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DEGRADATION OF PROPERTIES OF $YBa_2Cu_3O_x$ SUPERCONDUCTORS SINTERED IN CO_2-CONTAINING ATMOSPHERE*

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ABSTRACT

Stability of the $YBa_2Cu_3O_x$ (YBCO) superconductor toward reacting with CO_2 in CO_2/O_2 gas mixtures during sintering was investigated as a function of the partial pressure of CO_2 and temperature. The transport critical current density, J_c, of the superconductor decreased drastically with increasing partial pressure of CO_2 in the gas mixture. As the partial pressure of CO_2 was increased, J_c became zero (at 77 K) even though the major phase of the sample was still a superconductor as determined by magnetic susceptibility measurements. Microstructures and compositions of the samples were investigated by transmission electron microscopy in conjunction with energy-dispersive X-ray spectroscopy. Two types of grain boundaries were observed: ~10% of the grain boundaries contained a second phase; the regions near the remaining grain boundaries were tetragonal. At high partial pressures of CO_2, the YBCO completely decomposed to $BaCO_3$, Y_2BaCuO_5, and CuO.

INTRODUCTION

The transition temperature, critical current density, and the width of superconducting transition of YBCO superconductors are influenced by atmospheric contaminants such as CO_2 and H_2O[1-6]. Jahan et al.,[7] indicated the formation of insulating phases when YBCO is reacted with water vapor. Reaction of YBCO with CO_2 has been reported by several researchers[1,5,6,8]. Gallagher et al.,[1] reported that at 1000°C in a 1% CO_2/O_2 mixture the YBCO phase was not decomposed, while in a 10% CO_2/O_2 mixture the YBCO phase was completely decomposed, forming $BaCO_3$, $Y_2Cu_2O_5$, and CuO. Fjellvag et al.,[8] concluded that the reaction occurred in two steps. Below 730°C the reaction products are $BaCO_3$, Y_2O_3, and CuO, while above this temperature the products are $BaCO_3$, $Y_2Cu_2O_5$, and CuO. Because of limitations of the X-ray diffraction technique, both Gallagher et al.,[1] and Fjellvag et al.,[8] were unable to study the spatial origin of the reaction between YBCO and CO_2, which may be very important with regard to the low value of the critical current density found in ceramic superconductors. Recently Cooper et al.,[9] employed in-situ electrical conductivity measurements to study the kinetics of decomposition of YBCO in flowing 5% CO_2/95% O_2 atmosphere at 815°C.

In this paper, we report on the degradation of properties (critical temperature, T_c, and critical current density, J_c) of YBCO superconductors sintered in CO_2-containing atmospheres. The microstructures and compositions of the samples were investigated by transmission electron microscopy, analytical electron microscopy, and secondary ion-mass spectroscopy. The relations between the properties and the partial pressure of CO_2 will be discussed in terms of the microstructural changes.

EXPERIMENTAL

Phase-pure, orthorhombic powders of YBCO were prepared by mixing and grinding stoichiometric amounts of Y_2O_3, $BaCO_3$, and CuO, and calcining in flowing oxygen at a reduced total pressure of about 2 mm Hg at about 850°C, followed by low temperature annealing in ambient pressure oxygen[10]. The reduced pressure used in this process ensured the efficient removal of the CO_2 gas generated during the formation of the YBCO phase, resulting in the production of phase-pure, orthorhombic powders. These powders were pelletized and sintered in the temperature range 900 - 1000°C for about 5 h in flowing (~ 1 atm) O_2/CO_2 gas mixtures. The portion of CO_2 in the mixtures was 0 - 5%. The samples were cooled slowly to room temperature. A 12 h hold at 450°C was incorporated in the cooling schedule for oxygenation of the ceramics. J_c was measured by standard four-probe resistivity measurement in liquid nitrogen. A criterion of 1 $\mu V/cm$ was used for J_c measurement. T_c values were obtained by resistivity and magnetization techniques. A low field rf SQUID magnetometer was used for the magnetization measurements. Transmission electron microscope (TEM) specimen discs (3 mm diameter) were cut from the sintered bulk samples, polished, and dimpled from both sides until a thin area at the center obtained. The final TEM specimens were argon-ion thinned at liquid nitrogen temperature.

