Novel oxygen sensor using hot spot on ceramic rod

M TAKATA*, Y NOGUCHI, Y KURIHARA, T OKAMOTO and B HUYBRECHTS

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

Abstract. A novel oxygen sensor using hot spot on ceramic rod of high- T_c superconductor $\text{RBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (R: rare earth element) has been developed. The hot spot appears by the self-heating of the local part on the $\text{RBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ceramic rod when a voltage above threshold is applied at room temperature. This sensor operates without any separate heater by taking advantage of the high temperature of the hot spot wherein oxide ions can diffuse easily. The oxygen concentration is determined from the value of the current flowing through the rod by utilizing the change in the resistivity of the hot spot depending on oxygen partial pressure in atmosphere. Oxygen concentration of 0–100% can be detected with high sensitivity and the response time is several seconds. The response performance of this oxygen sensor is almost the same as that of limiting-current-type zirconia sensor operating at 500°C.

Keywords. Oxygen sensor; hot spot; oxide ion; self-heating.

1. Introduction

With increasing worldwide interest in environmental problems and need for more comfortable life, oxygen sensor has been playing an active part in many industries. Among them, the solid state oxygen sensor using zirconia (ZrO_2) electrolyte has been in most widespread use for controlling the combustion of automotive engines (Fleming 1977; Anderson and Graves 1981). This sensor consists of a thimble shaped nonporous ZrO_2 with Pt electrodes and detects oxygen concentration due to electromotive force (emf) generated between the electrodes. The inner and outer electrodes are exposed to reference gas (air) and to the measurement gas mixture, respectively. The emf, which is output signal of the sensor, is determined by the oxygen concentration ratio between the reference gas and the measurement gas mixture, given by the Nernst equation. Since this emf-type oxygen sensor is useful for sensing below a few percent of oxygen, most automotive cars have installed this to detect even small amount of oxygen from the exhaust gases, and for the optimum use of the three-way catalyst. Limiting-current-type oxygen sensor, using ZrO_2 , has been also developed for the sensing of the wide range of oxygen concentration from a few to 100% (Asada *et al* 1984; Saji *et al* 1984). This sensor is comprised of ZrO_2 electrolyte and diffusion determining hole. When a voltage is applied to the electrolyte, oxide ions in the electrolyte move towards the positive electrode, resulting in oxygen diffusion owing to the applied voltage, i.e. oxygen gas is pumped from the cathode side to the anode side. This diffusion is restricted by a hole, which

is provided in the system, and the current flowing in the circuit is limited by this diffusion determining hole. Therefore, this sensor can detect wide range of oxygen concentrations from the limiting-current which is proportional to the oxygen concentration in the environment.

These ZrO_2 -type sensors need to be heated above 400°C to operate because the ZrO_2 cannot work well as an electrolyte below 400°C (Usui *et al* 1989). Recently, Taniguchi *et al* (1998) have developed the limiting-current-type oxygen sensor, using $\text{BaCe}_{0.8}\text{Gd}_{0.2}\text{O}_{3-\alpha}$ as an electrolyte, operating at lower temperature, 300°C. However, even this sensor must be heated by a separate heater, and is not so cost effective because of its complex structure and the use of Pt electrodes. Thus, it is necessary to construct a simpler and less expensive sensor that operates without any separate heater.

Okamoto and co-workers (1994) in our group have discovered a phenomenon that when a dc voltage above threshold is applied to a ceramic rod of high- T_c superconductor, $\text{RBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (R: rare earth element, hereafter R123), a very stable visible hot region—the hot spot—appears on the rod, which moves towards the negative electrode with a velocity of a few mm/min. Furthermore, the authors have developed a novel oxygen sensor using the self-heating of the hot spot phenomenon which operates at room temperature, i.e. without any separate heater (Fukuoka and Takata 1997). So far the combination of emf-type and limiting-current-type ZrO_2 sensor has been commonly used in case of sensing of oxygen concentration from 0 to 100%. On the other hand, the proposed sensor using the hot spot not only has the great advantage of the simple structure but can also detect oxygen, 0–100%, with high sensitivity. Moreover, the response time is only several seconds, and the

*Author for correspondence

response performance of this sensor is almost the same as that of the limiting-current-type oxygen sensor, using ZrO_2 , operating at 500°C.

