Transactions of the Materials Research Society of Japan 28 [3] 743-746 (2003)

Sheet Heater Composed of PTCR Composite Particles

Mikihiko Kobayashi, Mitsuru Egashira, Takehiro Dan*,
Kyoko Saito and Norio Shinya
National Institute for Matrials Science, Sengen 1-2-1, Tsukuba, Ibaraki 305-0047, Japan
Fax: 81-29-859-2401, e-mail: KOBAYASHI.Mikihiko@nims.go.jp
*Soi 2425-3, Odawara, Kanagawa 250-0851, Japan

We fabricated a thin ceramic heater having PTCR property from the composite particles of semiconducting $BaTiO_3$ and solder. The composite particles were prepared by a low cost and high productivity method as follows. The semiconducting $BaTiO_3$ particles and solder particles were charged in a cylindrical vessel and rotated for a few hours. The solder particles were flattened and stuck to the surface of semiconducting $BaTiO_3$ particles. A packed bed of the composite particles was placed between two foil-like electrodes. It was enveloped in an air-tight and heat resistant bag, and the bag was sealed after evacuation. Thickness of the sheet was about 1mm. It was flexible and showed PTCR property. The trial sheet heater overcame the defect of ceramic PTCR heaters. The brittleness limited the size of ceramic heaters. Advantages and disadvantages of the trial sheet heater are discussed comparing with the previous results.
Keywords: PTCR, sheet heater, composite particle, $BaTiO_3$

1. INTRODUCTION

Resistance of some electroceramics varies steeply with the temperature at around the Curie point. When the resistance increases with an increase in temperature, they are PTCR (positive temperature coefficient of resistivity) materials. The unique property of the PTCR materials is utilized to protective devices, heaters, demagnetization devices, etc.

Ceramic heater made of PTCR material has a self-control function of temperature. When a constant voltage is applied to the heater, the temperature rises by the Joule's heat. The intensity of the current is depressed by the increasing resistance at around the Curie point, and the heater keeps the temperature constant. The Curie point can be controlled by addition of elements with 3 or 5 valence.

In spite of the useful self-control function, PTCR heaters are produced for limited use. The size of the PTCR heaters are less than a few cm. Ceramics brittleness becomes severe defect, when the size is large. Thus, they are not used for floor heating system or electric radiators.

We showed that compact of composite particles of semiconducting $BaTiO_3$ and In has a good PTCR property without sintering [1]. The results led us to flexible PTCR sheets. In this paper, we described how to fabricate the ceramic sheet heater of PTCR.

2. CONCEPT OF CERAMICS SHEET HEATER

Table I is the summary of our previous results [1], which are the starting point of this research.

Table I Summary of the previous results

Specimen	PTCR property
Sintered bulk	Standard PTCR
Compact of PTCR particles	PTCR but extremely high resistivity
Compact of composite particles	PTCR but a little worse than the standard bulk

The PTCR property of two particulate samples was measured. One was a PTCR powder and the other was composite particle of PTCR and In. In the composite particles, In particles adhered dispersively at the surface of PTCR particles, and each In particle was electrically separated from other In particles. The disk sample was prepared from the same PTCR powder for reference.

The PTCR property of the particulate samples was measured after packing in the cell of 6mm diameter.

When the PTCR particles were packed in the cell of 6mm diameter, the resistance of the cell was more than $10^5\Omega$ at room temperature. On the other hand, the resistance of the composite particles' cell was about $2x10^3\Omega$, almost the same with the disk sample.

The results of Table I are explained as follows. For the PTCR powder sample, contact resistance between the neighboring particles is very high, because of large Shottky barrier [2]. The resistance of the cell, therefore, becomes very high.

When the composite particles are filled in the cell, In particles always lie between the PTCR particles. Indium particles markedly lower the high contact resistance between the PTCR particles to the ohmic resistance [3].

The results indicate that the compact of PTCR composite particles shows good PTCR property without sintering process. It leads us to a flexible PTCR sheet heater.

The sheet heater, in which the composite particles are sandwiched between two foil-like electrodes as shown in Fig. 1, will be flexible. As the particles are only filled between the electrodes, the sheet is deformed by the rearrangement of the particles when the stress is added.