RESULTS AND DISCUSSION

The J_c (at 77 K) values decrease as the CO_2 partial pressure in the sintering atmosphere is increased. Depending on the sintering temperature, up to a certain value of the CO_2 partial pressure, the J_c value decrease, and finally become zero. Resistivity measurements show that the materials with $J_c = 0$ are semiconductive. Figure 1 shows the stability region for transport superconductivity with respect to the partial pressure of CO_2 at the four sintering temperatures (910, 940, 970, and 1000°C). Magnetization measurements for samples with $J_c = 0$ (semiconductive behavior by resistivity measurements) indicate that the majority phases of these materials are still superconducting. The onset temperature of superconductivity, about 90 K, is almost the same for all of the samples. The resistivity and magnetization measurements on samples with high and zero J_c suggest a strong blockage of superconducting current at the grain boundaries in the latter samples. A possible cause of the blockage could be a thin layer of second phase at grain boundaries, formed during sintering, due to the reaction of YBCO with CO_2 in the gas atmosphere.

TEM observations show the presence of secondary phases at some grain boundaries. An example of one such secondary phase is shown in Figure 2 for the sample sintered at 970°C in 0.5% CO_2/O_2 gas mixture. The second phase is determined to be $BaCuO_2$ and $BaCO_3$ by X-ray energy-dispersive spectroscopy (XEDS). The width of this grain boundary phase is much larger than the coherence length in YBCO superconductor. Such a phase therefore can obstruct the superconducting current passing across the grain boundaries so that the overall critical current density may decrease. This type of grain boundary accounts for only about 10% of the observed grain boundaries, while the majority of the grain boundaries appear quite sharp with no obvious evidence for a second phase. Because of the multitude of possible percolation paths, the value of J_c would not become zero if only 10% of the grain boundaries are coated with a second phase. Therefore, a majority of the grain boundaries have to be resistive enough to block the flow of superconducting current across the boundaries. By careful study of high-resolution electron microscopy (HREM) images, it is found that the structure near the sharp grain boundaries is not orthorhombic, but tetragonal. Figure 3 shows a HREM image of lattice fringes of (001) planes. By careful measurement of the inter-planar spacing, it was found that the spacing is about 1.19 nm at the region near the grain boundary while the spacing is approximately 1.17 nm in the region far from the grain boundary. From neutron diffraction data[11], it is known that the structure with c = 1.19 nm is tetragonal. Another indication of the presence of the tetragonal structure is the termination of the twin structure as marked by T in Fig. 3. This can be taken as the signature of the demarcation line between the orthorhombic and tetragonal structures, since the tetragonal structure has no twins. A possible cause of the phase transformation from the orthorhombic to the tetragonal structure is the incorporation of carbon into the lattice due to the CO_2 in the sintering atmosphere[5,6]. Carbon diffuses into the lattice, and expells the oxygen in the orthorhombic structure, thus forming a tetragonal structure. Secondary ion mass spectroscopy (SIMS) was used to detect the carbon signal. The SIMS results show that there is carbon segregation at grain boundaries or at regions near grain boundaries[6]. It should be noted that Fig. 3 is a special example which has a particularly large tetragonal region. We observed, in most cases, that such tetragonal regions near grain boundaries vary from a few nanometer to several tens of nanometers. Therefore, they are very difficult to detect and are not readily identifiable in most boundaries. The width of these tetragonal regions are quite large compared to the coherence length, and these regions block the superconducting current and therefore the J_c goes to zero.

