

A New Class of NTC Thermistors

Kazuya Kato, Toshitaka Ota, Yasuo Hikichi, Hidero Unuma, Minoru Takahashi and Hisao Suzuki

CRL, Nagoya Institute of Technology, Tajimi, 507, Japan
Shizuoka University, Hamamatsu, 432, Japan

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VO₂ ceramics exhibiting a negative temperature coefficient (NTC) of resistivity have been widely used as temperature dependence resistors. The NTC effect similar to VO₂ ceramics was observed when a low-thermal-expansion ceramic matrix was loaded near the percolation threshold with conductive metal particles. The resistivity in a composite made from silica glass and 20 vol% Ag filler suddenly decreased from 10⁷ to 10³ Ωcm at about 300°C.

Key words: Thermistor, Composite, Resistivity, Percolation, Expansion

I. Introduction

Thermistor is a resistor whose resistance depends upon changes in temperature. There are three kinds of thermistors: PTC (Positive Temperature Coefficient), NTC (Negative Temperature Coefficient), CTR (Critical Temperature Resistor). Usually they are prepared from ceramic materials such as BaTiO₃, NiO-CoO-MnO or VO₂, respectively. However, a PTC thermistor is also prepared from composite materials such as polyethylene-carbon composite.^{1,2)} In this study, we tried to prepare a NTC thermistor and/or CTR from composite materials.

The resistivity of composite materials containing randomly dispersed conducting filler in an insulating polymer matrix is reasonably explained by percolation theory.³⁾ For a small volume fraction of conducting filler, the resistivity of the composite is basically that of the polymer matrix as shown in Fig. 1(a). As the volume fraction of the filler increases, the particles come into contact with one another to form the conduction paths through the composite. As a result, the resistivity drops by many orders of magnitude at a critical threshold. Once a saturation region is reached, there are a large number of conduction paths, resulting in low resistivities.

The composite in the percolation region near the saturation region exhibits a strong positive temperature coefficient (PTC) of resistance as shown in Fig. 1(b). The conducting particles are barely in contact at room temperature, giving a low resistivity. As the temperature increases, the polymer matrix expands much more than the conducting particles. Thereby the conducting particles are separated to break up the conduction paths, resulting in a PTC effect.

On the contrary, if conducting particles have larger thermal expansion as compared with matrix, we would

expect to see a negative temperature coefficient (NTC) of resistance for the composite in the percolation region near the critical threshold as shown in Fig. 1(c). At room temperature, the composite resistance is high because the conducting particles are essentially not in contact. As the temperature increases, the conducting particles expand to come into contact with one another, resulting in a NTC effect. In particular, this type of composite would become an attractive candidate for a critical temperature resistor (CTR) similar to VO₂ ceramic thermistor. CTR character of VO₂ ceramic is caused by the phase transition from semiconductor to metal which occurs at about 70°C. Consequently, the critical temperature is almost constant, although it can be slightly altered by adding additives. On the other hand, composite CTR should reveal different

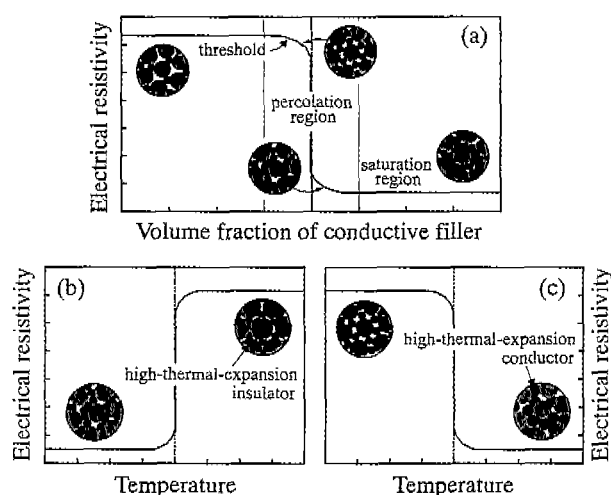


Fig. 1. Mechanism of composite thermistor. (a) Percolation curve, (b) PTC effect and (c) NTC effect (CTR).

critical temperatures, which are influenced by choice of filler and matrix materials.

