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Preparation, electrical resistivity and its temperature dependence of RuO_2–polystyrene composite powder

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RuO_2–polystyrene composite powder was prepared by admixing fine powdered RuO_2 and polystyrene beads thoroughly in ethanol. RuO_2-coated polystyrene beads were also prepared by direct suspension polymerization of styrene in an aqueous phase in the presence of a suspended RuO_2 powder. The apparent d.c. volume resistivity, ρ_a, of the hot-pressed composite was measured at various temperatures (20 to 80° C), pressures (3.5 to 35 MPa) and volume fractions of RuO_2, ϕ, (0.008 to 0.10). The volume resistivity increased linearly with temperature on a double logarithmic scale. The equilibrium volume resistivity at constant temperature, ρ_{aT}, decreased remarkably when ϕ increased from 0.025 to 0.04 for the mixed material, due to the establishment of a continuous network of RuO_2 in this region, as revealed by scanning electron microscopy. The composite prepared by direct polymerization completed a network of the conductive phase at a much smaller volume fraction of RuO_2. The average size of RuO_2 aggregates covering the surface of polystyrene agreed fairly well with the calculated value based on the simple geometry.

1. Introduction

Among many kinds of inorganic–plastic or metal–plastic composite materials, plastic-cored particles coated with fine electrically conducting particles have scientific and applicational interests [1]. After we had published detailed properties of a silver–polystyrene powder mixture [2], we developed a composite powder comprising of ruthenium oxide and polystyrene. RuO_2, used widely for modern electronic devices, has a specific electrical resistance which is as low as those for metals [3]. Since the primary particle of RuO_2 is much smaller than usual metal powders and has no problem with insulating oxide layers on conducting metal particles, RuO_2 is one of the most suitable materials for making thin conductive layers on plastic surfaces.

Homogeneous coating of plastic beads with fine powdery RuO_2 is not very easy because of its strong aggregating tendency in liquids. Once the plastic beads are successfully coated and compacted subsequently by a suitable method, very high apparent specific conductivity can be obtained with a small content of the conducting phase, due to the ordered mixing of the conducting powder particles [4].

The main purpose of the present study is divided into two parts. One is to prepare the RuO_2–polystyrene composite powder with a uniform coating of well dispersed RuO_2 on polystyrene beads. The other is to elucidate the electrical resistivity and its temperature dependence of the compacted composite and to discuss in conjunction with its microstructure.

2. Experimental details

2.1. Starting materials

RuO_2 was supplied by Shoei Kagaku Ltd. The median diameter of the polygonal primary particles is approximately 0.1 μm. The surface of RuO_2 was cleaned with benzene in a Soxhlet extractor for 30 h. Sieved polystyrene beads, supplied by Showa Denko Co., has a narrow particle size distribution around the median

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value, 50 μm. True densities are 6.84 g cm^{-3} for RuO_2 and 1.06 g cm^{-3} for polystyrene. Specific electric resistivity of RuO_2 single crystals is 3.4×10^{-5} Ω cm [3].

2.2. Preparation of composite powders

Two different methods were employed. (a) Mixing method: after washing the polystyrene beads and RuO_2 separately in ethanol, a 3 g batch containing two constituents in a predetermined ratio was mixed thoroughly together in 150 cm^3 ethanol in an ultrasonic bath for 20 min. Ethanol was then evaporated at 70° C for 4 h by agitating constantly with a magnetic stirrer. (b) Polymerization method: with the aid of ultrasonic vibration, one gram RuO_2 was dispersed in 10 g distilled styrene monomer containing 1 g benzoyl peroxide as an initiator. The monomer was mixed subsequently with 200 ml H_2O. Polymerization was carried out at 80° C in a 1 litre glass reactor in N_2 atmosphere for 6.5 h. Details of the polymerization technique will be published separately.

2.3. Hot-pressing

A cylindrical die cavity of 10 mm diameter was filled with a 0.3 g composite powder. The material was then compressed under the predetermined pressure and heated at a constant rate of heating, 0.5 K min^{-1}, up to the maximum temperature (40 to 160° C), kept constant for 0 to 6 h, and then cooled down by simply turning the heater off. The applied pressure was taken off only after the compact had been cooled down to the room temperature.