Our previous work[5] indicates that the reaction rate with CO_2 depends on the grain boundary orientation and structure. Therefore, at low partial pressures of CO_2 (up to few hundred parts per million), only a fraction of the grain boundaries may be modified sufficiently by such reactions to cause interruption of the superconducting current. For the samples sintered in 5% CO_2/O_2, no superconducting transition is observed. At this high level of CO_2, the YBCO phase completely decomposed into three different phases. From the XEDS analyses, it is found that these phases are $BaCO_3$, CuO, and Y_2BaCuO_5.

CONCLUSIONS

YBCO react strongly with CO_2 at high temperatures, leading to a decrease in J_c. The secondary phases formed at the grain boundaries as a result of reaction of YBCO with CO_2 blocks the flow of superconducting currents. The secondary phases are identified as $BaCuO_2$, and $BaCO_3$ and appear as a thin layer, coating the grain boundaries. The carbon segregation results in a phase transformation of the orthorhombic phase to the non superconducting tetragonal phase. At CO_2 level as high as 5%, the YBCO completely decomposes to $BaCO_3$, Y_2BaCuO_5, and CuO.

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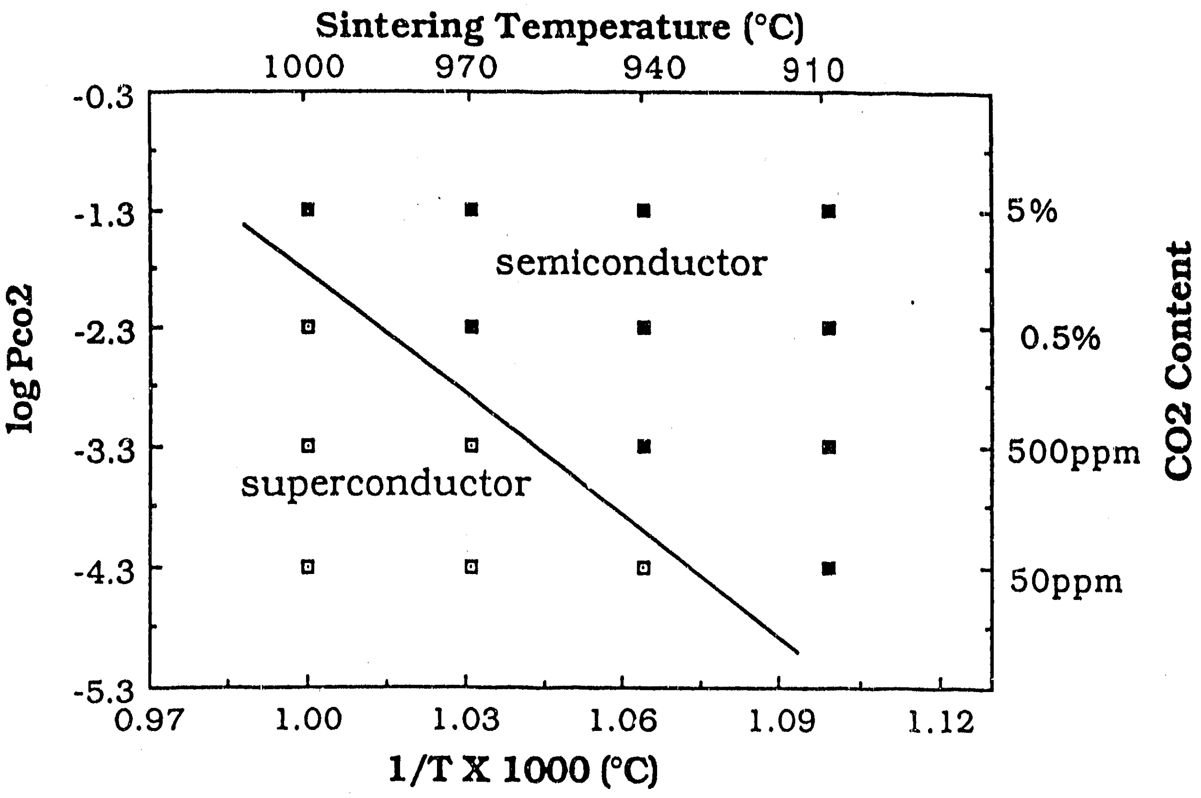
FIGURE CAPTIONS

Figure 1. The stability of YBCO with respect to partial pressure of CO_2 at various temperatures.

