries were observed in the samples that were sintered in 0.5% CO₂ + 99.5% O₂. Approximately 10% of the grain boundaries were found to be wet by a thin layer of a second phase, as shown in Fig. 10. EDS spectra obtained

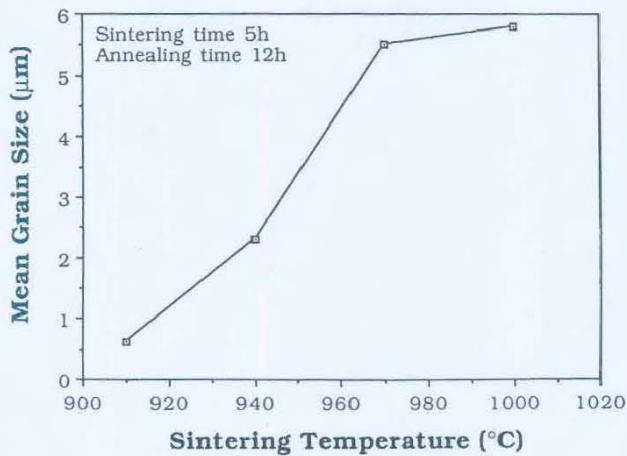


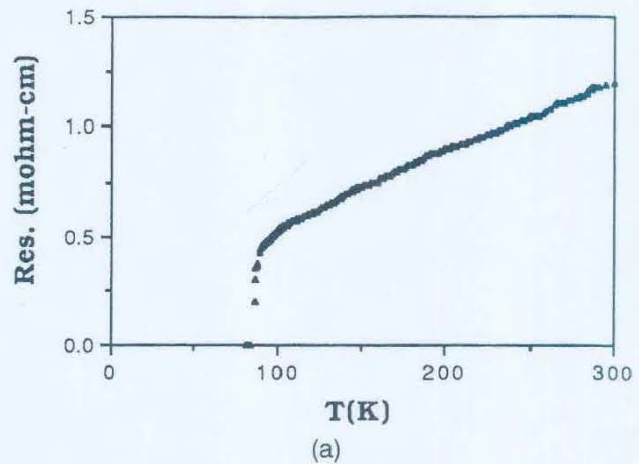
FIG. 7. Grain size of samples sintered under 100% O₂.

from locations along this boundary indicated that the composition of this layer was rich in barium and copper, but depleted in yttrium, and was likely to be BaCuO₂. At some locations this layer was found to be extremely rich in copper, and it is likely that the composition may be due to the eutectic reaction between BaCuO₂ and CuO, in accordance with the phase diagram.¹⁰ The remaining boundaries were sharp grain boundaries, and free from the presence of second phases.

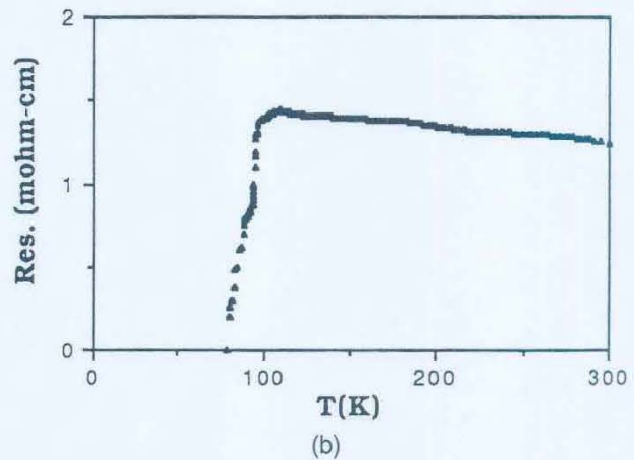
By using high-resolution transmission electron microscopy (HRTEM), it was also found that the structure near the sharp grain boundaries was not orthorhombic, but tetragonal, as shown in Fig. 11. The lattice fringes in the [001] direction were clearly observed, and it was found that $c = 1.19$ nm near the grain boundary whereas $c = 1.17$ nm in the region far from the grain boundary. From neutron diffraction data¹¹ it is known that $c = 1.19$ nm for the tetragonal structure and $c = 1.17$ nm for the orthorhombic structure. The region having $c = 1.17$ nm was also found to have twin structures, whereas the region having $c = 1.19$ nm was found to have no twins. A boundary could be observed between these two regions. The orthorhombic phase exhibits twinning, but the tetragonal phase does not.¹² This was used as further evidence to conclude that the region adjacent to the grain boundaries is tetragonal, while the region farther away is orthorhombic.

EDS also revealed the presence of precipitates of Y₂BaCuO₅ ("211") for the samples sintered in 0.5% CO₂, as shown in Fig. 12. Based on the findings here, and the fact that the samples were phase pure before they were sintered, it can be concluded that the 123 compound decomposes in the presence of CO₂, yielding Y₂BaCuO₅, BaCO₃, and CuO.