2.4. Measurement of electrical resistivity of compacts

Two square silver electrodes (6 mm × 6 mm) were cemented on both ends of the cylindrical compact with an electroconductive paste. Overall apparent electrical resistivity, ρ, was measured with a precise d.c. double bridge (Yokogawa, Type 2752) ($\leqq 100\,\Omega$) or a digital ohmmeter (Takeda, TR 6834) ($> 100\,\Omega$) in a dry N_2 atmosphere. The volume resistivity, ρ_a, was calculated by

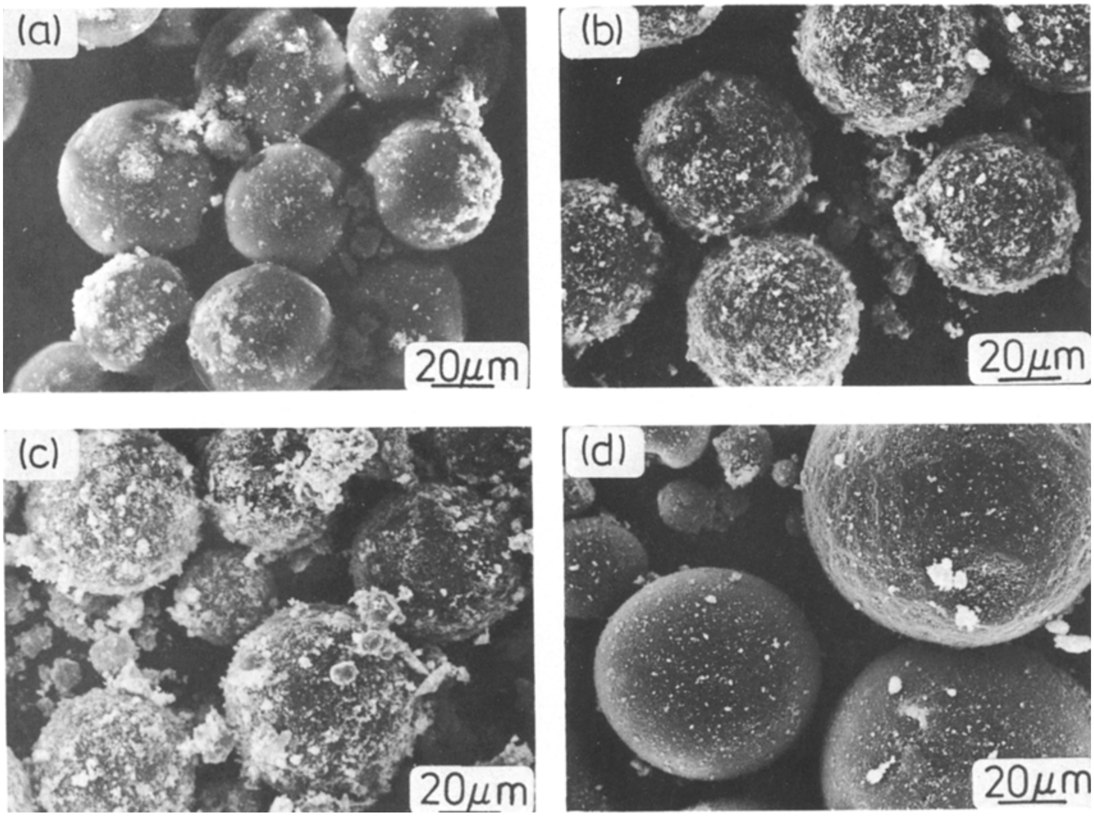

Figure 1 Scanning electron micrographs of the RuO_2–polystyrene composites. (a) mixing method, $\phi = 0.025$; (b) mixing method, $\phi = 0.04$; (c) mixing method, $\phi = 0.06$; (d) polymerization method, $\phi = 0.0078$.