In the present paper, the general features of the hot spot phenomenon for R123 ceramic rod: appearance of the hot spot, thermal equilibrium, migration of the hot spot, and oxygen partial pressure dependence of current-voltage characteristics are described. Further, we have shown that the current, when the hot spot is on the rod, strongly depends on oxygen partial pressure, and this fact is the basic principle of the oxygen sensor using the hot spot. Finally, the characteristics of the proposed sensor are demonstrated, and we have shown that this sensor is economically and efficiently superior to ZrO_2 -type sensors.

2. Experimental

R123 ($\text{R} = \text{Gd}, \text{Sm}$) ceramics were prepared by the conventional solid-state reaction method. The details have been described elsewhere (Okamoto *et al* 1994). The density of the sintered sample was 60–70% of the theoretical density. The sample was cut in rectangular shaped rod (0.65 mm in height and in width). The current-voltage characteristics were measured for several oxygen partial pressures by the four-probe method to avoid any influence of the contact resistance. The temperature of the hot spot was measured by infrared camera. For the evaluation of the sensing characteristics, the oxygen concentration was changed by using the mixture of oxygen and nitrogen. The measurements were carried out at room temperature and atmospheric pressure.

3. General features of hot spot

In this paper the hot spot phenomena of $\text{GdBa}_2\text{Cu}_3\text{O}_{7-\delta}$; appearance of hot spot, migration of hot spot, and oxygen partial pressure dependence of current-voltage characteristics are described. The grain boundary in ceramics is essential for the appearance of the hot spot, and the stable existence of the hot spot on the local part of the rod can be explained by considering the balance between the generated joule heat and the heat dissipated to the environment. The appearance of the hot spot is observed in the ceramic materials showing positive temperature coefficient of resistivity (PTCR) characteristic, and the movement of the hot spot towards the negative electrode is believed to be caused by ionic conduction of oxide ions.

3.1 Appearance of hot spot

Figure 1 shows photographs of the hot spot appearing on $\text{GdBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ceramic rod when a dc voltage was

applied in air (Okamoto *et al* 1994; Takata *et al* 1996). Figure 1a shows that with the joule heating concentrated on a local part, a hot spot appeared on the rod. The temperature of the hot spot was around 900°C, as measured by infrared camera, while the rest of the rod remained cold at 200–300°C. Figure 1b presents a sequence photograph of the hot spot taken at 3 min intervals after the hot spot appearance, when a dc voltage of 9 V was applied. The spot moved towards the negative electrode, and the direction of movement reversed itself time after time when the polarity was reversed. Figure 1c shows sequence photographs with an increase of applied voltage every 30 sec at 0.5 V after the appearance of the hot spot. The size of the hot spot increased with increasing applied voltage, and the hot spot simultaneously moved towards the negative electrode as time passed. The details of the migration of the hot spot will be described later.

Figures 2a and b respectively show current-voltage characteristic and spot size as a function of applied voltage in air. The current increased linearly with increasing voltage in low voltage region. When the applied voltage reached a threshold value, the current abruptly decreased and at the same time the hot spot appeared on the rod. After that the current was almost constant. The spot size increased linearly with increasing voltage. It has been already observed that the temperatures of the hot spot is around 900°C in air, independent of voltage (Takata *et al* 1996). Since the electric power accumulatively applied to the rod is consumed for the heating of the near part of the hot spot region, the spot size lineally increases with increasing voltage.