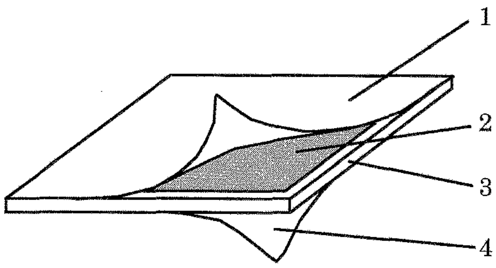

Fig.1 Structure of flexible sheet heater

1: upper electrode, 2: packed bed of composite particles, 3: insulating frame and 4: lower electrode

3. EXPERIMENTAL

3.1 Sample preparation

Row powder material of $BaTiO_3$ was supplied from Mitsui Mining Material Co. Ltd. The powder was granulated, sieved and baked in the atmosphere at 1330°C for two hours, and cooled down at a rate of 130°C/h to give the PTCR property.

In the previous experiments, composite particles of semiconducting $BaTiO_3$ and In were prepared by the forced electrification method [4]. Practical aspects were neglected and we concentrated only to demonstrate the flexibilty of the sheet. The preparation method was, therefore, not proper for the practical use.

Here, cheap solder particles instead of In particles were used in the experiments and another preparation process, a low cost and high productivity process, was developed [6]. Semiconducting $BaTiO_3$ and solder particles were charged in a cylindrical vessel of about 4cm in diameter. The mixture was agitated by a desk top ball mill. The agitating conditions were shown in Table II.

Table II Preparation of composite particles

Charges	
Core particle	$BaTiO_3$ of 600-700μ m
Child particle	Solder of -20μ m
Weight ratio	4:1
Agitation	
Rotation speed	200rpm
Agitating time	3hrs

After several hours treatment, the solder particles adhered dispersively at the surface of $BaTiO_3$ as shown in Fig. 2. The solder particles were flattened out by the impulse of collision during the agitation. The cross section of the composite particle suggests that a good electrical contact is expected between the core particles and adherents.

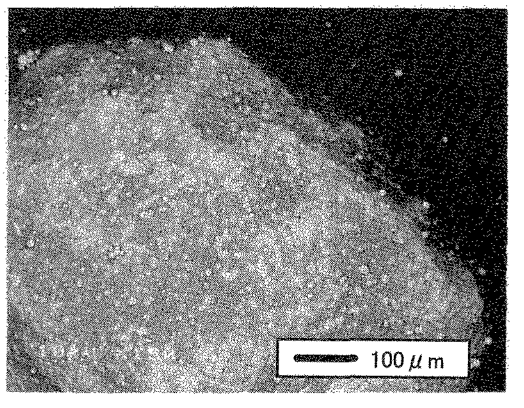

Fig. 2 Composite particle of $BaTiO_3$ and solder

3.2 Fabrication

An aluminum foil of 3x3cm was used for the electrodes. Insulating plastic frame of 0.9mm thickness were put on one electrode and the composite particles were filled within the frame. Another electrode covered the upper side of the frame and composite particles.

The whole was inserted in an air-tight and heat resistant bag used for the food preservation. The bag was sealed by heat after evacuation. As the inside was kept vacuum, the electrodes were always compressed by the atmospheric pressure of about 0.1MPa. Relative position of composite particles and the electrodes was fixed by the compressive pressure. The compression also ensured the contact between the electrodes and particles and between particles. Two lead wires, each connected to each electrode, were taken out through the small holes on the bag. An adhesive agent filled the holes.

3.3 Measurement

The relationship between the temperature and resistance was measured for the composite particles and for the trial sheet heater.

The PTCR property of the composite particles was measured by the same way described in the previous paper [1]. The sample was packed in a cell of a silica tube and pressed by the stainless rods. The cell was heated up and cooled down at a rate of 0.25°C/min in an oven, and the resistance of the cell was measured by a digital electrometer (TR8652, Advantest Co. Ltd.).

The electrometer sent a very small current from 100nA to 100μA to measure the resistance. When the heater was used, more current will be sent. Self-heating test was, therefore, carried out for the sheet heater, i.e., constant voltages were applied to the sheet covered with the heat insulator. The equilibrium temperature and the current were measured ranged from 0 to 95V.