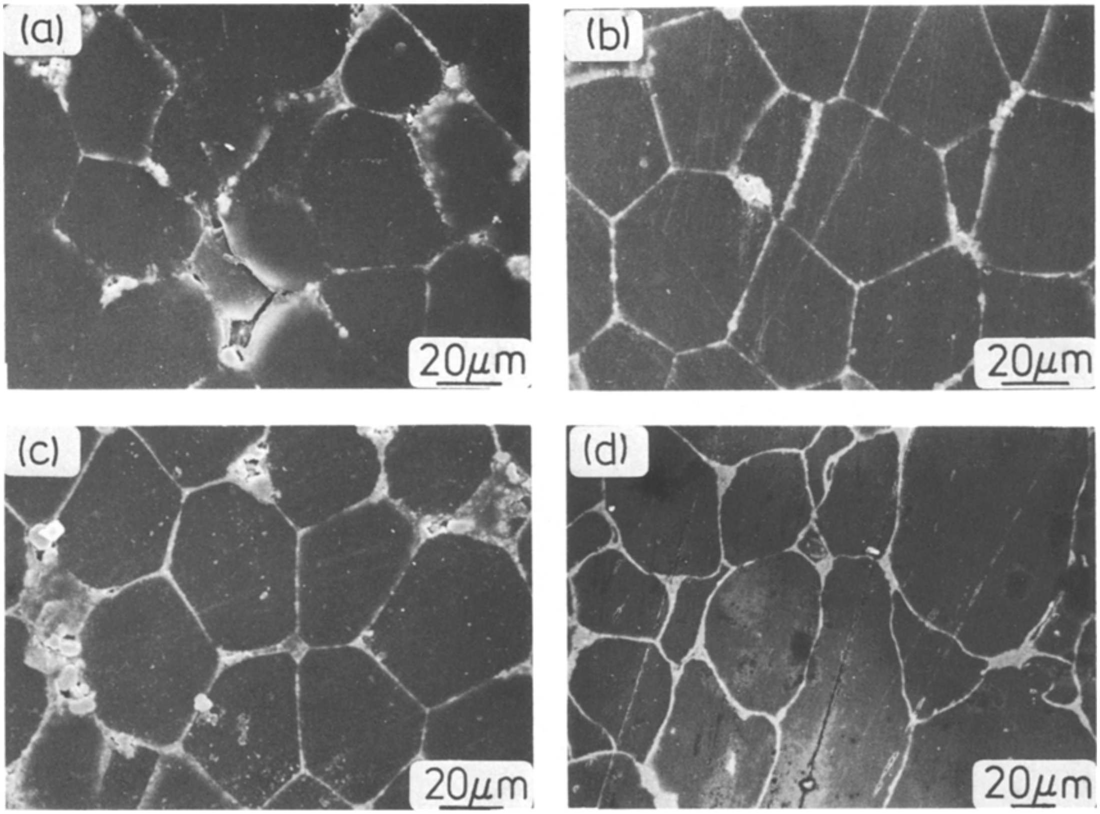

Figure 2 Cross sectional views of composites compacted at 3.5 MPa. Symbols (a) to (d) correspond to those used in Fig. 1.

multiplying ρ by l/s, where l and s are the thickness and the cross-sectional area of the compact, respectively.

3. Results

3.1. Microscopic observations

Scanning electron micrographs of some composites are given in Fig. 1. By the mixing method, the surface of polystyrene seems to be covered entirely with RuO_2 at $\phi = 0.04$ as shown in Fig. 1b. Since the degree of dispersion of RuO_2 is better in the polymerization method, the surface looks much smoother as shown in Fig. 1d. The size of aggregates of RuO_2 on the surface of polystyrene are between 1 to 5 μm, whereas larger aggregates are often found in the interspherical voids. Fig. 2 shows cross sectional views of the hot-pressed composites. The bright polygonal boundaries are RuO_2 layers, as confirmed by an electron probe microanalysis. Fig. 2 clearly shows the completeness of the network at $\phi = 0.04$ for the mixing method (Fig. 2b), and $\phi = 0.0078$ for the polymerization method (Fig. 2d).