We shall briefly mention how the visible hot spot appears and coexists stably with the cold region in equilibrium. Further, we shall also explain that the current flowing through the rod is determined by the balance between the generated joule heat and the heat dissipated to the environment. Figure 3 schematically describes temperature distributions in the process of the appearance of the hot spot. The resistivity of $\text{GdBa}_2\text{Cu}_3\text{O}_{7-\delta}$ in air steeply increases above 400°C due to the loss of oxygen (Kishio *et al* 1987). The appearance of the hot spot is related to such a steep increase in resistivity above a certain temperature T^* . As a voltage is applied to the rod, the whole rod heats up by joule heating. When the rod is heated up to T^* , it is possible that a part of the rod with a higher resistance per length than the rest of the rod has a temperature higher than T^* . This can be owing to the inhomogeneity of local composition, cross section, microstructure, etc. The resistivity of this area increases further due to the PTCR characteristics above T^* , and the electric field over this area increases rapidly. Finally the rod develops a distinct hot region at T_3 , which is clearly visible, while the rest of the rod is much colder at T_1 .

Figure 1. (a) The hot spot appearing on a $\text{GdBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ceramic rod. A dc voltage of 10 V is applied over the rod. (b) Sequence photograph after applying a dc voltage of 9 V. The pictures were taken at 3 min intervals. It is clear that the hot spot moved toward the negative electrode. The direction of movement reversed itself time after time when the polarity was reversed. (c) Sequence photograph after applying a dc voltage of 6 V. Voltage was increased every 30 sec with 0.5 V. The pictures were taken at 30 sec intervals.

The temperatures of the hot and cold regions can be obtained by considering the heat balance of the rod as:

$$C \frac{\partial T}{\partial t} = j^2 \rho(T) - W(T) + \frac{\partial}{\partial x} \lambda(T) \frac{\partial T}{\partial x}, \quad (1)$$

where C is the heat capacity per unit volume, j the current density, $\rho(T)$ the resistivity, $\lambda(T)$ the thermal conductivity, and $W(T)$ is the heat dissipated to the environment per unit volume (Abramov *et al* 1985). When the system is in equilibrium, and if each region is assumed to be at a constant uniform temperature, the balance can be written as:

$$j^2 \rho(T) = W(T). \quad (2)$$

Figure 2. Voltage dependence of (a) current and (b) spot size. In low voltage region the current increases linearly with increasing voltage. The current drastically decreases with the appearance of hot spot. After that, the spot size increases almost linearly with increasing voltage.

Figure 4 schematically shows generated joule heat, $j_{eq}^2 \rho$, and heat dissipated, W , to the environment as a function of temperature. The generated heat balances the dissipated heat in an equilibrium at three different temperatures, namely T_1 , T_2 , and T_3 . However, T_2 is unstable. Assuming, for example, that there is a slight increase in temperature around T_2 , the generated heat becomes larger than the dissipated heat and consequently the temperature increases to T_3 . If the temperature is decreased slightly, the dissipated heat becomes larger than the generated heat and the temperature decreases to T_1 . Therefore, T_3 is the temperature of the hot spot and T_1 is that of the rest of the rod.

The rod here is assumed to have enough length to neglect heat sinking into electrodes. The condition for coexistence of the states $T=T_1$ and T_3 , is given as:

$$\int_{T_1}^{T_3} \lambda(T) \{W(T) - j_{eq}^2 \rho(T)\} dT = 0, \quad (3)$$

where j_{eq} is the current density in equilibrium. The dissipated heat as a function of temperature is written as:

$$W(T) = k \{ h (T - T_0) + \sigma (T^4 - T_0^4) \}, \quad (4)$$

where $k = P/A$, P is the perimeter and A the area of the cross section of rod, h the heat transfer coefficient

Figure 3. Schematic representation of the appearance process of the hot spot.

between the rod and the atmosphere, T_0 the ambient temperature, and σ the Stefan-Boltzmann constant. The current density j_{eq} is controlled automatically as (3) is satisfied.

To consider the process of the appearance of the hot spot in detail, the relation between the generated and the dissipated heat at each applied voltage, as shown in the inset of figure 5 is, discussed (Kurihara *et al* 1999):

① → ②: At low voltage, $j^2\rho(T)$ curve intersects with $W(T)$ at one point, and the temperature of the whole rod increases from T_0 to the temperature of the intersection. With increasing applied voltage, j becomes higher and $j^2\rho(T)$ curve shifts upward. Then the curve of $j^2\rho(T)$ becomes tangent to $W(T)$, and consequently the whole rod is in a metastable state at the temperature of the point of tangency T_m .

