JOURNAL OF MATERIALS SCIENCE 12 (1977) 509–516

Electrical resistivity of hot-pressed silver-polystyrene powder mixture

RITSU MATSUSHITA, MAMORU SENNA, HIROSHI KUNO
Faculty of Engineering, Keio University, Hiyoshi, Yokohama, Japan

Electrical volume resistivity and bulk density during hot-pressing were measured simultaneously on silver–polystyrene equal-sized binary powder mixture under three different conditions: (1) at constant rate of temperature increase under constant pressure; (2) at constant temperature and pressure, and (3) at constant temperature and constant rate of pressure increase. Volume resistivity decreased with increasing pressure at all temperatures studied (50 to 164° C). Above the softening temperature of polystyrene (101° C) volume resistivity under the constant pressure increased with time even after the bulk density of the compact became constant. Judging from the scanning electron micrographs, contiguity of silver particles seems to be gradually hindered due to the penetration of thin films of polystyrene between silver particles after the onset of softening of polystyrene. A new method of preparing plastic-based composites with desired electrical resistivity is therefore possible through appropriate hot-pressing of metal–polymer powder mixture.

1. Introduction

Densification processes during hot-pressing have been investigated over the last decades and a number of possible mechanisms have been proposed [1, 2]. Changes in the pore or the packing structures on densification are, however, not yet clarified [3, 4].

Electrical resistivity measurement is one of the most convenient tools in studying such structural changes of powder compacts [5–7], and has the advantage that the resistivity can be measured continuously throughout the whole densification process.

A metal–polymer binary system was chosen in the present study because changes in the electrical resistivity in such a system are a direct measure of the contiguity of the metal phase [6], and the rate of densification of the compact is controllable by choosing an appropriate temperature and pressure. By measuring the volume resistivity and the thickness of the mixed powder simultaneously, information on the contiguity of the metal phase, and the packing structure of hot-pressed mixtures as well as the overall densification, were obtained. Silver was chosen as a metal component, because of the small effect of its surface oxide. Since the softening behaviour is well known [8], polystyrene was very suitable for the polymer phase. Scanning electron microscopy of hot-pressed materials was also carried out to directly observe changes in the structure of hot-pressed composites.

2. Experimental

2.1. Materials

Electrolysed silver comprising polyhedral particles (99.95%, Ishifuku Metal Co) was sieved to a fraction of 140/200 mesh and cleaned by a Soxhlet's extractor with benzene for 30 h. As-received spherical polystyrene ($M_{av} = 174\,000$, Nippon Polystyrene Co) was sieved to a fraction of the same size as the silver and used without further treatment. Photomicrographs of the starting materials are given in Fig. 1. The desired amount of each powder was mixed in a 275 ml V-mixer for 20 to 40 min until an homogeneous mixture was obtained. The composition of the mixture throughout the present study is expressed as the volume fraction of silver, ϕ_{Ag}.

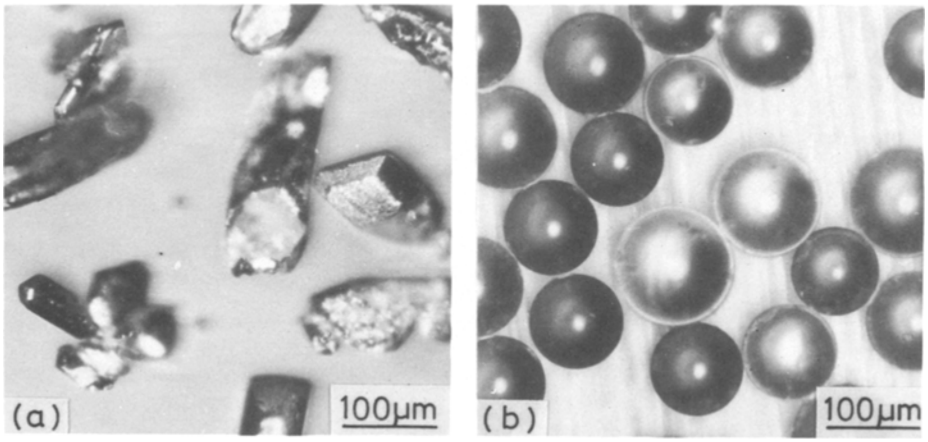


Figure 1 Photomicrographs of the starting materials: (a) electrolysed silver; (b) polystyrene.

