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PTCR property in carbon–NaCl composites

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The composition dependence of resistivity and the positive temperature coefficient of resistivity (PTCR) were investigated in composites of electrically conducting carbon and insulating NaCl. Resistivity at 20 °C of the composites decreased rapidly with increasing carbon volume fraction above a critical volume fraction, V_c, which was well expressed by an equation of the percolation theory. The value of V_c decreased from 25 vol % to 4 vol % when the particle size ratio of NaCl/carbon increased from 0.5 to 50. When the carbon volume fraction was close to the value of V_c, the composites showed pronounced PTCR properties with a resistivity increase of five orders of magnitude and a temperature coefficient of 15%–17% K^{-1}. A composite of all inorganic materials with a controllable PTCR property is suggested to be possible.

1. Introduction

Materials showing positive temperature coefficient of resistivity (PTCR), represented by rare-earth-doped $BaTiO_3$, are used in a variety of applications, such as temperature sensors, self-regulating heaters and devices for circuit protection. A series of composite PTCR materials based on combinations of conducting particles such as carbon black and an insulating polymer matrix such as polyethylene has been investigated by a number of researchers [1–9] and is already commercially available. The PTCR effect in the composite occurs at the melting temperature of the polymer. At that temperature, the polymer undergoes a large volume increase that results from the crystalline to amorphous phase transition. This volume expansion breaks continuous conduction pathways made of carbon blacks, resulting in an abrupt increase in resistivity of the composite. The PTCR effect was reported to occur also in carbon–cristobalite composites, though the resistivity increase was not large [10]. In this system, thermal expansion by polymorphic transition of cristobalite was utilized.

These carbon black–polymer composites exhibit a substantial PTCR effect of several orders of magnitude and have several advantages over conventional $BaTiO_3$ PTCR thermistors, including a low room-temperature resistivity and better thermal shock resistance. However, it is difficult to control the critical temperature of rapid resistivity increase at a desired temperature due to the use of the melting point of the polymer. In the carbon–cristobalite composites, the critical temperature is fixed at the polymorphic transition temperature. A composite consisting of inorganic materials with widely different resistivity and thermal expansion coefficients could be a candidate to realize a controllable PTCR property and high durability.

In the present study, dependences of resistivity on composition and temperature in the carbon–NaCl composites were investigated to confirm the feasibility of an inorganic materials composite with a controllable PTCR property.

2. Experimental procedure

Sodium chloride powder (Wako Chemical, Co., purity 99.5%) was ball-milled with ZrO_2 balls and classified with sieves into three kinds of powder with average particle sizes of 25, 150 and 250 μm. Three kinds of commercial carbon particle (PC series, Nippon Carbon Co., Ltd) with average particle sizes of 5, 20 and 50 μm, were used as the conducting particles. The carbon particles had a low resistivity of 10^{-1}–10^{0} Ω cm and a narrow size distribution, i.e. 90% of particles were in the range within ± 30% of the average diameter, as shown in Fig. 1. Powders of NaCl and carbon were mixed in propanol, dried and pressed into pellets (10 mm diameter × 2 mm thickness) at a pressure of 2 t cm^{-2}. A small amount of water was added when pressing to improve the density of the compact. The obtained pressed compacts had relative densities above 95%. Microstructure of the composites was examined with a scanning electron microscope.

Silver paste was applied to opposite surfaces of the pellet with silver wires. Electrical resistivity was measured by a d.c. two-probe method at an applied voltage of 0.1 V using a digital electrometer (advantest, TR8652) and a programmable d.c. standard (Hioki,

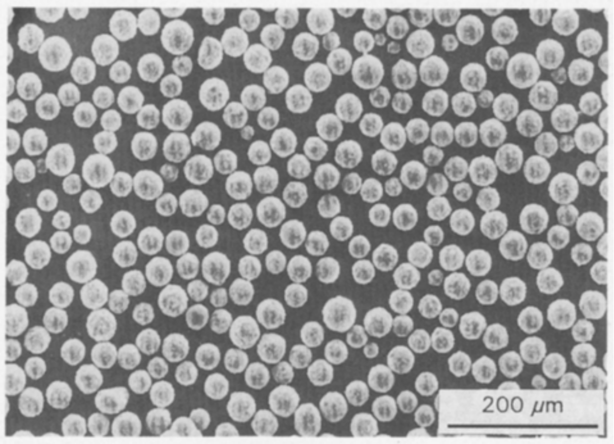

Figure 1 Scanning electron micrograph of carbon particles with an average diameter of 30 μm.

