Mechanical Response to Reducing Gases in PZT/ZnO Actuator

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PZT/ZnO アクチュエーターにおける還元性ガスへの機械的応答

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Electrostrictive behavior responding to reducing gas (CO, H₂) atmospheres was investigated on a piezoelectric actuator consisting of a dense PZT plate (Pb_{0.995}Nb_{0.01}(Zr_{0.53}Ti_{0.47})_{0.99}O₃) and a porous ZnO plate (ZnO + 0.2 mol% Li₂O + 10 mol% NiO). The dense PZT and press-formed ZnO disks were bonded by hot-pressing using glass frits. The PZT side of the actuator showed a shrinkage by a d.c. bias at 250°C, and its value was larger in reducing gas atmosphere than in air. When measured on the separated plates, the PZT and ZnO plates had high resistivities in the same level in air but only the ZnO showed a decrease in resistivity by introduction of reducing gas. It is assumed that the applied voltage is distributed to both plates in air, but concentrated to the PZT part in reducing gas atmospheres due to a decrease in resistance of the ZnO part. The bending displacement of the actuator was also observed in reducing gas atmosphere, although the precise value was not obtained due to the high temperature in measurements.

Key-words : Gas sensor, Piezoelectric actuator, PZT, ZnO, CO, H₂

1. Introduction

Piezoelectric actuators have attracted an attention as mechanical devices instead of oil driving devices, electromagnetic valves or motors. Recently, piezoelectric actuators have been used for VTR head actuators, ink jet devices of printers and driving devices of fatigue testing machines etc. The value of bending displacement is usually controlled by the intensity of applying electric field. A monomorph type actuator of PZT single plate was reported to show a change of bending displacement by an increase in humidity,¹⁾ and present authors reported that an unimorph type actuator consisting of a porous and a dense PZT plate shows a bending displacement depending on environmental humidity.²⁾ Such a device is expected as one of the intelligent materials, which can sense the environmental atmosphere and actuate responding to a change of atmosphere by itself.³⁾ However, it has not yet been reported that a mechanical displacement is controlled by environmental reducing gases.

In the present study, piezoelectric actuator was prepared by stacking a dense PZT plate with a

porous ZnO plate, which was well known as a gas sensing material.^{4),5)} Its electrostrictive behavior responding to reducing gases was measured at 250°C.

2. Experimental procedure

2.1 Specimen preparation

PZT ceramics (Pb_{0.995}Nb_{0.01}(Zr_{0.53}Ti_{0.47})_{0.99}O₃) were prepared from reagent oxides (purity 99.9%) of PbO, Nb₂O₅, ZrO₂ and TiO₂. These powders were ball-milled for 50h with ZrO₂ balls as a milling media in a polyethylene pot. The mixing powder was calcined at 850°C for 6h in air and ball-milled again for 50h. The calcined PZT powder was pressed into disks and, then sintered at 1150°C for 2h in air to obtain dense PZT samples. ZnO ceramics (ZnO + 0.2 mol% Li₂O + 10 mol% NiO) was prepared from powders (purity 99.9%) of ZnO, LiNO₃ and NiO. These starting materials were ball-milled for 8h and calcined at 600°C for 5h in air. The calcined powder was pressed into disks under 50MPa.

The dense PZT and press-formed ZnO disks were stacked and hot-pressed together in air at 700°C for 1h under 8 MPa. Before hot-pressing, a small amount of glass frits (softening point: 630°C) were applied to the interface between dense PZT disk and press-formed ZnO disk. The hot-pressed bulk was then cut into a test piece (with 6 mm × 11 mm × 1 mm in size) consisting of dense PZT and porous ZnO plates which were both 0.5 mm in thickness. A dense PZT plate was cut off with 4 mm × 10 mm × 1 mm (thickness) in size from the hot-pressed bulk to measure its displacement induced by electric field and gas sensitivity. A porous ZnO plate also was cut off in the same manner to measure its gas sensitivity. Silver paste was applied and fired on PZT, and gold was sputtered on ZnO, as ohmic electrodes.

2.2 Measurement

The electrical measurements were performed using an electrometer (Advantest Co., Ltd., Model R8340A) which has a constant voltage supply within. The DC electrical resistivities of the dense PZT plate and the porous ZnO plate were measured at 250°C under controlled gas atmosphere, separately. Air, air-balanced 0.40 vol% H₂ gas and air-balanced 0.40 vol% CO gas were used as testing gases, and

gas flow rate was fixed at $3.33 \times 10^{-6} \text{ m}^3/\text{s}$ (200 cc/min). Mechanical displacement was measured at 250°C in the direction perpendicular to electric field (along the length direction) using a strain gauge (Tokyo Sokki Kenkyujo Co., Ltd., Type ZFLA-I-002LE) attached on the PZT side of PZT/ZnO actuator, under an electric field of 0–250 kV/m in various atmospheres. Mechanical displacement of single PZT plate was also measured under an electric field of 500 kV/m.

