Fabrication of PTC Sheet with Semiconducting BaTiO₃ Particles*

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A mono-layer sheet of 24 mm × 24 mm and a multi-layer sheet of 12 mm × 12 mm were fabricated as follows. Semiconducting BaTiO₃ particles were packed between two electrodes of aluminum foil. As the particles and electrodes were enclosed in a plastic bag, evacuated and heat-sealed, they were fixed and compressed by atmospheric pressure. One layer is formed by the packed particles in the mono-layer sheet, and two to three layers are formed in the multi-layer sheet. The particles are semiconducting BaTiO₃ for the mono-layer sheet and composite particles of semiconducting BaTiO₃ and In for the multi-layer sheet. Indium particles always exist between the semiconducting BaTiO₃ particles in the multi-layer sheet and lower the contact resistance between the semiconducting particles. The properties of the sheets are investigated and the following results are obtained. (1) Both the mono-layer sheet and the multi-layer sheet are flexible and show the PTC property. (2) The performance of the multi-layer sheets is almost the same with that of the mono-layer sheet. (3) The apparent resistance is higher than that of the sintered disk, because of the imperfect contact in the sheet. (4) The thickness is about 1.1 mm and it is thinner than commercial thin PTC plates.

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1. Introduction

Shape memory alloys and piezoelectric materials are the typical “smart” or “intelligent” materials. PTC materials are also one of the “smart” or “intelligent” materials by their unique temperature dependence of the resistance.

As the temperature is increased, the resistance of PTC materials steeply increases about five or six orders of magnitude near the Curie point.¹⁾ When a constant voltage is applied to a PTC material, the temperature of the material is increased by the Joule’s heat. The current and also the exothermic rate are depressed owing to the increasing resistance. As the results, the temperature of the PTC materials keeps a constant value without any external circuits. The PTC materials are used to heaters, which temperature are self-controllable and protective devices which limit the current against overheating.

Semiconducting barium titanate (BaTiO₃) is a representative PTC material. It has the defect of brittleness same as the usual ceramics. It is employed to a practical use like small parts of home electronic appliances, because of its useful PTC property. If the flexibility is given to the PTC materials by improving the mechanical property, they will use more widely.

We have engaged in the research project of particle assemblage and developed various methods to treat fine particles.²⁾ One of them is a technique to produce composite particles of ordered mixture. We reported that the packed bed of the composite particles of semiconducting BaTiO₃ and In showed the same PTC property with that of the sintered disk.^{3,4)} The results suggest that flexible PTC sheet will be produced if it can form sheet by packing the composite particles.

We try to produce the flexible sheet and measure the PTC property to prove the above consideration to be valid in this paper.

2. Concept of Flexible PTC Sheet

Figure 1 shows the schematic structure of the flexible PTC sheet. PTC particles are sandwiched between two thin metallic electrodes. Insulating frame and partitions are also inserted between the electrodes and the inside of the sheet is divided into cells (four cells in case of Fig. 1).

The particles are only filled the cells, not fixed to ensure the flexibility. The problems are, therefore, that how to fix the particles and the electrodes and how to keep the contact between the particles and the electrodes, and also among the particles.

To solve the problems, the sheet shown in Fig. 1 is inserted in a bag and the bag is sealed after evacuation. The sheet is always compressed by the atmospheric pressure of about 0.1 MPa. The compressive stress will solve the above problems. When the PTC property of the disk was measured, the electrode was pressed to the disk at a load of 0.16 MPa.^{5,6)} The value is comparable with the atmospheric pressure.

To enclose stuffs in an evacuated bag is a general method especially in the food industry. The airtight and heatproof bag will be, therefore, easily available.

3. Experimental

3.1 Fabrication of flexible PTC sheet

Two kinds of sheet are fabricated. One is mono-layer sheet and the other is multi-layer sheet. The cross section

Fig. 1 Schematic structure of the flexible PTC sheet.

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Fig. 2 Cross section of the mono-layer sheet (a) and the multi-layer sheet (b).

of the former and that of the latter are shown in Figs. 2(a) and (b), respectively. Semiconducting BaTiO₃ particles are filled between the aluminum foil electrodes. The numbers of particle's layer are one for the mono-layer sheet and two to three for multi-layer sheet as shown in Fig. 2. The particles are semiconducting BaTiO₃ for the mono-layer sheet and composite particles of semiconducting BaTiO₃ and In for the multi-layer sheet.

The frame and partitions are a paper or a plastic of 0.6 mm thickness. Two copper wires, each connected to each electrode, are lead out from the bag through holes for the examination of the electrical properties. The holes are sealed with a filling agent and the bag is heat-sealed.

3.2 Measurement of electrical properties

The PTC property is decided by measuring the resistance at various temperatures as follows. The trial product of the sheet is placed in an oven. The oven is heated up to 100°C and cooled down to room temperature at a rate of 0.25°C/min. As the rate is very slow, the temperature of the sheet is considered to be almost the same with that for the oven. Two copper wires from the sheet are connected to a digital electrometer (TR8652, Advantest Co. Ltd.) for the measurement the resistance of the sheet.