7005). For measurements of the temperature dependence of resistivity, the heating and cooling rates were kept constant at 7 K min^{-1} and nitrogen gas was passed above 400 °C to prevent the oxidation of carbon particles.

3. Results and discussion

3.1. Composition dependence of resistivity

The resistivity of the NaCl compact without carbon particles was very high and above the measurable limit ($> 10^{10}$ Ω cm) below 200 °C. The resistivity of composites at 20 °C decreased abruptly when the carbon volume fraction exceeded a critical value, and then continued to decrease down to below 10^1 Ω cm with increasing carbon volume fraction. Fig. 2 shows a typical carbon volume fraction (vol %) dependence of resistivity in composites of 50 μm NaCl and 20 μm carbon particles.

The composition dependence of resistivity in a conductor–insulator composite is well expressed with the percolation theory [11, 12]

$$\rho(V) = A(V - V_c)^{-t} \qquad (1)$$

where V_c is the critical carbon volume fraction required to make a continuous conduction path, $\rho(V)$ is the resistivity at carbon volume fraction V, and A, t are constants ($t = 1.5$–1.6).

According to Equation 1, $\log \rho$ and $\log(V - V_c)$ should follow a linear relationship when the carbon volume fraction, V, is above the critical value, V_c. Fig. 3 shows the $\log \rho$ and $\log(V - V_c)$ plot for $V_c = 0.167$ in the system shown in Fig. 2. The plot gives a linear relation with a slope ($-t$) of -1.58, suggesting the percolation theory can hold in the present system. The resistivity calculated by applying the values $V_c = 0.167$, $t = 1.58$ and $A = 1.86$ was also indicated in Fig. 2.

The value of V_c is reported to be dependent on the arrangement of particles, and has been calculated statistically to be 0.31 for single cubic and 0.20 for face-centred cubic lattice arrangements [11]. Observed values of V_c were largely dependent on the ratio of particle size of NaCl and carbon particles, R_d ($= d_{\mathrm{NaCl}}/d_{\mathrm{carbon}}$), in the present system. V_c decreased from 0.25 at $R_d = 0.5$, to 0.04 at $R_d = 50$, as shown in Fig. 4. Fig. 5 shows fracture surfaces of composites of 50 μm NaCl–50 μm carbon (40 vol % carbon), and 250 μm NaCl–5 μm carbon (10 vol % carbon). The spherical shape of the carbon particle is found to be unaltered in the composites. The carbon particles were randomly dispersed in a composite of equal-size particles (Fig. 5a), while carbon particles were located inhomogeneously in a manner to surround large NaCl particles in the composite with a large R_d (Fig. 5b). In a composite with a large R_d, a continuous conduction path is expected to be formed at a low carbon volume fraction due to the segregated arrangement of carbon particles. The percolation theory assumes a random distribution of specific sites or bonds in the regular lattice network, that is, a homogeneous distribution of two kinds of same-size particles. Accordingly, it is reasonable that the observed V_c in a composite with $R_d = 1$ corresponded to the statistically calculated V_c and it decreased with increasing R_d as shown in Fig. 4.

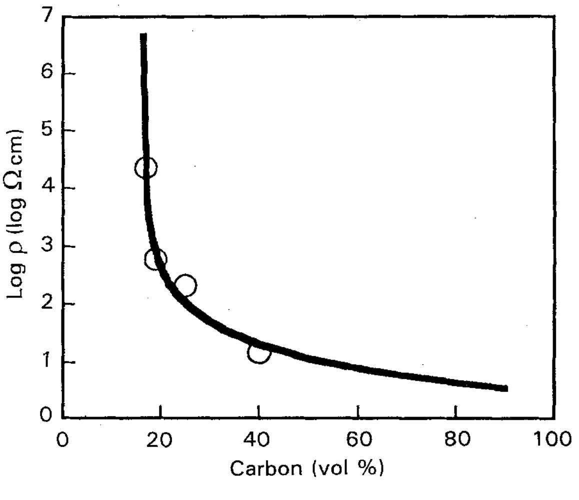

Figure 2 Composition dependence of resistivity at 20 °C (○) in composites of 50 μm NaCl–20 μm carbon. (——) Calculated resistivity; $V_c = 16.7$ vol %, $-t = -1.58$.