4. RESULTS AND DISCUSSION

4.1 PTCR property of the composite particles

Figure 3 shows the PTCR property of the packed bed of the composite particles. The temperature dependence of the resistance is almost the same with that of the composite

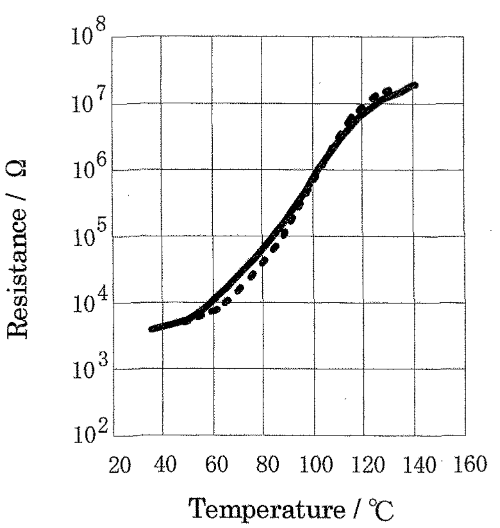

Fig. 3 PTCR propertyies of the packed beds of composite particles

Solid line and broken line is for the composite particles prepared by the ball mill method and thoseprepared by the forced electrification method, respectively.

particles of semiconducting $BaTiO_3$ and In prepared by the forced electrification method.

The ball mill method is fit for a mass production of composite particles in comparison with the forced electrification method. Furthermore, the products by the former method have some advantages. Solder is cheaper than In. The adherent force of the solder particles is tougher than the In particles. Indium particles in the composite particles easily peel off during the fabrication process. On the other hand, no solder particle peel off, even then the composite particles are immersed in ethanol and agitated by the ultrasonic wave. The reasons are that the bonding area is enlarged by the flattening, and that bonding strength of newly born surface is tough. The tough bonding suggests a good electrical contact as described above.

4.2 PTCR property of the trial sheet heater

The appearance of the trial heater is shown in Fig. 4. A thin copper plate of 1x3cm is put upon the aluminum foil electrode to solder the lead wire. The copper plate is seen on the left side of the electrode. The thickness of the heater is about 1mm.

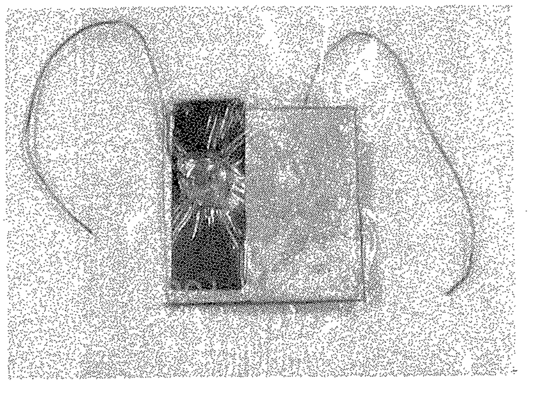

Fig. 4 Photograph of the trial sheet heater

The result of the self-heating test is shown in Fig. 5. When the applied voltage was less than 20V, equilibrium current increased from 0 to 0.05A with the voltage. Above 20V, the current decreased with the voltage, about 0.022A at 95V. The equilibrium temperature increased monotonously to about 85°C at 95V.

The resistance was estimated from the applied voltage and equilibrium current in Fig. 5. Calculated resistance was plotted against the equilibrium temperature in Fig. 6. The resistance increased with temperature from the minimum resistance of 300Ω at about 35°C to 5kΩ at 85°C. Figure 6 shows that the sheet has a PTCR property, though the increasing rate is not steep as expected from Fig. 3.

We fabricated the sheet heaters from the composite particles of semiconducting $BaTiO_3$

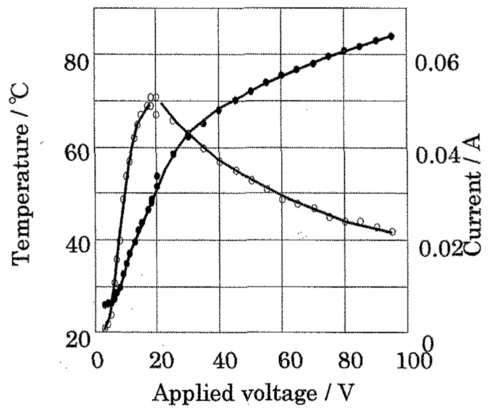

Fig. 5 Relationships between applied voltage and equilibrium temperature and between applied voltage and equilibrium current

