Fabrication of bulk Y-Ba-Cu-O superconductors with artificial holes through oxidation of carbon rods

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Abstract. We fabricated bulk Y-Ba-Cu-O superconductors with artificial holes that were created by oxidizing carbon rods embedded in the precursor pellets. Twenty carbon rods 500 μm in diameter and 5 mm in length were compacted with bulk Y-Ba-Cu-O precursor pellets such that carbon rods were parallel to the thickness direction. Then the precursors were heated at 1000 °C and 1050 °C. During the heating process, carbon rods reacted with ambient oxygen and twenty holes were successfully produced. With oxygen annealing treatment, the bulk Y-Ba-Cu-O superconductors with 20 holes exhibited superconductivity. Microstructural observations showed that the grain size around carbon rods was larger than that of the interior region. This was probably due to the fact that the temperature near the carbon rod was raised since the reaction of carbon and oxygen is exothermic. We also noticed that the formation of pores was largely inhibited near the holes.

1. Introduction
Bulk Y-Ba-Cu-O superconductors are attractive for various engineering applications, since they can levitate permanent magnets without active control, and can trap a significant magnetic field much higher than those of permanent magnets [1-3]. The stable levitation of permanent magnets has been applied to the fabrication of magnetic bearings without contact, which was further employed for the production of superconducting flywheel system for energy storage. High trapped field magnets were employed for various high field applications such as water-purification system and magnetron sputtering devices. Transfer of rotational torque without contact is another interesting application area [4]. When magnet circuits are made such that multiple magnetic poles like NSNS face the superconductor, rotational torques are transferred without contact by making a configuration of two permanent magnets with a bulk superconductor placed in between.

Bulk superconductors are however brittle ceramics with low thermal conductivity and thereby suffer from low cryo-stability and poor mechanical properties. Hence mechanical reinforcement and an increase in thermal conductivity have been performed to enhance their feasibility and robustness for practical applications and a trapped field of 17 T has been achieved [5].

One such treatment is the incorporation of metals. For this it is common to mechanically drill the holes into a bulk superconductor followed by the insertion of metal rods and the impregnation of low melting-temperature alloys such as Pb-Sn-Bi [6]. Machining prior to melt processing is also commonly performed [7], since mechanical machining after melt processing may cause damage to the superconducting properties. Once holes are introduced into bulk materials, various compounding treatments are possible. Recently we have incorporated ferromagnetic Fe bars into bulk Y-Ba-Cu-O, which showed stronger coupling forces with permanent magnets [8].
rotational torque forces were greatly improved for rotational devices such as a superconducting mixer. Mechanical machining of melt-processed Y-Ba-Cu-O either before or after the melt growth is likely to cause damage such as cracking to bulk superconductors. It is thus desirable to introduce holes into bulk superconductors without any mechanical treatments. In this context, we sought for the method to make holes without mechanical drilling.

During the calcination process of Ba-containing oxides, carbon is released from BaCO$_3$ raw powders. Based on this fact, we reached the idea to create holes by firing carbon rods incorporated into Y-Ba-Cu-O precursor. When one can prepare the composite of carbon and Y-Ba-Cu-O and heats it at high temperatures in air, carbon will be released from the precursor in the form of CO$_2$ gas, leading to the formation of pores. In this study, the fabrication of artificial holes was carried out by heating the Y-Ba-Cu-O precursor in which carbon rods were embedded.

2. Experimental

Powders of YBa$_2$Cu$_3$O$_y$ and Y$_2$BaCuO$_5$ were made by mixing Y$_2$O$_3$, BaO$_2$ and CuO powders for two hours. The mixed powders were sintered at 900°C for 24 hours and pulverized, which was repeated three times. Then, the YBa$_2$Cu$_3$O$_y$ and the Y$_2$BaCuO$_5$ powders were compounded in a molar ratio of 5:2 and mixed for two hours. The mixed powder of 15 g incorporated with 20 carbon rods of 500 μm in diameter and 5 mm in length was compacted into a pellet of 30 mm diameter and 5 mm in thickness. Figure 1 shows a green compact with 20 carbon rods embedded.

Figure 2 shows thermal schedules employed for melt processing. The maximum temperature was set to be 1000 °C and 1050 °C to study the effects on the oxidation of carbon rods. After the melt process, oxygen annealing was carried out at 400 °C for 100 hour.

![Figure 1. Top view of Y-Ba-Cu-O bulk precursor with twenty carbon rods embedded. The spots with bright contrast seen on the surface are carbon rods.](image1)

![Figure 2. Schematic diagram of thermal schedule.](image2)

For sample characterization, we measured the trapped magnetic fields. To magnetize the superconductors, we used an Fe-Nd-B permanent 25 mm in diameter and 10 mm in height. The field of the permanent magnet at 1 mm above the surface was 0.361 T. The superconductor was cooled by liquid nitrogen with the distance between the magnet and the superconductor fixed to be 1 mm. After removing the magnet, the trapped field was measured by scanning a Hall sensor in the area of 50×50
mm² at 1 mm above the sample surface. In order to observe pore structure and crystal grains, the samples were polished using abrasive papers and subjected to optical microscopic observations.