II. Experimental Procedure

Starting materials were silica glass (Towa Refractory Engineering Co., Ltd., 15 μm) as an insulating matrix and two kinds of Ag particles (2 μm and 30 μm) (Kojundo Chemical Laboratory Co., Ltd.) as conductive filler. The particle size was measured with a laser diffraction particle size distribution analyzer (Horiba LA-500NA). Besides a small amount of binder, Aron Ceramic (Toagosei Co., Ltd.), was used in order to increase strength of composite. Table 1 shows some properties of starting materials.

These materials were homogeneously mixed in the desired composition ratio with acetone. This mixture was

Table 1. Properties of Starting Materials

	Silica glass	Ag
Particle size (μm)	15	2, 30
Density (g/cm^3)	2.2	10.5
Electrical resistivity (Ωcm) at r.t.	$>1.00 \times 10^{12}$	1.08×10^{-4}
Thermal expansion coefficient	0.50×10^{-6}	19.68×10^{-6}

Table 2. Conditions for Measurement

Temperature range	30~550°C
Heating rate	2°C/min
Bias voltage	1 V
Frequency	1 kHz

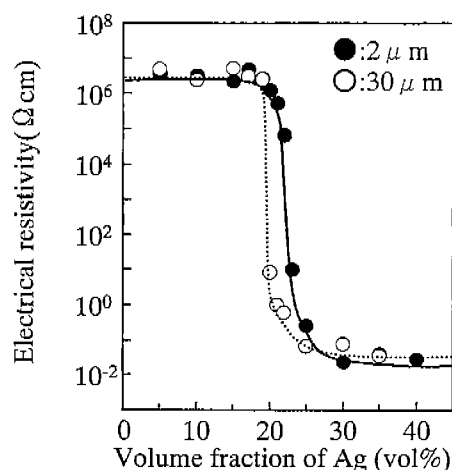


Fig. 2. The electrical resistivity of silica glass/Ag composite plotted as a function of volume fraction of Ag.

formed by die pressing under 100 MPa in the shape of 16mm diameter tablets. The tablets were then hardened at 150°C for 1 h.

Measurements of the electrical resistivity were carried out under the conditions shown in Table 2 using YHP-4284A LCR meter. Silver paste was applied on both sides of tablets as electrodes for the two-point method. Thermal expansion of the samples was measured by dilatometer (Shimazu TMA-50) from room temperature to 650°C.