Figure 2. TEM picture of a grain boundary (GB) in a YBCO sample sintered at 970°C in 0.5% CO_2/O_2 atmosphere. The thick second phase layer at GB is identified as $BaCuO_2$.

Figure 3. HREM image of a grain boundary in a YBCO sample sintered at 970°C in 0.5% CO_2/O_2 atmosphere.



Sintering Temperature (°C)
1000
970
940
910
-0.3
-1.3
-2.3
-3.3
-4.3
-5.3
log Pco2
5%
0.5%
500ppm
50ppm
CO2 Content
semiconductor
superconductor
0.97
1.00
1.03
1.06
1.09
1.12
1/T X 1000 (°C)

Fig. 1

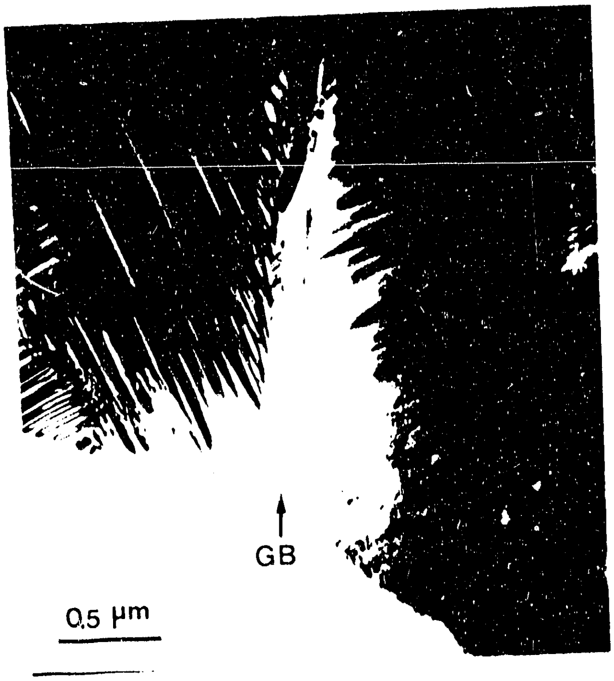


Fig. 2

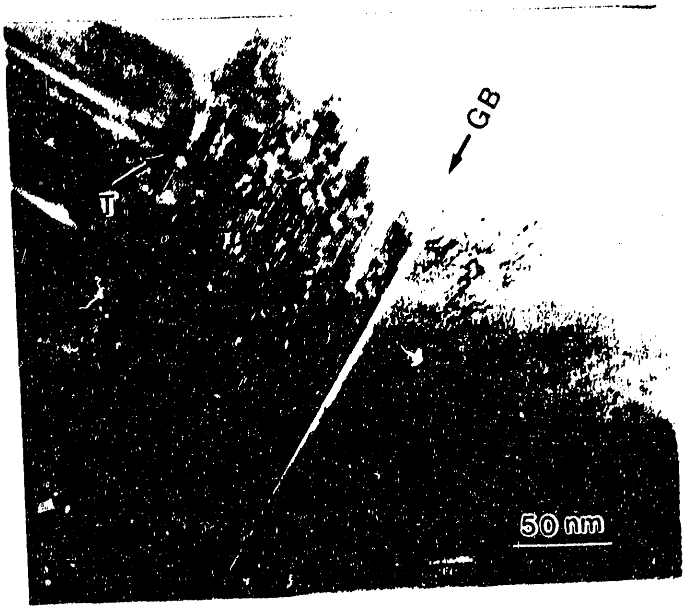


Fig 3

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