Novel sponge-like structure created in GdBa$_2$Cu$_3$O$_{7-\delta}$ ceramics by hot spot

Tomoichiro Okamoto, Yoshifumi Tsutai, Masasuke Takata*

Department of Electrical Engineering, Nagaoka University of Technology, 1603-1 Kamitomioka, Nagaoka, Niigata 940-2188, Japan

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Abstract

A hot spot, which is a local area glowing orange, appears in a GdBa$_2$Cu$_3$O$_{7-\delta}$ ceramic rod when a voltage exceeding a certain value is applied to the rod at room temperature. The rod with the hot spot shows various functional characteristics that give rise to applications in devices. We found that the hot spot created a sponge-like structure in the rod. The elemental map revealed that the sponge-like structure was composed of Gd$_2$BaCuO$_5$ grains. The hot spot is considered to decompose GdBa$_2$Cu$_3$O$_{7-\delta}$ into Gd$_2$BaCuO$_5$ and liquid phase, and the liquid phase moves toward the periphery of the rod, leaving sponge-like structure composed of Gd$_2$BaCuO$_5$ grains. The novel sponge-like structure created in the GdBa$_2$Cu$_3$O$_{7-\delta}$ rod by the hot spot may bring about new applications for magnetic separations of fluids.

Keywords: Hot spot; Sponge-like structure; Decomposition; Scanning electron microscopy; Energy dispersive X-ray spectroscopy; Superconductor; Magnetic separation

1. Introduction

LnBa$_2$Cu$_3$O$_{7-\delta}$ (Ln: rare earth element), which is well known as the high-$T_c$ superconductor, is a typical non-stoichiometric oxide. Oxygen deficiency $\delta$ increases with increasing temperature above 400 $^\circ$C [1]. The carrier density decreases with increasing $\delta$, which results in a steep increase of the resistivity [2–4]. In other words, the material shows a positive temperature coefficient of resistivity (PTCR).

The present authors observed the phenomenon that a local area of a LnBa$_2$Cu$_3$O$_{7-\delta}$ ceramic rod glows orange once a voltage exceeding a certain value is applied at room temperature (Fig. 1) [5]. The visible glowing area was named a hot spot. The temperature of the hot spot in air was about 900 $^\circ$C that is almost the same as its sintering temperature [6–8]. The hot spot moves to the negative electrode with the velocity of a few mm/min. The direction of movement can be reversed by switching the polarity [5]. The appearance of the hot spot is related to the PTCR characteristic [5–7]. The movement of the hot spot is considered to be caused by the diffusion of oxide ions in the electric field over the hot spot [5,6]. The heat treatment using the moving hot spot can be used as an improvement technique for its transport critical current density [8].

The current through the rod decreases abruptly when the hot spot appears, and remains constant with increasing voltage [6–9]. This is possible because the size of a hot spot with high resistivity increases linearly with increasing voltage [5–7]. The rod with the hot spot can be used as a constant-current generator without any active component. The current after the appearance of the hot spot depends on the oxygen partial pressure in ambient atmosphere, which acts as an oxygen sensor without the need for any heating system [6,10]. The current is also sensitive to the gas flow around the rod, and the rod can be used as a high sensitive gas flow sensor [11]. Under low oxygen partial pressure, the current vibrates in the form of damped sinusoidal oscillation [12]. The rod with hot spot can be used as a new type of sine wave oscillator.

We have schemed to apply the hot spot to create a new structure in the GdBa$_2$Cu$_3$O$_{7-\delta}$ ceramics. In this paper, it is reported that a novel sponge-like structure have been created in the GdBa$_2$Cu$_3$O$_{7-\delta}$ ceramics rod by the hot spot. The mechanism of the formation of the structure is discussed from the elemental analysis of the rod.

* Corresponding author. Tel.: +81 258 47 9509; fax: +81 258 47 3604. E-mail address: takata@vos.nagaokaut.ac.jp (M. Takata).
2. Experimental

GdBa$_2$Cu$_3$O$_{7-\delta}$ ceramics was prepared by conventional solid-state reaction. The starting powders Gd$_2$O$_3$, BaCO$_3$ and CuO (Soekawa Chemical, >99.9% purity) were weighed in the ratio of Gd: Ba: Cu = 1: 2: 3, mixed for 2 h in ethanol, dried, calcined at 900°C for 10 h in air, and then ground into powder. The powder was uniaxially pressed at 40 MPa into pellet of 20 mm × 50 mm × 5 mm. The pellet was sintered at 900°C for 5 h in air. The X-ray diffraction pattern of the sintered pellet showed only GdBa$_2$Cu$_3$O$_{7-\delta}$ peaks. The pellet was cut into rods that had the cross-section of 0.65 mm × 0.65 mm. The electrical characteristics were measured by a four-probe method with the distance between voltage electrodes being 40 mm. Oxygen partial pressure ($P_{O_2}$) of the ambient was controlled by changing the flow rates of N$_2$ and O$_2$. The microstructure of the rod was observed by scanning electron microscopy (SEM; JEOL, JSM-5510) and energy dispersive X-ray spectroscopy (EDS; JEOL, JED-2201).