② → ③: If there is a slight increase in temperature on the local part of the rod, the generated heat is larger than the dissipated heat, and the temperature on this part increases further. Then the resistance of this part increases due to the PTCR characteristic of the sample, which leads j to the lower value and $j^2\rho(T)$ curve shifts downward. As the system reaches equilibrium, the temperature of this part becomes T_3 , while the rest of the rod cools down to T_1 . The part having the maximum

Figure 4. Schematics of generated joule heat $j_{eq}^2\rho$ and dissipated heat W as a function of temperature. Resistivity of $\text{GdBa}_2\text{Cu}_3\text{O}_{7-\delta}$ steeply increases above 400°C due to the loss of oxygen. T^* indicates the temperature above which generated heat steeply increases. When the rod is in equilibrium, $j_{eq}^2\rho$ and W balance each other at three different temperatures, T_1 , T_2 and T_3 . However, only T_1 and T_3 are stable, while T_2 is unstable.

resistance per length is a nucleus of the phase with T_3 for a hot spot. After the appearance of the hot spot, the current density is automatically adjusted to be j_{eq} as (3) is satisfied, and the temperatures of the hot and cold regions become T_3 and T_1 , respectively.

3.2 Migration of hot spot

As shown in figures 1b and c, the hot spot moved towards the negative electrode, and the direction of its movement was reversed by switching the polarity. Figure 6 shows the P_{O_2} dependence of the spot velocity at dc 8 V (Takata *et al* 1996). The spot velocity increased with increasing P_{O_2} (≥ 3 kPa). These results indicate that the migration of hot spot is closely related to the diffusion and the conduction of oxide ions.

Figure 7 presents schematic illustration of the migration of the hot spot. The oxide ions move easily in the hot spot due to the high temperature, high concentration of oxide vacancies, and the high electric field over the hot spot. Since oxide ions move to the positive potential in

Figure 5. Schematics of generated joule heat $j^2\rho$ for various current density and dissipated heat W as a function of temperature in the appearance process of the hot spot during increasing applied voltage. The inset shows typical current density-voltage characteristics. Each $j^2\rho$ curve numbered from ① to ③ corresponds to the generated heat at applied voltage shown in the inset.

the hot spot, the oxygen content of the negative side in the hot spot decreases, which results in the increase of the resistivity. The generated heat is therefore larger on the negative side than on the positive side, consequently the temperature increases at the negative side in the hot spot and decreases at the positive side. Oxygen diffuses from the environment into the sample at the positive side, which further decreases the resistivity and temperature. On the other hand, at the negative side, oxygen is released from the sample, hence the resistivity and temperature increase. As a result, the hot spot moves towards the negative electrode as can be seen in figures 1b and c. Figure 6 indicates that the diffusion of oxygen becomes faster with increasing P_{O_2} , which suggests an increase in temperature of the hot spot.

3.3 Oxygen partial pressure P_{O_2} dependence of current-voltage characteristics

Figure 8 shows current-voltage characteristics for several P_{O_2} . The current linearly increased in low voltage region. The applied voltage at which the current abruptly decreased was almost the same for all P_{O_2} , and the appearance voltage of the hot spot was independent of P_{O_2} . It should be noted that the current after the appearance of the hot spot depended strongly on P_{O_2} . This experimental result means that the oxygen concentration in environment can be determined from the current value and is the principle of the novel oxygen sensor proposed by the authors.

When the oxygen content $(7-\delta)$ of R123 is higher than 6.2, the R123 behaves like an oxygen excess (metal deficit) oxide (Kakinuma and Fueki 1997). If the R123

Figure 6. P_{O_2} dependence of the velocity of the hot spot when dc 8 V was applied.

is kept at high temperature and the P_{O_2} is raised, the R123 absorbs oxygen which dissociates into holes and oxide ions. The overall reaction is expressed as:

where O_i^{2-} is an interstitial divalent oxide ion and h^+ is a hole. Therefore, the R123 essentially has a p -type

Figure 7. Schematic representation of the migration of the hot spot.