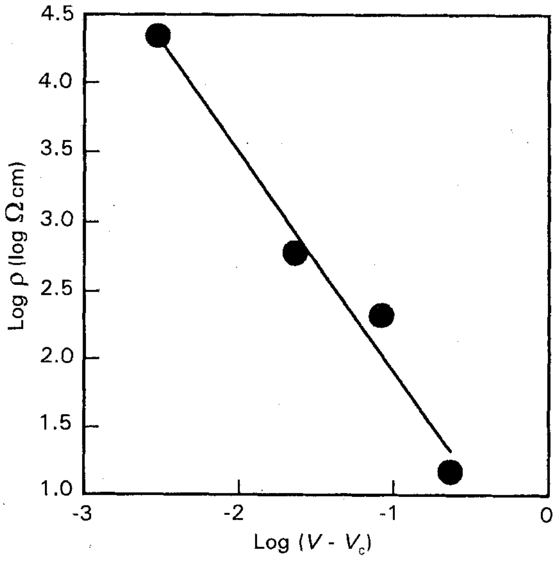

Figure 3 Log ρ–log($V_c - V$) plot ● in composites of 50 μm NaCl–20 μm carbon. $V_c = 0.167$ vol %, $-t = -1.58$.

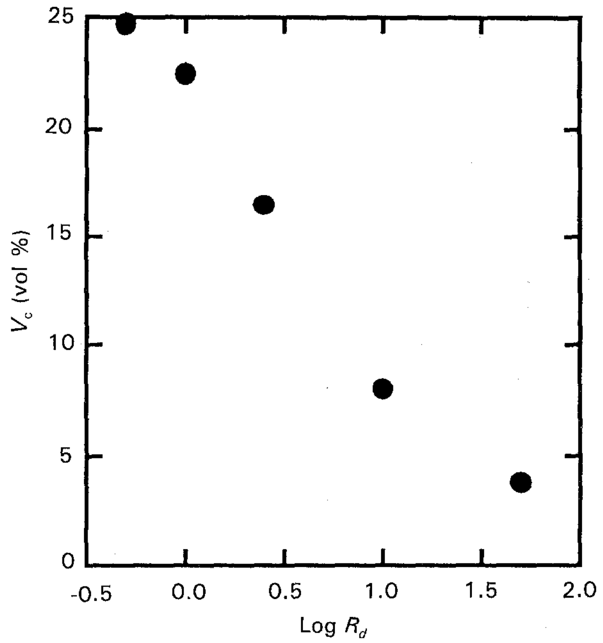

Figure 4 Critical carbon volume fraction, V_c, as a function of particle size ratio, R_d ($= d_{NaCl}/d_{carbon}$).