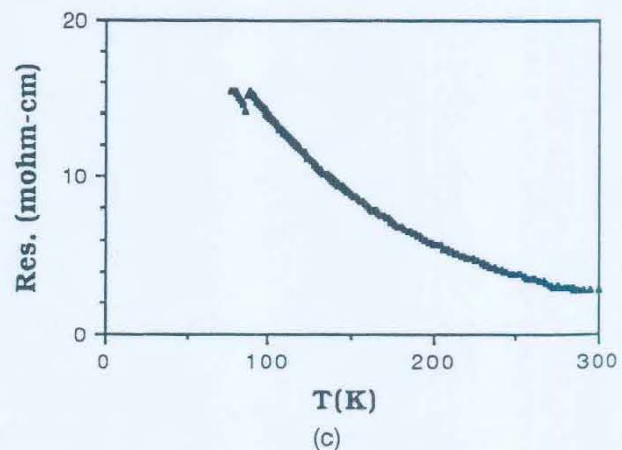
For samples sintered in 5% CO₂ + O₂, the initial 123 phase was found to be completely decomposed. Both EDS and XRD showed that the decomposition products were 211, BaCO₃, and CuO.



(a)



(b)



(c)

FIG. 8. Resistivity versus temperature for samples sintered at 940 °C, with (a) pure O₂, (b) O₂ + 50 ppm CO₂, and (c) O₂ + 0.5% CO₂.

IV. DISCUSSION OF RESULTS

Effect of CO₂

The results show that J_c decreases with an increase in CO₂ content in the sintering atmosphere, implying that

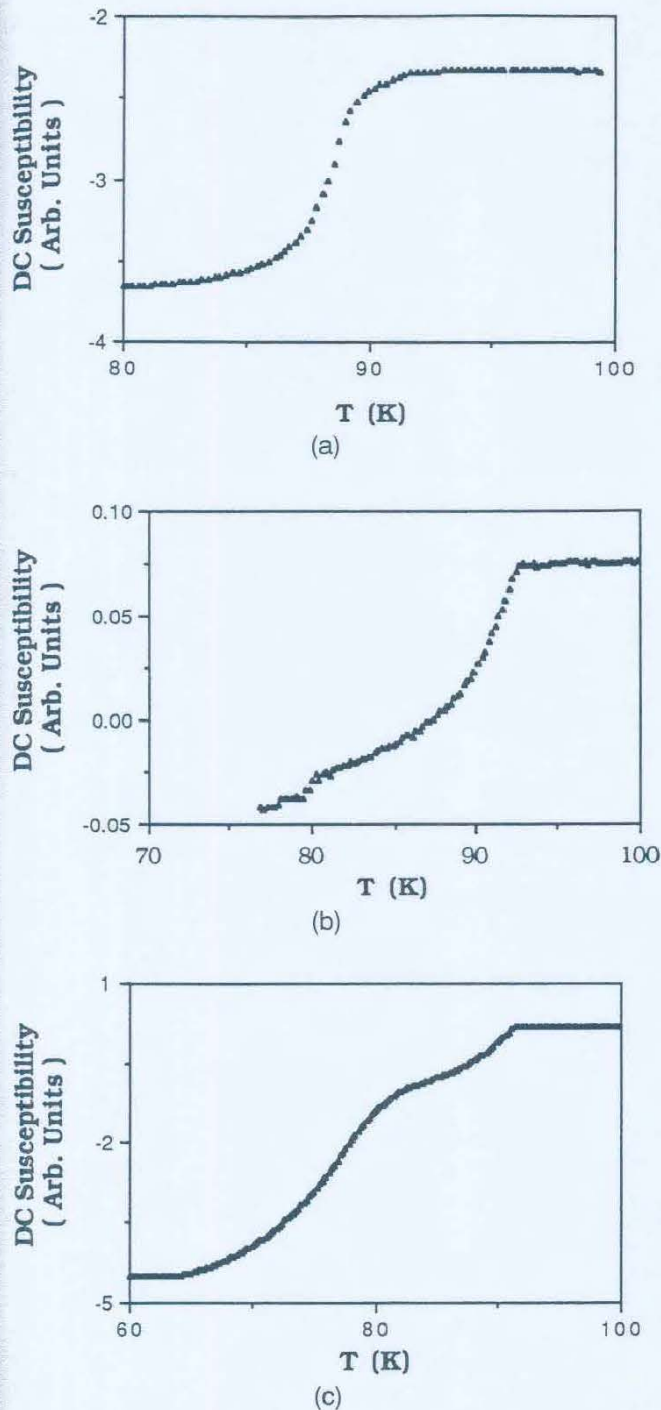


FIG. 9. R.F. susceptibility versus temperature for samples sintered at 940 °C, with (a) pure O₂, (b) O₂ + 50 ppm CO₂, and (c) O₂ + 0.5% CO₂.