Figure 8. Current-voltage characteristic for several P_{O_2} . The voltage was increased every 6 sec with 0.1 V. At around a voltage of 7 V, the spot appeared and the current decreased abruptly. The current was almost constant after the appearance of the hot spot.

conduction, since the excess oxygen plays the role of acceptor. The mass action law for (5) is

$$K = \frac{[O_i^{2-}]^2 \cdot [h^+]^4}{[O_2]}, \quad (6)$$

where K is the equilibrium constant, and $[O_i^{2-}]$, $[h^+]$ and $[O_2]$ represent the concentrations of interstitial oxide ion, hole, and oxygen ($= P_{O_2}$), respectively. When the formation of defects represented by (5) is predominant, the insertion of the relation $2[O_i^{2-}] = [h^+]$ into (6) yields

$$[h^+] \propto P_{O_2}^{1/6} \quad (7)$$

Since the conductivity σ is proportional to $[h^+]$, the σ is proportional to $P_{O_2}^{1/6}$.

Figure 9. Sensing characteristics between 20 and 100% oxygen concentration for $\text{SmBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ceramic rod.

Figure 10. Output current of the sensor as a function of oxygen concentration for $\text{SmBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ceramic rod.

The temperature of the hot spot increases with P_{O_2} as described later. Above description is valid for a constant temperature, but a qualitative explanation can be made using (7) in case of the hot spot. As mentioned before, the temperature of the hot spot is much higher than that of the cold region. Since the hot spot decides the resistance of the whole rod, the resistance of the hot spot determines the current flowing through the rod.

4. Oxygen sensing characteristics

Figure 9 shows sensing characteristics between 20 and 100% oxygen concentration for $\text{SmBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ceramic rod when the hot spot was on the rod. In case of changing the oxygen concentration from 20 to 100%, the current flowing through the rod abruptly increased and was saturated within several seconds. For the change from 100 to 20%, the current decreased rapidly to the initial level, and the reproducibility of this sensor was found to be excellent. Furthermore, the response time of several seconds is almost the same as that of the limiting-current-type ZrO_2 oxygen sensor operating at 500°C. Here, the current in equilibrium state is defined as output current. The relation between the output current and oxygen concentration in the environment is presented in figure 10. At high concentration region above 20%, the output current slowly decreased with decreasing oxygen concentration, while the decreasing tendency was much larger at lower concentration. These results indicate that the sensitivity is high enough at usual oxygen concentration like air and is further improved at lower concentration. Therefore the sensor using the hot spot can detect oxygen concentration from 0 to 100%, while the combination of emf-type and limiting-current-type ZrO_2

Figure 11. Relation between log of output current and log of oxygen concentration for $\text{SmBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ceramic rod.

Figure 12. Oxygen concentration dependence of hot spot temperature for $\text{SmBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ceramic rod.

sensor has been commonly used in the same range. Figure 11 shows log of output current vs log of oxygen concentration characteristics. It is clear that the linear relation is obtained in this figure, and the slope is 0.15. This value is very close to 1/6 for the ideal case of oxygen excess materials given in (7), whereas the temperature of the hot spot is varied from 780°C (0.5% O_2) to 940°C (100% O_2) as shown in figure 12. This tendency of the hot spot temperature is attributed to the fact that the current with the existence of the hot spot was reduced at lower oxygen concentration as shown in figure 10.

5. Summary

The general features of the hot spot on the ceramic rod of high- T_c superconductor $\text{RBa}_2\text{Cu}_3\text{O}_{7-\delta}$ have been

described, and a novel oxygen sensor using the hot spot has been developed. This sensor operates at room temperature, i.e. without any separate heater by taking advantage of high temperature of the hot spot wherein oxide ions can diffuse easily. The sensitivity is high enough at usual oxygen concentration like air and is improved with lower concentration. Therefore the sensor using the hot spot can detect oxygen concentration from 0 to 100%, while the combination of emf-type and limiting-current-type ZrO_2 sensor has been commonly used in the same range. The response performance of this oxygen sensor is almost the same as that of the limiting-current-type zirconia sensor operating at 500°C.

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