3. Results and discussion

3.1 Structure

A schematic illustration of the actuator, prepared in the present study, is shown in Fig. 1. Table 1 shows the relative densities and average grain sizes of dense PZT and porous ZnO plates those were cut off from stacked body. The distinct differences in density and grain size were observed between two plates.

3.2 Gas sensing property

The porous ZnO ceramics showed a high electrical resistivity of about $2 \times 10^8 \Omega \cdot \text{m}$ at 250°C in air, which was a little higher than that of dense PZT ceramics at the same temperature. Figure 2 shows gas sensing properties of porous ZnO and dense PZT plates, measured at 250°C under application of 10 V d.c. The porous ZnO ceramics added with Li_2O and NiO showed a large decrease in resistivity by CO or H_2 gas. Especially, in 0.40 vol% CO gas, the decrease in resistivity reached more than one and half orders of magnitude. In contrast, electrical resistivity of dense PZT was kept constant in both 0.40 vol% H_2 and CO gases. As a result, electrical resistivity of ZnO became much lower than that of dense PZT in reducing gas atmospheres.

3.3 Displacement characteristics

Under application of electric field, piezoelectric ceramics expand in the direction of applied electric field and shrink in the direction perpendicular to applied electric field. Figure 3 shows the displacement

Fig. 1. A schematic illustration of actuator.

Fig. 2. Resistivity changes of porous ZnO and dense PZT by CO and H_2 gases at 250°C. Gas concentration is 0.40 vol% balanced with air.

Fig. 3. Displacement of PZT plate as a function of temperature at 500 kV/m.

of single dense PZT plate at 500 kV/m in air as a function of temperature. Here, mechanical displacements were represented by a ratio of the change to the original length ($\Delta L/L$). Generally, PZT ceramics do not exhibit good electrostrictive characters at high temperatures near the Curie point (375°C). However, it was confirmed that the present PZT ceramics kept a stable displacement in the direction perpendicular to electric field up to 250°C.

Figure 4 shows the values of mechanical displacements at the PZT side of the actuator as a function of applied electric field in various atmospheres. The dis-

Table 1. Relative Density and Average Grain Size of Dense PZT Plate and Porous ZnO Plate

Specimen	Relative density	Average grain size
Dense PZT plate ($\text{Pb}_{0.995}\text{Nb}_{0.01}(\text{Zr}_{0.53}\text{Ti}_{0.47})_{0.99}\text{O}_3$)	98 %	5.0 μm
Porous ZnO plate ($\text{ZnO} + 0.2 \text{ mol\%Li}_2\text{O} + 10 \text{ mol\%NiO}$)	51 %	0.4 μm

Fig. 4. Displacements at PZT side of PZT/ZnO actuator as a function of applied electric field at 250°C in various atmospheres.

placements almost in proportion to the induced electric field were observed in the measured electric field range. The values of displacements were larger in the order of those in CO, H₂ and air.

In air, both of the dense PZT and the porous ZnO parts have high resistances in an almost same level and hence the applied d.c. voltage is distributed to the both parts. However, in reducing gas atmospheres, resistance of the ZnO part becomes smaller than that of the PZT part. This leads to a concentration of applied voltage to the PZT part. Consequently, the value of shrinkage would be larger in reducing gas atmosphere than in air. It is reasonable that the shrinkage was larger in CO gas than in H₂ gas, because a decrease in resistivity of the porous ZnO plate was larger in CO gas than in H₂ gas.

Measurement of bending displacement was tried on the present actuator fixed at one end, using non-contact laser sensor. The value of bending displacement was approximately 4–12 μm under an electric field of 250 kV/m at 250°C in reducing atmospheres.

However, correct values of bending displacement have not been measured yet because of difficulties of non-contact measurements at high temperatures. From the results of shrinkage, the value of bending displacement is also expected to increase by introduction of reducing gases.

From the present results, it is suggested to be possible to fabricate an actuator responding to reducing gases, provided that a PZT plate is combined with a ceramic material having a high resistivity in air and a good gas sensitivity. The addition of Li₂O and NiO was found effective to give such properties to porous ZnO.

4. Conclusions

(1) The porous ZnO ceramics (ZnO+0.2 mol% Li₂O+10 mol% NiO) showed a high electrical resistivity ($2 \times 10^8 \Omega \cdot \text{m}$), which was higher than that of dense PZT ceramics in air at 250°C, and exhibited large decreases in resistivity by CO and H₂ gases.

(2) The values of shrinkage by a d.c. voltage at PZT side of the PZT/ZnO actuator was larger in reducing gas atmospheres than in air. It is supposed that the applied voltage is concentrated to the PZT part by introduction of reducing gas due to a decrease in resistance of the ZnO part.

(3) The bending displacement of the actuator was also observed in reducing gas atmosphere, although the precise value was not obtained due to the high temperature in measurements.

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