When the resistance is measured, the electrometer sends a very small current of 10 nA–100 μA according to the magnitude of the objective resistance. In the practical use, more current will be sent to the PTC sheet. We, therefore, obtain the relationship between the voltage and current at a practical condition. Constant voltages of 0 to 200 V are applied to the sheet covered with the heat insulator. The sheet becomes hot by the Joule's heat. The temperature and the current are measured after the temperature becomes constant. We call it self-heating test.

The relationship between the current and the voltage at room temperature is also obtained. The measurement is carried out as quickly as possible to avoid the effect of the Joule's heat.

3.3 Specimen

Semiconducting BaTiO₃ particles of 600–710 μm and 300–355 μm are prepared as follows. Raw powder material supplied from Mitsui Mining Material Co. Ltd. was granulated, sieved, baked in the atmosphere at 1330°C for two hours, and cooled down at a rate of 130°C/h. The Curie point is 51°C. In-

Fig. 3 Relationship between the resistance and the temperature of the mono-layer sheet. Arrows show the order of the measurement.

dium particles of –20 μm are supplied from Mitsuwa Chemical Industry Co., Ltd.

Composite particles of semiconducting BaTiO₃ and In are produced by the forced electrification processing.⁷⁾ Mother particles of semiconducting BaTiO₃ and child particles of In are separately electrified positive and negative, respectively, and are sprayed at a same place. Composite particles are formed by the Coulomb's force. Details of the process are described in a previous paper.^{3,4)}

Plastic bag is a commercial product by Asahi Kasei Co., Ltd. for food storage.

4. Results and Discussion

4.1 Mono-layer sheet

The mono-layer sheet is prepared using semiconducting BaTiO₃ of 600–710 μm. The sheet consists of four cells and the size is 24 mm × 24 mm. The thickness is about 1.1 mm and it can be bent.

Figure 3 shows the values of the resistance at various temperatures of the mono-layer sheet. The resistance is about 20 kΩ at room temperature, and it increases steeply with the temperature, showing that the sheet has PTC property. As shown by arrows in Fig. 3, the resistance jumps up at about 90°C when the temperature goes up. When the temperature goes down, it suddenly falls down at about 50°C.

The discontinuous jump and fall of the resistance occurs when the intensity of the current is changed, *i.e.*, the current is 100 μA for the resistance less than 200 kΩ, 1 μA for the resistance of 200 to 20 MΩ and 10 nA for the resistance of above 20 MΩ. The discontinuity in Fig. 3 occurs at 200 kΩ. As described before, the electrometer sends a small current during the measurement. The intensity of the current is automatically changed according to the magnitude of the object resistance.

The effect of the current intensity can be negligible in the usual measurement, because the Ohm's law is valid at the low current region for ordinary specimens. The Ohm's law, however, cannot apply to the mono-layer sheet even for the small

Fig. 4 Relationship between the current and the applied voltage for the mono-layer sheet.

current of less than 100 μA as shown in Fig. 4.

The I-V characteristic of the disk specimen of semiconducting BaTiO_3 is almost linear different from Fig. 4. The hysteresis does not appear for the disk specimen. We, therefore, ascribe the hysteresis for the mono-layer sheet to the non-linearity shown in Fig. 4. If we can measure the resistance at a constant current, the hysteresis will disappear.

The electrodes are formed by the evaporation of In for the electrical measurement of the disk specimen. The good contact between the metallic electrode and the semiconducting specimen is ensured. On the other hand, the semiconducting particles attached to the metallic foil only by the atmospheric pressure. Thus, the non-linearity will be derived from the imperfection of the contact.

The resistance estimated from Fig. 4 decreases with an increase in applied voltage. It means that the effect of the imperfection decreases at a high current region.

Figure 5 shows the result of the self-heating test for the mono-layer sheet. The current and the temperature of the sheet are measured at a voltage of 0 to 120 V. The applied voltage is raised at intervals of 10 V after the current and the temperature attain equilibrium.

The equilibrium current and temperature are plotted against the applied voltage in Fig. 6. The current increases steeply until the applied voltage reaches about 55 V. Above 55 V the current monotonously decreases. The reason is that the resistance increases with an increase in temperature. The temperature attains about 85°C at 120 V.

4.2 Multi-layer sheet

The multi-layer sheet, which consists of one cell, is fabricated using composite particles. The photograph is shown in Fig. 7. The area of the multi-layer sheet is one fourth of the mono-layer sheet, because the number of cell is one. Semiconducting BaTiO_3 particles of 300–355 μm are used to prepare the composite particles. The size of the particles used in the multi-layer sheet is about half that used in the mono-layer sheet. The thickness is, therefore, almost the same with that

Fig. 5 Variation of the current and the temperature with the applied voltage for the mono-layer sheet.

Fig. 6 Relationships between the equilibrium current and the applied voltage and between the equilibrium temperature and the applied voltage for the mono-layer sheet.

of the mono-layer sheet.