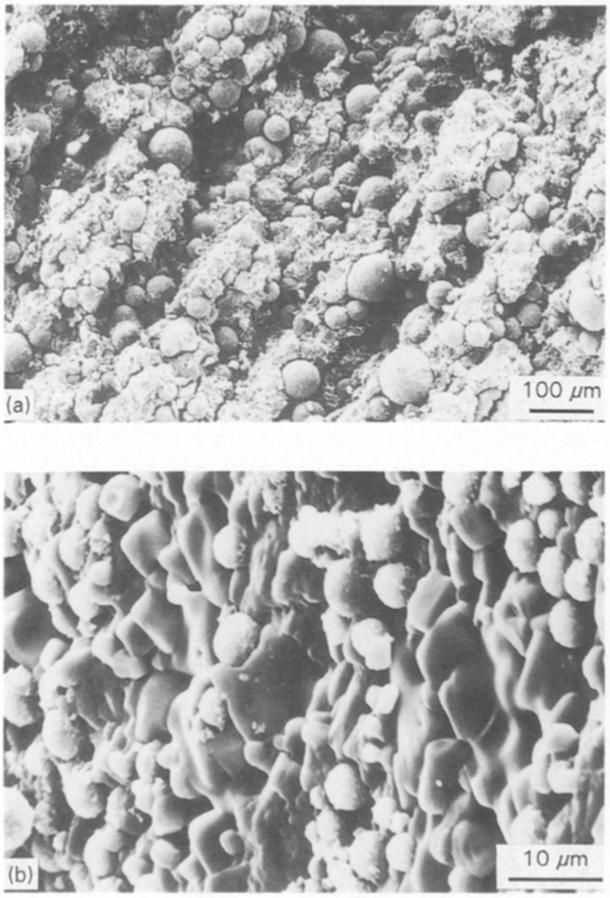

Figure 5 Scanning electron micrograph of the fracture surface of a composite of (a) 50 µm NaCl–50 µm carbon (carbon 40 vol %), and (b) 250 µm NaCl–5 µm carbon (carbon 10 vol %).

This variable behaviour of V_c has been proposed theoretically [13] and confirmed in the carbon–polymer and carbon–cristobalite composites [6, 10]. In the present system, all the observed t values were in the range 1.0–2.0.

3.2. PTCR effect

All the composites with carbon volume fractions above V_c exhibited the PTCR effect. Figs 6 and 7 show resistivity–temperature characteristics of composites of 50 µm NaCl–20 µm carbon and of 50 µm NaCl–5 µm carbon, respectively. When the carbon volume fraction was close to the critical value V_c, increases of resistivity were large, up to five orders of magnitude, and the changes were sharp with a temperature coefficient of resistivity, α, of 15%–17% K^{-1}. As the carbon volume fraction increased, the magnitude and temperature coefficient of the resistivity change, decreased. At a composition much above V_c, the log ρ–T plot showed an almost linear relation over a wide temperature region, in some cases up to 600 °C.

These PTCR properties are derived from a large difference in thermal expansion coefficient of the components. It is reported that NaCl has a linear thermal expansion coefficient of $40.4 \times 10^{-6}\ K^{-1}$ [14] and carbon (graphite) has 1.2×10^{-6}–$8.2 \times 10^{-6}\ K^{-1}$ depending on crystallinity and anisotropy of the graphite crystal [15]. Because the carbon particles used in the present study were found to be amorphous from the X-ray measurement, a low thermal expansion coefficient is expected. As temperature increases, the volume fraction of conducting carbon, V, decreases relatively, approaching the critical volume fraction, V_c. In the vicinity of the temperature at which V reaches V_c, resistivity increases sharply by breaking the conduction paths. Accordingly, if values of V_c of the composite and the thermal expansion coefficients of the components are known, it is possible to estimate the temperature ($T + \Delta T$°C) showing the sharp increase of resistivity in the composite with a carbon

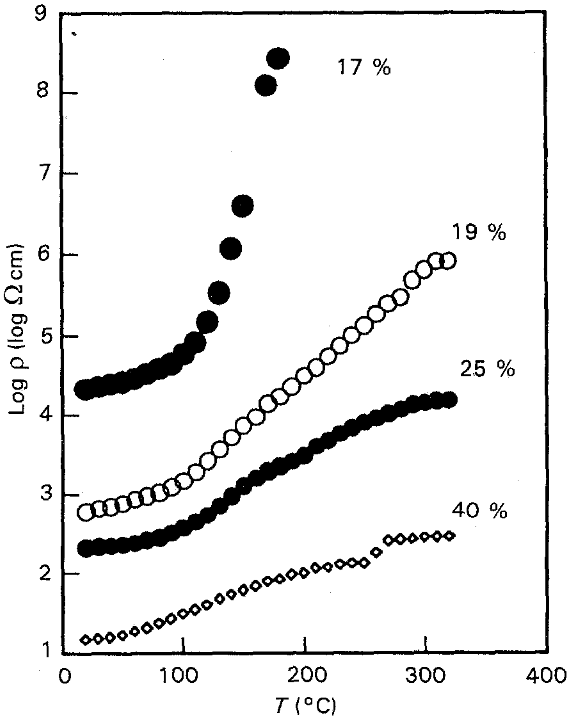

Figure 6 Resistivity–temperature characteristics in composites of 50 µm NaCl–20 µm carbon. Numbers indicate the volume per cent of carbon (V_c = 16.7 vol %).