CO₂ plays a critical role in the phase relationships in the Y–Ba–Cu–O system. CO₂ was also found to lower the decomposition temperature of 123. As the CO₂ content in the atmosphere increased, there was clear evidence of an



FIG. 10. Sample sintered at 970 °C in 0.5% CO₂ + 99.5% O₂. TEM micrograph for the grain boundary, as marked by G.B., which is wet by a layer of BaCuO₂ second phase.

increasing fraction of the BaCuO₂, CuO, and Y₂BaCuO₅ secondary phases.

Available phase diagram information¹³ shows that 123 melts incongruently at ≈1000 °C in air and forms a liquid and 211. The reverse reaction occurs as the temperature is decreased. The 211 phase and the liquid phase must coexist for the growth of the 123 phase. Once the 211 phase is trapped inside the 123 phase and separated from the liquid phase no more reaction occurs, and 211 will show up as a second phase with the 123 grains. During further cooling, there is a small variation in stoichiometry in the direction of BaCuO₂ + CuO, since the 211 phase is trapped inside the 123 phase. Because of the occurrence of local variations in stoichiometry,



FIG. 11. Sample sintered at 970 °C in 0.5% CO + 99.5% O₂. HRTEM image of a grain boundary (G.B.) whose normal is [001]. The lattice fringes of 1.19 nm spacing correspond to the tetragonal structure (T), while the lattice fringes of 1.17 nm spacing correspond to the orthorhombic structure (O).

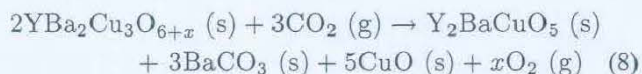


FIG. 12. TEM micrograph of sample sintered in 0.5% CO₂ + O₂. The second phases, marked S, were identified to be Y₂BaCuO₅.

the eutectic reaction takes place and BaCuO₂ and CuO form at the grain boundaries.

The decomposition at the grain boundaries weakens the path for the current, thereby decreasing the overall J_c value. The wetting of the boundaries with non-superconducting phases decreases the effective contact area between the superconducting grains and therefore decreases J_c . From the data shown in Fig. 10, the width of the second phase region along the grain boundaries was determined to be approximately 50 nm, which is much larger than the coherence length in this material.¹⁴ Therefore, it is reasonable to conclude that these second phases block the passage of currents.

The finding that higher CO₂ partial pressures can be tolerated at higher sintering temperatures is thermodynamically consistent. The interaction of 123 with CO₂ can be represented by the following reaction:



The Gibbs free energy change, ΔG , for this reaction can be expressed as follows:

$$\Delta G = \Delta G^\circ + RT \ln \left\{ \frac{(p_{\text{O}_2})^\delta}{(p_{\text{CO}_2})^3} \right\} \quad (9)$$

Since $p_{\text{O}_2} \approx 1$ atm, and $0 < \delta < 0.5$, the above equation can be simplified as follows:

$$\Delta G = \Delta G^\circ - 3RT \ln p_{\text{CO}_2} \quad (10)$$

At equilibrium, $\Delta G = 0$, and therefore:

$$\Delta G^\circ = 3RT \ln p_{\text{CO}_2} \quad (11)$$

For values of $p_{\text{CO}_2} < 1$, T must increase as p_{CO_2} increases in order to maintain the same value of ΔG° . Therefore, increasing the temperature results in a higher p_{CO_2} .

The manner in which CO₂, contained in the sintering atmosphere, reacts with the bulk material is obviously extremely important. As pointed out at the beginning of this paper, two sources of CO₂ are the decomposition of BaCO₃ during calcination and/or the CO₂ contained in the O₂ gas used during sintering and annealing. An additional potential source is the organic binders that are used in the formulation of 123 compounds. The CO₂ formed by the interaction of the organic binders and the oxygen from the atmosphere could have a deleterious effect on the performance capabilities of the final product.

Sintering temperatures can be lowered if p_{CO_2} can be lowered, and one expedient means of doing this is to remove the CO₂ contained in the O₂ gas. The CO₂ content of O₂ gas varies, depending upon the purity of the gas purchased. While research purity oxygen gas, with a minimum purity of 99.998%, is reported to have a CO₂ content of less than 0.1 ppm,¹⁵ commercial purity O₂ gas could have a significantly higher CO₂ content. Therefore, when using oxygen gas of uncertain CO₂ content, it is recommended that a CO₂ removal system, such as LiOH, be incorporated in the experimental equipment.

V. CONCLUSIONS

The present study has shown that 123 compounds can be successfully prepared, from BaCO₃ and other oxides, only under conditions to the left of the equilibrium boundary in Fig. 4. The critical current density and transition temperature both depend strongly on the sintering conditions, particularly the partial pressure of CO₂ and temperature. The 123 compound reacts with CO₂, resulting in compositional inhomogeneity which accumulates at grain boundaries, thereby impeding the current path.

The tendency of the 123 compound to react with CO₂ also depends on the sintering temperature; increasing temperatures raise the equilibrium CO₂ partial pressure.

ACKNOWLEDGMENTS

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