Black circles: temperature and white circles: current

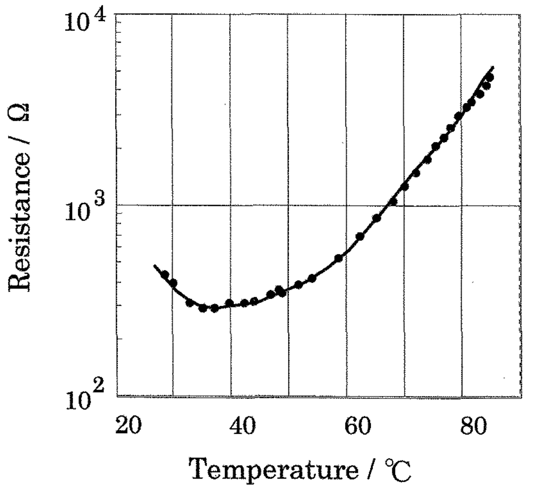

Fig. 6 PTCR property of the trial sheet heater

and In by the same way. In that case, the heaters were frequently short-circuited at about 50V. The cause of the short-circuit was considered to be the free In particles in the evacuated bag. The composite particles by the ball mill method yielded no free solder particles. The short-circuit is, therefore, not observed in the trial sheet heaters fabricated here.

4.3 Possibility of the ceramic sheet heater

Deterioration of the PTCR property may not be avoided due to the fabrication of sheet. As the spatial rate of the closed-pack is 23%, more voids will be in the packed bed. The voids do not give any contribution to the PTCR property.

The heater is, however, shows PTCR property and it will bring more benefits. The thickness is more than 3mm for mass-produced ceramic heaters. The thickness of the trial sheet is about 1mm and it is flexible, not fragile different from the ceramic heaters.

Besides the deterioration the most serious disadvantage is the structure. As the heater is enveloped in the evacuated bag, it cannot work only by a pinhole. Large size is difficult to produce.

Flexible sheets are fabricated to produce a large-scale heater applicable to the floor heating system. Next step of this research is, therefore, to develop a new process to fix the composite particles and electrodes. The process must be fit for the scaling-up. One way is to use a heat resistant resin. If the composite particles are embedded in the resin, and heaters are fabricated by spreading or spraying the mixture of the resin and composite particles, flexible ceramic sheet heaters will be widely used.

5. CONCLUSION

The flexible ceramic sheet heater was fabricated from the composite particles of semiconducting $BaTiO_3$ and solder. The composite particles were prepared by agitating the mixtures with a ball mill. The solder particles in the composite particles were flattened out and they adhered toughly to the semiconducting $BaTiO_3$ particles.

The composite particles were packed between the thin aluminum foil electrodes, and the whole was inserted in an evacuated bag to fix the particles and electrodes. The trial sheet heater was flexible and had PTCR property. Advantages and disadvantages of the sheet heaters were enumerated and problems for the practical use were discussed.

REFERENCES

[1] T. Dan, M. Egashira, J. Kyono, H. Fudoji and N. Shinya, *J. Soc. Powder Technol., Japan*, **33**, 848-854 (1996).
[2] "Semiconducting Barium titanate", Ed by Electro-ceramics Publication Committee, Giken, Tokyo(1980) pp. 27.
[3] T. Dan, M. Egashira, J. Kyono, H. Fudoji and N. Shinya, *Advanced Powder Technol.*, **13**, 425-435 (2002).
[4] T. Dan, M. Egashira, J. Kyono, H. Fudouzi and N. Shinya, "Preparation method of composite particles by electrification", Japanese Patent, Reg. No. 2694895 (1997.9.12).
[5] T. Dan, M. Egashira, M. Kobayashi and N. Shinya, *Mater. Trans.*, **43**, 956-960 (2002).
[6] M. Egashira, K. Saito, T. Dan, M. Kobayashi and N. Shinya, "Preparation method of composite particles", Japanese Patent, Appl. No. 2001-288212 (2001.9.21).

(Received Febuary 21, 2003; Accepted March 19, 2003)