Semiconducting BaTiO_3 particles in the multi-layer sheet are in contact with the electrode and/or neighboring BaTiO_3 particles through In particles. The contact resistance between the semiconducting BaTiO_3 particles drastically decreases by the intermedial In particle.

When the multi-layer sheet is fabricated using the semiconducting BaTiO_3 particles, the resistance of the sheet at room temperature is more than 100 M Ω . The resistance of the multi-layer sheet prepared with the composite particles is about 100 k Ω . The value will be reduced to 25 k Ω for the multi-layer sheet of four cells.

Figure 8 shows the relationship between the resistance and the temperature of the multi-layer sheet. Discontinuous jumps and falls are again seen in Fig. 8 similar to Fig. 3. We identify the reason of the discontinuity with that for the mono-layer sheet.

The electrometer changes the intensity of the current two times through the measurement. Two discontinuities correspond to the two changes of the current intensity. Non-linear

Fig. 7 Appearance of the multi-layer sheet.

Fig. 8 Relationship between the resistance and the temperature of the multi-layer sheet. Arrows show the order of the measurement.

relation similar to Fig. 4 is obtained between the current and the voltage.

The multi-layer sheet shows the PTC property. The slope of the curves in Fig. 8 is, however, not steep. The phenomenon is seen to PTC materials, which have high resistance. Small area of the sheet will be the cause of the high resistance.

Figure 9 shows the result of self-heating test for the multi-layer sheet. The current and the temperature vary with voltage basically in a similar manner as those for the mono-layer sheet, see Fig. 6. The current increases and then decreased. When the applied voltage is about 140 V, the current reaches a peak point and the temperature is about 60°C. The resistance of the disk shows a rapid increase at the same value of 60°C. It means that the effect of PTC will be remarkable above about 60°C. In the case of the mono-layer sheet, the temperature, at which the current reaches peak, is also about 60°C.

4.3 Comparison of mono-layer sheet and multi-layer sheet

Two kinds of sheet are fabricated and the properties are investigated. Both sheets are flexible and show the PTC property. The resistance at room temperature is 100 kΩ for the multi-layer sheet, and is five times larger than that for the mono-layer sheet. The size of the multi-layer sheet is, however, one fourth. Thus, the resistances at room temperature

Fig. 9 Relationships between the equilibrium current and the applied voltage and between the equilibrium temperature and the applied voltage for the multi-layer sheet.

are 20 kΩ for the mono-layer sheet and 25 kΩ for the multi-layer sheet, if the resistance of the latter is converted to that for the 24 mm × 24 mm sheet.

The resistance will be higher than that of sintered specimens, because of the imperfection of the contact in the sheets. The sheets have, however, the advantage that the thinner product is possible as described later.

The apparent performance of the mono-layer sheet is better than that of the multi-layer sheet. If we fabricate a multi-layer sheet of four cells, the performance will not be so different from that of mono-layer sheet.

When the multi-layer sheet is fabricated, composition step must be added to the fabrication process of mono-layer sheet. In the other words, the cost performance for the mono-layer sheet is better than that for the multi-layer sheet. The advantage of the multi-layer sheet is its prospective future.

We produce the mono-layer sheet and multi-layer sheet to verify our idea of a flexible PTC sheet. For the practical application, several problems to be solved have remained. The problems are, for example, preparation of finer PTC particles, development of a practical composition technique and a practical production technique of sheet, improvement of PTC property of particles and composite particles, etc.

Some of them have been already undertaken.⁸⁾ When the sheet is produced from finer particles, the packed particles must be a multi-layer from the practical viewpoint. Current flexible PTC heaters are produced by enveloping small plates of BaTiO₃, which are connected parallel, in the plastic films. The thickness of the plates cannot be lowered less than 2 mm, because of the problem of mechanical strength. On the other hand, both the mono-layer sheet and multi-layer sheet is about 1.1 mm of thickness. Our method has a potential to fabricate thinner film by using finer particles.

5. Conclusions

Sheets are formed by packing PTC particles between two aluminum foil electrodes and enclosing in an evacuated bag.

When only one layer of particles is inserted between the electrodes (mono-layer sheet), semiconducting BaTiO₃ particles of 600–710 µm are used. When two or more particles are piled up between the electrodes (multi-layer sheet), composites of semiconducting BaTiO₃ of 300–355 µm and In of –20 µm are used to decrease the contact resistance between the semiconducting particles.

A mono-layer sheet of 24 mm × 24 mm and a multi-layer sheet of 12 mm × 12 mm are fabricated. The properties of the sheets are investigated and the following results are obtained.

(1) Both the mono-layer sheet and the multi-layer sheet are flexible and show the PTC property.

(2) The performance of the mono-layer sheets is almost the same with that of the multi-layer sheet.

(3) The apparent resistance is higher than that of sintered specimens, because of the imperfect contact in the sheet.

(4) The thickness of the sheet is about 1.1 mm. The sheet is thinner than commercial thin PTC plates.

(5) When semiconducting BaTiO₃ particles are used for the multi-layer sheet, the resistance of the sheet is extremely high. The resistance is drastically lowered by using the composite particles of semiconducting BaTiO₃ and In.

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