3.2. Variation of apparent volume resistivity

The volume resistivity, ρ_a, varied with time and temperature as shown in Fig. 3, for the sample with $\phi = 0.04$, hot pressed at 35 MPa. Since ρ_a did not return to the initial value at the end of the first temperature cycle, all resistivity data were taken from the second temperature cycle, which was closed. The volume resistivity increased with increasing temperature and decreased with time under constant temperature, reaching an equilibrium value, ρ_{aT}. When temperature is lowered, ρ_a went down again and reached an initial value of ρ_a, thus the resistivity change was reversible.

3.3. Variation of ρ_{aT} with RuO_2 content

The volume resistivity at constant temperature (80° C) decreased with increasing RuO_2 content and compressive stress, as shown in Fig. 4. Between $\phi = 0.025$ and 0.04, the decrease in ρ_{aT} is particularly steep for the samples prepared by the mixing method. For the purpose of comparison, some mixtures were prepared by mixing poly-

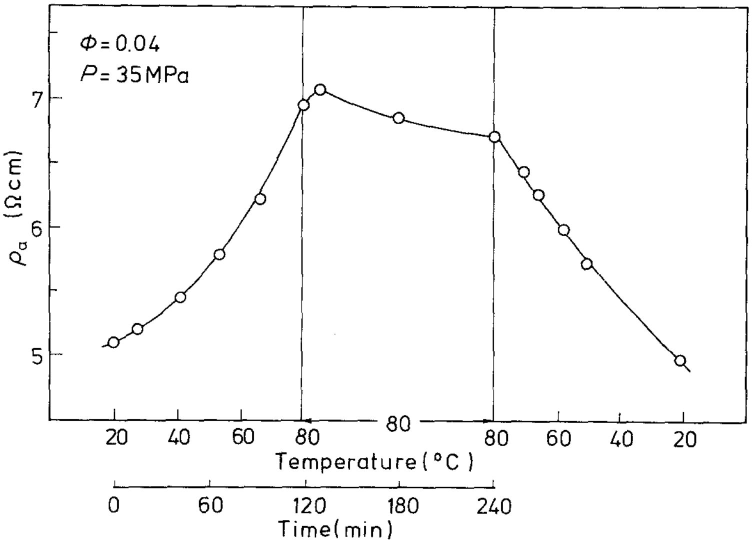

Figure 3 Variation of volume resistivity with time and/or temperature.

styrene and RuO_2 simply by a V-mixer in air. The results with these composites are shown in Fig. 4 with triangles. With poorer dispersion of RuO_2, ρ_{aT} is much higher than those thoroughly admixed. No data for the polymerization method was plotted in Fig. 4, because the wide variation of ϕ with the polymerization method was not possible. However, the better dispersion of RuO_2 on polystyrene was obvious from the equilibrium volume resistance shown in Table I.

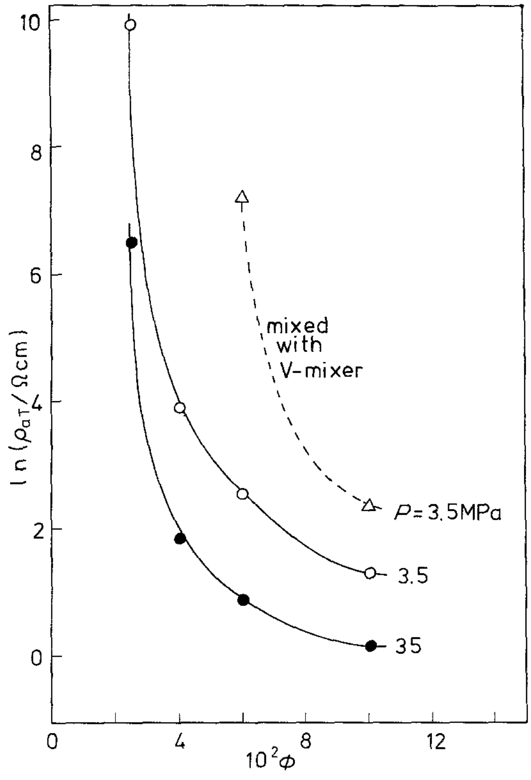

Figure 4 Relation between ln ρ_{aT} at 80° C and ϕ.