3. Results and discussion

Fig. 2 shows SEM images of a cross-section of the rod before the appearance of the hot spot. The rod had porous microstructure. The relative density of the rod was 68%. The distribution of the density was almost homogeneous. The hot spot appeared in the rod when the voltage of certain value was applied to the rod in each $P_{O_2}$ ranging from 1 to 100 kPa. After the certain duration, the rod broke in two due to melting at the hot spot. The duration tended to decrease with increasing $P_{O_2}$; e.g. about 7 and 1 h for air and O$_2$ atmosphere, respectively.

The presence of partial melt in the hot spot is considered to be the cause of the breaking at the hot spot [10,13]. It is thought that the viscosity of liquid phase generated by the partial melt decreases with increasing $P_{O_2}$, since the temperature of the hot spot increases with increasing $P_{O_2}$ [6]. The lower viscosity of the liquid phase leads to the easier migration of the elements, resulting in the acceleration of the structural change in the ceramics. In other words, the structure change is easier in higher $P_{O_2}$, and this accounts for the decrease of the duration with increasing $P_{O_2}$. For the above discussion, it is thought that the hot spot appearing in O$_2$ atmosphere is the most effective in changing microstructure.

A hot spot whose size was 2 mm appeared after applying a dc voltage of 6 V in O$_2$ atmosphere. After about 1 h, the rod broke in two due to melting at the hot spot. Fig. 3 shows the cross-section of the rod. The observed surface was about 2 mm far from the breaking point. There was remarkable density distribution in the rod. The inside of the rod (Fig. 3(b)) showed a sponge-like microstructure composed of needle-shaped grains. The density near the periphery of the rod (Fig. 3(c)) was higher than the initial one (Fig. 2). Fig. 4 presents SEM image and EDS elemental maps for Gd, Ba and Cu. Compared to the periphery, the centre of the rod showed high concentration of Gd and low concentration of Ba and Cu. The quantitative analysis revealed that the needle-shaped grains were Gd$_3$BaCuO$_5$.

The above results suggest the following formation mechanism for the sponge-like structure in the rod. Though the temperature of the hot spot in O$_2$ atmosphere was measured at about 950°C using infrared radiation thermometer [6], the temperature near the center of the hot spot is considered to be around 1000°C. From the report about YBa$_2$Cu$_3$O$_{7-\delta}$ [14], the decomposition of GdBa$_2$Cu$_3$O$_{7-\delta}$ is expected to occur at 1000°C, resulting in the formation of...
Fig. 3. SEM images of a cross-section of the rods after the sustained presence of the hot spot. For the hot spot appearance, dc voltage of 6 V was applied to the rod in O₂ atmosphere. The section was about 2 mm far from the breaking point. (a) Whole cross-section, (b) near the center of the rod and (c) near the periphery of the rod.

Fig. 4. SEM image and EDS elemental maps for Gd, Ba and Cu for the cross-section of the rods after the sustained presence of the hot spot appearing at 6 V in the O₂ atmosphere.
Gd$_2$BaCuO$_5$ and liquid phase. The liquid phase is moved toward the periphery of the rod by capillarity because the rod has porous microstructure. Consequently only Gd$_2$BaCuO$_5$ grains remain near the centre of the rod.

The unique structure created by the hot spot may bring about new applications such as magnetic separations for mixed fluids [15–18]. For effective magnetic separations, it is necessary to increase the magnetic field and field gradient in the separators. The superconducting GdB$_2$Cu$_3$O$_{7−δ}$ remaining near the periphery of the rod may generate high magnetic field and high field gradient in the sponge-like structure.

4. Conclusion

A novel sponge-like structure created in the GdB$_2$Cu$_3$O$_{7−δ}$ ceramics rod by the hot spot was reported and the mechanism of the formation of the structure was discussed. The elemental map revealed that the sponge structure was composed of Gd$_2$BaCuO$_5$ grains. It is considered that the hot spot decomposes GdB$_2$Cu$_3$O$_{7−δ}$ into Gd$_2$BaCuO$_5$ and liquid phase, and the liquid phase moves towards the periphery of the rod, leaving sponge-like structure composed of Gd$_2$BaCuO$_5$ grain. The unique structure created by the hot spot may bring about new applications for magnetic separations.