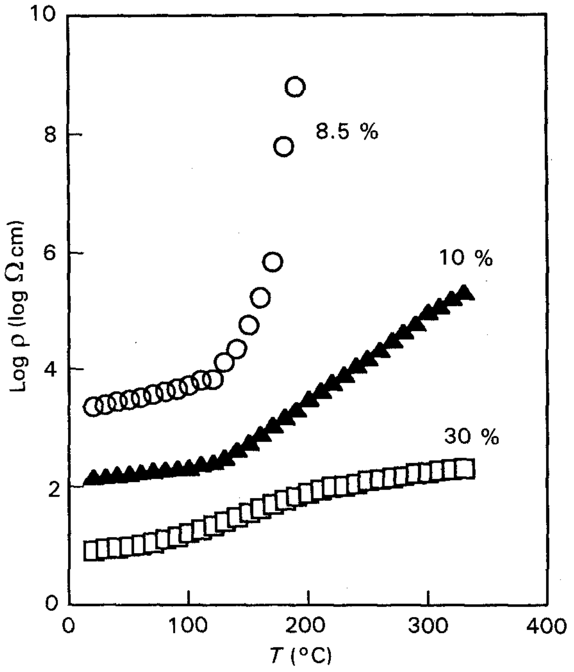

Figure 7 Resistivity–temperature characteristics in composites of 50 μm NaCl–5 μm carbon. Numbers indicate the volume per cent of carbon (V_c = 8.3 vol %).

volume fraction V at T°C, using the following equation

$$\frac{V + 3\alpha_c V \Delta T}{1 + 3[\alpha_c V + \alpha_i(1 - V)]\Delta T} = V_c \qquad (2)$$

where α_c and α_i are the linear thermal expansion coefficient of conducting carbon and insulating NaCl, respectively, and ΔT is the required temperature increase from T°C. By using $V = 0.17$ at 20 °C, $V_c = 0.167$ and tentative values of $\alpha_c = 2.0 \times 10^{-6}$, $\alpha_i = 40.0 \times 10^{-6}$, the ΔT was calculated to be 190 °C for the composite of 50 μm NaCl–20 μm carbon (17 vol %) shown in Fig. 6. In the same manner, using $V = 0.085$ and $V_c = 0.083$, ΔT of 230 °C was obtained for the composite of 50 μm NaCl–5 μm carbon (8.5 vol %) shown in Fig. 7. Taking into consideration that the calculated temperature is that at which resistivity reaches the value of the insulating matrix, the calculated temperatures are almost in agreement with the measured temperatures.

On the second and third heating–cooling cycles, resistivities slightly higher than that on the first heating were observed. However, the temperature dependence of resistivity was maintained constant after the third heating until at least the tenth heating. Preliminary heat treatment above 400 °C was found to be effective to stabilize the PTCR property.

From the above results, control of the resistivity–temperature relation, such as choice of abrupt or gradual resistivity change and setting of the temperature of the abrupt resistivity increase, etc., was found to be realized by selecting the composition and particle sizes in the NaCl–carbon system. All-inorganic materials composites with controllable PTCR properties, other than the NaCl–carbon system, would be possible if adequate materials systems with a thermally expansive insulator and a thermally unexpansive conductor are provided.

4. Conclusions

The composition dependence of resistivity at 20 °C in the NaCl–carbon system was well expressed by an equation of the percolation theory. The critical carbon volume fraction, V_c, decreased from 25 vol % to 4 vol % when the particle size ratio of NaCl/carbon increased from 0.5 to 50. When the carbon volume fraction was close to the value of V_c, the composites showed pronounced PTCR properties with a resistivity increase of five orders of magnitude and a temperature coefficient of 15%–17% K^{-1}. The temperature of the sharp resistivity increase estimated using V_c and thermal expansion coefficients, almost agreed with the measured temperature. A composite of all-inorganic materials with a controllable and reproducible PTCR property is suggested to be possible.

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