3.4. Change in ρ_a with the ambient temperature

When the volume resistivity is plotted against temperature on a double logarithmic scale, linear relations are always obtained as shown in Fig. 5. Hence the relation between ρ_{aT} and the temperature is expressed as

$$\rho_{aT} = AT^n \tag{1}$$

where A is a constant, similar to that for the RuO_2 single crystal [3]. The exponent, n, decreases also with increasing ϕ, approaching to the value of RuO_2 single crystal shown with a horizontal broken line in Fig. 6.

3.5. Effects of hot-pressing temperature and holding time

The equilibrium volume resistivity shows a minimum at 140° C when plotted against the maximum temperature of hot-pressing, as shown in Fig. 7 (indicated by circles). The temperature exponent, n, on the other hand, decreases monotonically with temperature, as shown by the squares in

TABLE I The equilibrium volume resistance, ρ_{aT}, of the hot-pressed RuO_2–polystyrene composites, at the temperature just above the softening point

Preparation method	ϕ	ρ_{aT}	T (° C)
Mixing	0.025	2.1×10^4	80
	0.04	52	80
Polymerization	0.0078	130	40

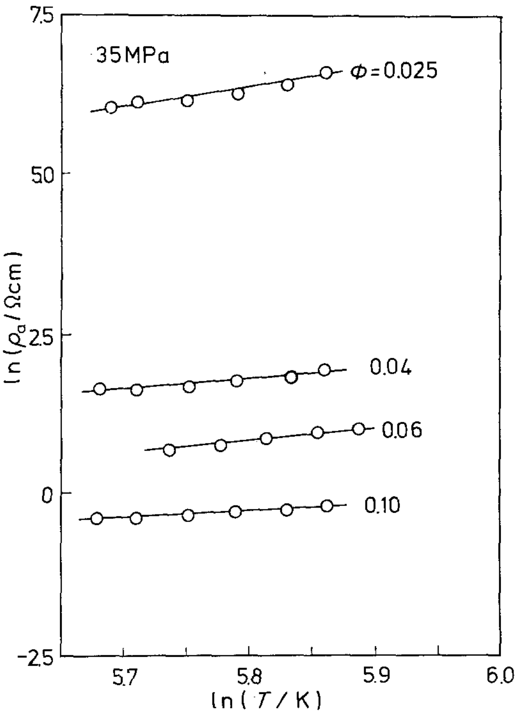

Figure 5 Relation between ln ρ_a and ln T.

Fig. 7. With a longer hold time at the maximum temperature, 140° C, during hot-pressing, both ρ_{aT} and n become larger, as shown in Fig. 8.

4. Discussion

4.1. Completion of RuO_2 network

As shown in Figs. 1 and 2, the network of RuO_2

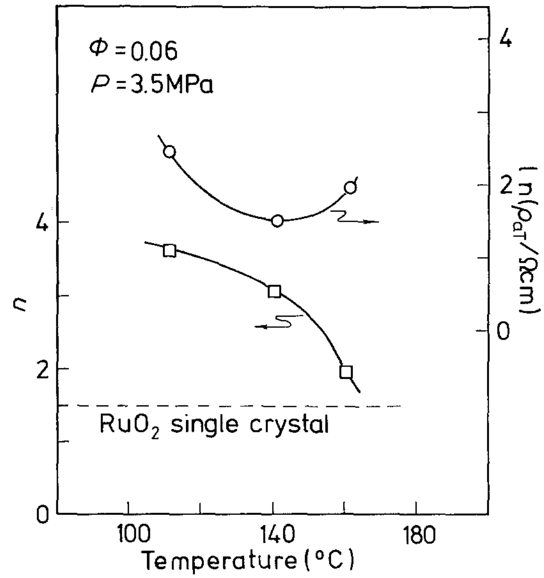

Figure 7 Variation of n with temperature.