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References

[1] K. Kishio, J. Shimoyama, T. Hasegawa, K. Kitazawa, K. Fueki, Determination of oxygen nonstoichiometry in a high-$T_c$ superconductor Ba$_2$YCu$_3$O$_{7−δ}$, Jpn. J. Appl. Phys. 26 (1987) L1228–L1230.
[2] V.A.M. Brabers, W.J.M. de Jonge, L.A. Bosch, C.v.d. Steen, A.M.W. de Groote, A.A. Verheyen, C.W.H.M. Vennix, Annealing experiments on and high-temperature behavior of the superconductor YBa$_2$Cu$_3$O$_{6−δ}$, Mater. Res. Bull. 23 (1988) 197–207.
[3] A.T. Fiori, M. Gurvitch, R.J. Cava, G.P. Espinosa, Effect of oxygen desorption on electrical transport in YBa$_2$Cu$_3$O$_{6−δ}$, Phys. Rev. B 36 (1987) 7262–7265.
[4] T.K. Chaki, M. Rubinstein, Normal-state resistivity of the high-$T_c$ compound YBa$_2$Cu$_3$O$_{6−δ}$, Phys. Rev. B 36 (1987) 7259–7261.
[5] T. Okamoto, B. Huybrechts, M. Takata, Electric field sensitive moving hot spot in GdB$_2$Cu$_3$O$_{7−δ}$ ceramics, Jpn. J. Appl. Phys. 33 (1994) L1212–L1214.
[6] M. Takata, Y. Noguchi, Y. Kurihara, T. Okamoto, B. Huybrechts, Novel oxygen sensor using hot spot on ceramic rod, Bull. Mater. Sci. 22 (1999) 593–600.
[7] H. Sunatori, T. Okamoto, M. Takata, Hot spot in La-doped BaTiO$_3$ ceramic rod, J. Ceram. Soc. Japan 111 (2003) 217–218.
[8] Y. Kurihara, Y. Noguchi, M. Takata, New sintering technique using the migrating hot spot on high-$T_c$ superconductor, Key Eng. Mater. 157-158 (1999) 127–134.
[9] Y. Kurihara, T. Okamoto, B. Huybrechts, M. Takata, Current–voltage hysteresis in GdB$_2$Cu$_3$O$_{7−δ}$ ceramics in air at room temperature, J. Mater. Res. 11 (1996) 549–551.
[10] T. Okamoto, M. Takata, Characteristics of oxygen sensor exploiting the hot spot in BaAl$_2$O$_4$-added GdB$_2$Cu$_3$O$_{7−δ}$ composite ceramic rod, J. Ceram. Soc. Jpn 112 (2004) S567–S571.
[11] K. Kikuch, M. Kanzaki, T. Neda, T. Kondo, M. Takata, A novel and highly sensitive gas flow sensor using a hot spot on YBa$_2$Cu$_3$O$_{7−δ}$ thin films, Jpn. J. Appl. Phys. 34 (1995) L1311–L1313.
[12] Y. Ibaraki, T. Okamoto, M. Takata, Oscillatory current in SmBa$_2$Cu$_3$O$_{7−δ}$ ceramic rod related to hot spot under low oxygen partial pressure, Trans. Mater. Res. Soc. Jpn 26 (2001) 23–26.
[13] Y. Tsutai, T. Okamoto, A. Kawamoto, M. Takata, Hot spot in GdB$_2$Cu$_3$O$_{7−δ}$–BaZrO$_3$ composite ceramics, J. Ceram. Soc. Jpn 112 (2004) S599–S601.
[14] M. Murakami, M. Morita, K. Doi, K. Miyamoto, H. Hamada, Microstructural study of the Y–Ba–Cu–O system at high temperatures, Jpn. J. Appl. Phys. 28 (1989) L399–L401.
[15] H. Nakajima, H. Kaneko, M. Oizumi, S. Fukui, M. Yamaguchi, T. Sato, M. Oizumi, H. Imai, M. Takanabe, Separation characteristics of open gradient magnetic separation using high-temperature superconducting magnet, Physica C 392–396 (2003) 1214–1218.
[16] K. Yokoyama, T. Oka, H. Okada, K. Noto, High gradient magnetic separation using superconducting bulk magnets, Physica C 392–396 (2003) 739–744.
[17] J. Gwak, A. Ayral, V. Rouessac, L. Cot, J. Grenier, E. Jang, J. Choy, Synthesis and characterization of porous inorganic membranes exhibiting superconducting properties, Mater. Chem. Phys. 84 (2004) 348–357.
[18] J. Svoboda, T. Fujita, Recent developments in magnetic methods of material separation, Miner. Eng. 16 (2003) 785–792.