3. Results and Discussion

Figure 3 shows a photo of top view of a Y-Ba-Cu-O bulk superconductor with 20 holes melt-processed at the maximum temperature of 1050 °C. Since we did not employ a top-seeded melt-growth method, the sample is poly-crystalline. One can also see that artificial holes were successfully created after melt-processing.

Figure 4 shows the results of trapped magnetic fields of the superconductor. The sample traps magnetic fields, showing that the sample is superconducting, although the field distribution is not uniform due to its polycrystalline nature.

Figure 5 shows optical micrographs of Y-Ba-Cu-O bulk superconductors with 20 holes melt-processed at the maximum temperatures of (a) (b) 1000 and (c) (d) 1050 °C. When one looks at the photos (a) and (b) for the sample melt-processed at 1000 °C, one can notice a significant difference in the grain sizes between two regions. The grain size of the region near the hole is much greater than that of the interior region. The reaction of carbon and oxygen is exothermic, and thus an increase in the temperature near the carbon rod may be responsible for a large grain size. In order to confirm this idea, we measured the temperature of carbon and furnace by using thermocouple in bulk of carbon and furnaces, respectively. As shown in Figure 6, the temperature of carbon is higher than that of the furnace. Hence we can conclude that enhanced grain growth near the hole was due to the temperature rise caused by the exothermic reaction of carbon rod. In the case of the sample heated at 1050 °C, however, we could not see a large difference in the grain size.

Another interesting feature of the microstructure is a small pore density near the hole. On heating oxides decompose and oxygen gas is released from the sample, which is trapped inside the sample as porosities due to a low diffusion rate. Near the hole, however, the gas can easily escape from the sample, leading to a small pore density.

Figure 3. Top view of a Y-Ba-Cu-O bulk superconductor with 20 holes melt-processed at the maximum temperature of 1050 °C.

Figure 4. Trapped magnetic field of Y-Ba-Cu-O bulk superconductor with 20 holes melt-processed at the maximum temperature of 1050 °C.
Here it should be noted that the average diameter of the holes for the sample heated at 1050 °C was 450 μm, which was smaller than the initial diameter of the carbon rod of 500 μm, presumably due to the liquid phase formation, which filled the wall of the hole. Hence, for the design of the final diameter, one should take account of such a shrinkage in the hole diameter. Heat generated from the

**Figure 5.** Microstructure of Y-Ba-Cu-O bulk superconductors with 20 holes melt-processed at the maximum temperatures: (a) (b) 1000 °C; and (c) (d) 1050 °C. The regions of (a) and (c) are near the hole, while the regions (b) and (d) are located in the interior region apart from the hole.

**Figure 6.** Temperatures for the carbon and furnace as a function of time when heated at a rate of 6 °C/min.
reaction of 1 mol carbon with oxygen is 396 kJ. Hence the heat is enough to raise the temperature of
the sample that the reaction will be generated near the carbon rod. The results presented in Figure 6
suggest that heat generation due to the carbon reaction takes place even at temperatures higher than
1000 °C, which may be useful for making thermal gradient in the furnace.

It is known that carbon starts to react with oxygen at around 400 °C in air. If one heats the
composite of Y-Ba-Cu-O and carbon rods at temperatures above 400 °C for a sufficiently long time,
the holes may be formed at low temperatures. The design of proper thermal schedule will enable us to
create holes into bulk Y-Ba-Cu-O without affecting microstructure through the oxidation of carbon
based materials.

4. Summary
We have studied the possibility to introduce artificial holes into bulk Y-Ba-Cu-O superconductors by
oxidizing carbon rods embedded in the precursor. Twenty carbon rods 500 μm in diameter and 5 mm
in length were incorporated into the powders of YBa2Cu3O7-Y2BaCuO5 and consolidated into the
pellet 30 mm in diameter and 5 mm in height.

Then the pellets were subjected to melt-processing at the maximum temperatures of 1000 and 1050
°C. In both cases, carbon rods fully reacted with oxygen in air, and twenty holes were successfully
produced into the bulk Y-Ba-Cu-O. Furthermore, we confirmed that both samples exhibited
superconductivity after oxygen annealing.

Microstructural observations clarified that the grain size near the hole was much larger than those
in the interior region. This could be ascribed to the temperature raise caused by the heat generation
associated with the reaction of carbon and ambient oxygen. It was also found that the pore density was
so small near the hole, due to the fact that the gas released from the decomposition of the oxides could
diffuse out of the sample through the holes.

Formation of the holes through oxidation of carbon rods is a practical and easy method and
applicable to engineering applications.

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