phase on the surface of polystyrene is almost completed between $\phi = 0.025$ and 0.04 when the mixing method is employed. This corresponds to the steep decrease in the volume resistivity shown in Fig. 4. When the coverage by RuO_2 is incomplete, the neighbouring polystyrene beads are readily coalesced and the RuO_2 network is discontinuous. By assuming that particles of both components are spherical, a theoretical relationship between the critical volume concentration of the conductive phase, V_c, at which the network is completed, and the diameter ratio of the con-

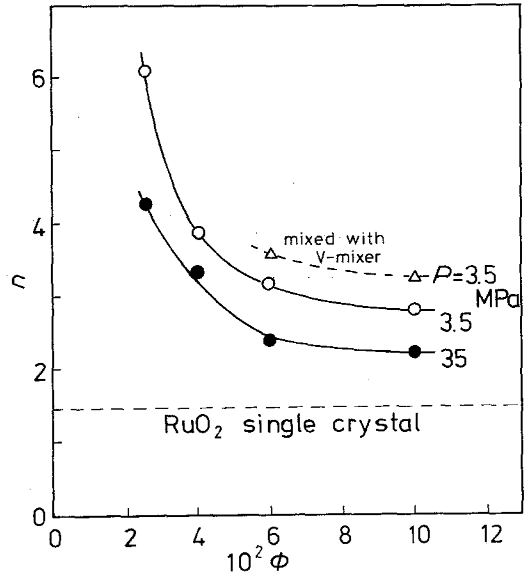

Figure 6 Relation between n and ϕ.

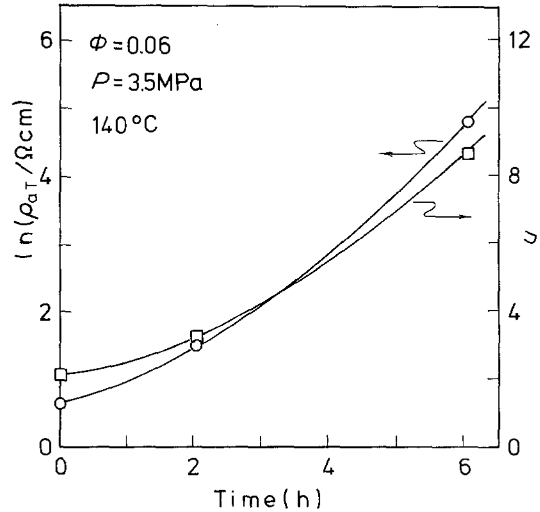

Figure 8 Variation of ln ρ_{aT} at 80° C with holding time. Holding temperature: 140° C.

ducting and the plastic phases has been proposed by Malliaris and Turner [5]. Kusy [6] modified the former equation and suggested an alternative one;

$$V_c = (1 + 0.756R_p/R_m)^{-1} \qquad (2)$$

where R_p and R_m are the diameters of polystyrene and RuO_2, respectively.

Starting from an assumption that RuO_2 particles are all ideally dispersed into primary particles and putting $R_p/R_m = 50/0.1$ or 500 into Equation 2, we obtain V_c as 0.0026. As shown in Fig. 4, the volume fraction of RuO_2 at the completion of the network was between 0.025 and 0.04, suggesting that in spite of thorough dispersing and admixing, RuO_2 particles are aggregated. This is actually observed in Fig. 2. Conversely, if we take the observed value of V_c as 0.0025 and 0.04, then R_p/R_m is 51.6 and 31.7, and accordingly, the average diameter of RuO_2 is estimated as 1.0 or 1.6 μm, which agrees fairly well with the observation shown in Fig. 1b. By the polymerization method, the RuO_2 network completed even at $V_c = 0.0078$. The corresponding average diameter of RuO_2 is 0.3 μm, which agrees reasonably well with the electron micrograph shown in Fig. 1d.