III. Results and Discussion

The electrical resistivity data of silica glass/Ag composites

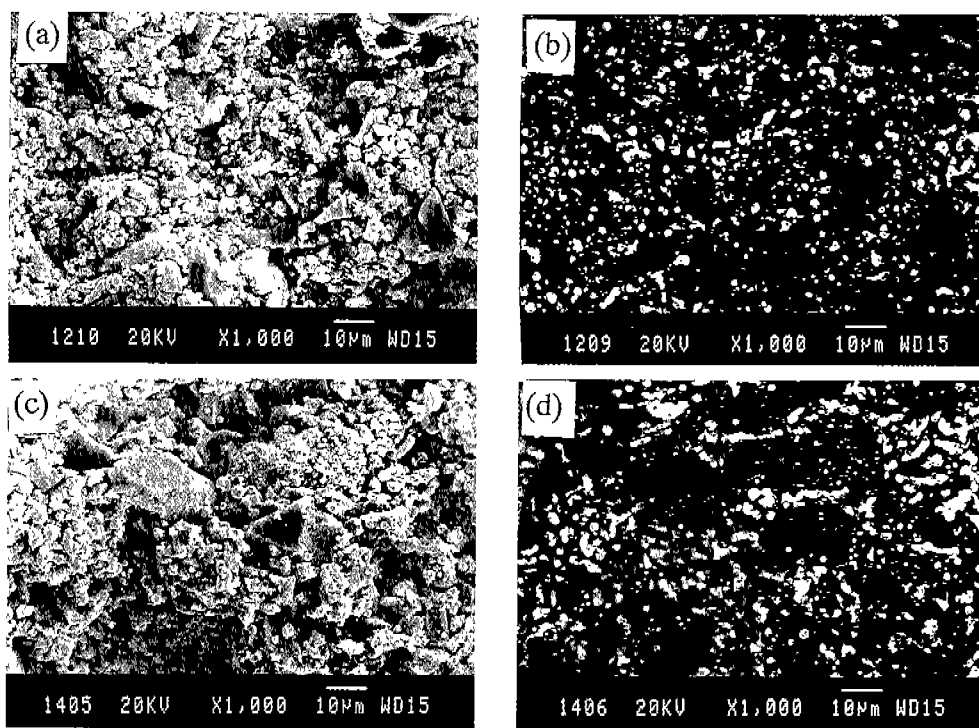


Fig. 3. Scanning electron micrographs of composites with (a) and (b) 20 vol% Ag and (c) and (d) 35 vol% Ag.

at 30°C were plotted as a function of volume fraction of Ag in Fig. 2. The electrical resistivity of the composites depended critically on the volume fraction of Ag. There was little difference due to the particle size of Ag. In the cases of composites with the volume fraction of Ag lower than 20vol%, the electrical resistivity of composites was high ($>10^6 \Omega\text{cm}$), and was basically that of the insulating silica glass. When the volume fraction of Ag was over the critical volume fraction (V_c) of about 20 vol%, the electrical resistivity drastically dropped by 8 orders of magnitude. This is because conduction paths through the composite were formed among Ag particles. Then the electrical resistivity gradually approached the resistivity of conducting Ag.

Fig. 3 shows the typical micrographs of the samples at the critical threshold (20 vol% Ag) and in the saturated region (35 vol%). In the BE images (Figs. 3 (b) and (d)), the white part must be Ag and the black part must be silica glass. The Ag particles were isolated from one another in the composite with 20 vol% Ag. (Fig. 3 (b)) While they came into contact with one another to form the conduction paths in the composite with 35 vol% Ag. (Fig. 3 (d))

Fig. 4 shows the temperature dependence of electrical resistivity of silica glass/Ag composites. The electrical resistivity of the matrix (0 vol% Ag) consisting of only silica glass and binder kept resistivity higher than $10^6 \Omega\text{cm}$ as shown in Fig. 4(b). Similarly, the electrical resistivity of composite with 10vol% Ag kept resistivity higher than $10^6 \Omega\text{cm}$ as shown in Fig. 4 (a), although it gradually decreased with increasing temperature in the temperature range over 300°C. This high resistivity is responsible for no conduction paths both at room temperature and at higher temperature. On the other hand, the electrical resistivity of composites with 30 vol% Ag, in which the conduction paths were completely formed by contact among Ag particles, was low in the whole temperature range from 30 to 550°C as shown in Fig. 4 (a) and (b). A remarkable CTR character was observed in composites with with 20 vol% Ag (2 μm) and 18vol% Ag (30 μm) near the critical threshold. The electrical resistivity dropped by 4~5 orders of magnitude at about 300°C(a) and 350°C(b). As mentioned in introduction, since Ag particles expanded with increasing the temperature, they would

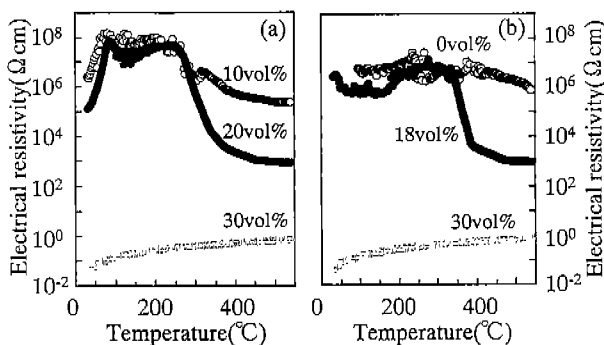


Fig. 4. Temperature dependence of electrical resistivity of silica glass/Ag composites which have various volume fraction of Ag. (a) 2 μm and (b) 30 μm .

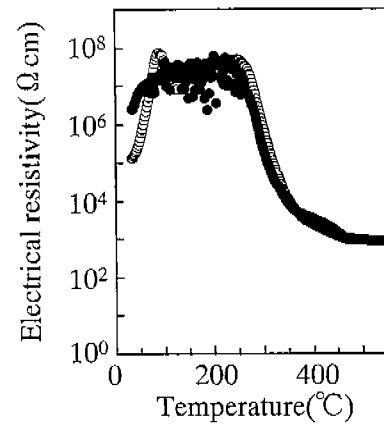


Fig. 5. Resistivity vs temperature of the composite with 20 vol% Ag (2 μm). ○: 1st cycle ●: 20th cycle.

come into contact with one another at a temperature. In this run, the conduction paths through the composite were formed at about 300~350°C, and then the electrical resistivity dropped by many orders of magnitude.

Fig. 5 shows the reproducibility of resistivity versus temperature of silica glass/Ag(2 μm) composites. The CTR character was almost the same from the first cycle to the 20th cycle, where the electrical resistivity dropped by 5 orders of magnitude. On the other hand, in silica glass/Ag(30 μm) composites the magnitude of the CTR character often became smaller and/or disappeared on repeating cycle of heating and cooling. Some composites had many cracks due to the large scale of expansion and shrinkage of large Ag particles after the measurement. It is thought that these cracks caused the irreproducibility. The difference between the 1st cycle and the 20th cycle for the silica glass/Ag(2 μm) composite in Fig. 4 might be also due to some changes of the microstructure.

Fig. 6 shows the thermal expansion curves of Ag and matrix. The thermal expansion of Ag was measured for a rod sample (ϕ 3 mm \times 10 mm). The thermal expansion coefficient ($19.68 \times 10^{-6}/^\circ\text{C}$) of Ag was apparently higher than that ($1.50 \times 10^{-6}/^\circ\text{C}$) of matrix. Consequently, it was thought that

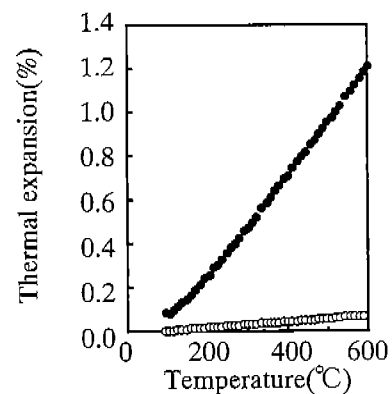


Fig. 6. Thermal expansion of Ag and matrix. ○: Matrix (silica glass+binder) and ●: Ag.

this difference of thermal expansion coefficient between Ag and matrix caused the CTR character. However, one of the most important questions arose: Why do we observe a very sizable and reproducible CTR character at 300°C. The PTC effect in a polyethylene-carbon composite occurs at the melting point of polyethylene, where polyethylene reveals an abrupt large volume change.²⁾ Similarly, it was expected that an abnormal expansion should occur at 300°C for the CTR character of silica glass/Ag composites. However, any sizable volume change was not observed at 300°C as shown in Fig. 6. So, further experimental work is needed to understand more clearly the nature of the CTR character in silica glass/Ag composites. In addition, the CTR character in some composites made up of other metals with different thermal expansion coefficients is presently being investigated.

IV. Conclusion

A new class of NTC thermistors was fabricated from sil-

ica glass/Ag composites. The electrical resistivity of the composite with 20 vol% Ag(2 μm) dropped by 5 orders of magnitude at about 300°C, in analogy with CTR character at 70°C observed in VO₂ ceramic. It was assumed that this phenomenon was due to the high thermal expansion of the conducting Ag filler in low-thermal-expansion silica glass matrix.

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