4.2. Temperature dependence of ρ_a

RuO_2 shows metallic conduction [3] and the specific resistance increases linearly with T^n, n being a constant. When $\ln \rho_a$ is plotted against $\ln T$ for the present composites, linear relations are obtained from which we calculated the exponent. n decreased with increasing RuO_2 loading, as shown in Fig. 6. The variation of n with ϕ is quite similar to those of ρ_{aT}. That the exponent n varies with polystyrene content implies that, in spite of the very high resistivity of polystyrene, the plastic phase is not completely inert for the electrical conductivity of the composite. In other words, the plastic phase in the present composite powder cannot be interpreted as a simple filler or a spacer. The role of polystyrene on the conduction mechanism of the present composite is not yet clear. It would be possible to assume that the tunnel effect is involved, as was suggested for the conduction mechanism of carbon black loaded rubbers [7].

4.3. Increase in ρ_{aT} with holding time

In the case of a silver–polystyrene mixture with similar particle sizes [2], the dominating factor for the increase in ρ_{aT} with holding time during hot-pressing was supposed to be the wetting of the silver phase by softened polystyrene. In principle, a similar mechanism would also explain the increase in ρ_{aT} with holding time shown in Fig. 8. Because of the much finer particles of RuO_2 than silver particles used in the previous work [2], some other mechanisms could also be included. With a prolonged hot-pressing, a remarkable change in the texture of the composite was observed as shown in Fig. 9. The micrograph strongly suggests that a part of RuO_2 migrated from the surface boundary of polystyrene into the interior of the plastic phase, resulting in the decrease in the volume resistivity of the whole

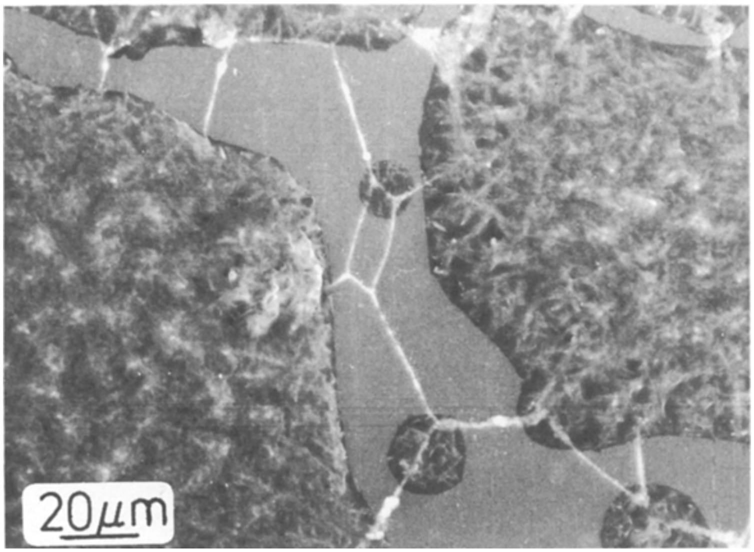

Figure 9 Cross sectional view of the compact of the composite prepared by the mixing method, $\phi = 0.06$, held at 140° C for 2 h during hot-pressing at 3.5 MPa.

hot-pressed composite. Although the precise mechanism of this kind of migration is not clear at the present step, the texture change shown in Fig. 9 should have disrupted the local RuO_2 network and accordingly cause the decrease in ρ_{aT}.

4.4. Concluding remarks

In order to obtain earlier completion of the network of the conductive phase with a minimum amount, good dispersion of the conductive phase is of vital importance. Although fairly good dispersion was achieved by admixing thoroughly the constituent powders, the average effective particle size of RuO_2 was still ten times as large as the primary RuO_2 particle, recognizable with an electron microscope. Direct polymerization, on the other hand, seems very promising for the purpose of better dispersion of RuO_2 on the surface of plastic globules.

It has been indicated that the temperature exponent, n, of the volume resistivity changes with the content of plastic matrix phase. The role of the plastic phase is thus obviously more than that of a spacer. The subtle change in the conduction mechanism due to the presence of the plastic matrix should, therefore, be studied further in order to elucidate the exact role of the polystyrene in the present composite.

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