2.2. Hot-pressing

Hot-pressing was carried out under three different heating and compressing conditions by a modified flow-tester (Shimadzu Seisakusho Co) [8]. A specimen was compressed uniaxially under normal stress ranging from 7 to 65 kg cm^{-2}, which was kept constant irrespective of the degree of deformation by using a beam and weights. It was also possible to increase the pressure at a constant rate by pouring water into a large vessel hung from the beam, instead of a weight pan. The change in thickness of the sample was determined by a built-in dial gauge to an accuracy of 10^{-3} mm. The upper and lower surfaces of the stainless steel punches were thoroughly polished to ensure a good contact with the surface of the powder bed.

In each case, an alumina die, 20 mm diameter, was preheated to 59° C and the die cavity was slowly filled by a desired amount (~3 g) of the mixed powder. Thereafter: in method 1 the powder bed was compressed at 29.3 kg cm^{-2}, and after the apparent density, d_a and resistivity, ρ, became constant, the temperature was raised at constant rate of 3° C min^{-1}, to 164° C; in method 2 the material was heated until the desired temperature (63 to 144° C) was reached and the mixture was then compressed under the desired constant pressure (7 to 65 kg cm^{-2}); for method 3 the powder mixture was heated until the desired temperature (63 to 144° C) was attained, and the powder bed then compressed at 7.2 kg cm^{-2} for 60 min and the pressure increased by a constant rate of 1.2 kg cm^{-2} min^{-1} to a maximum pressure of 29.3 kg cm^{-2}. The maximum pressure was held for about 20 min until the apparent density and the resistivity became constant.

2.3. Electrical resistivity measurements

Overall resistivity was measured using a precise double bridge (Yokogawa Electrical Co, 2752) to an accuracy of 10^{-5} Ω. The electric current during the measurement was chosen so small that the effects of Coulimbic heating was negligible. Contact resistance at the interface between the punch and the sample powder and any possible resistance other than that of the powder compact itself in the circuit, were obtained from the measurements on the samples with different thicknesses and by the extrapolation to zero, and were subtracted from each measured overall resistivity, ρ, to obtain

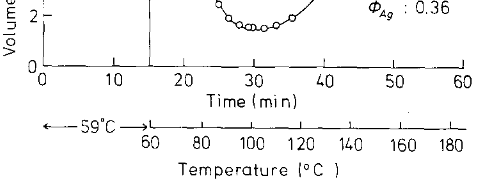


Figure 2 Variation of volume resistivity and bulk density with time and/or temperature on hot-pressing the mixture $\phi_{Ag} = 0.36$ with method 1.

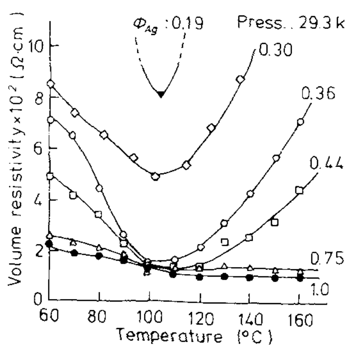


Figure 3 Variation of volume resistivity with temperature on hot-pressing mixtures of varying compositions with method 1.

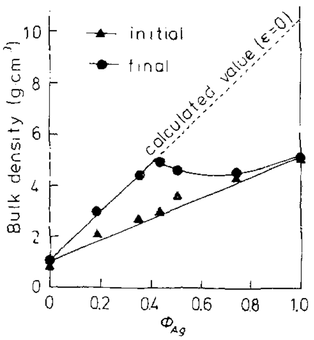


Figure 4 Initial and final bulk density of silver–polystyrene binary mixtures. Dashed line denotes the calculated true density by adding the true densities of the two components after their composition.

a net resistivity, ρ_n. The volume resistivity, ρ_a, was then calculated from the relation, $\rho_a = \rho_n\ (l/S)$, where l and S are the thickness and the cross-sectional area of the compact, respectively.

3. Results

3.1. Method 1

Changes in the bulk density and the volume resistivity for a mixture $\phi_{Ag} = 0.36$ are given in Fig. 2. At the beginning of compression at 59° C and 29.3 kg cm^{-2}, the volume resistivity decreased rapidly and fell to a constant value within 15 min, whereas the density remained nearly unchanged, except at the initial stage of compressing, when a rapid increase in the bulk density could not be followed. The change in the volume resistivity at this stage is attributed the the rearrangement and/or the reorientation of silver particles. Such rearrangement and/or reorientation can easily occur with little change in the bulk density. On increasing temperature, the volume resistivity began to decrease toward a minimum value at about 100° C, which is very near to the softening temperature of polystyrene, $T_s = 101°$ C [8]. The volume resistivity then increased continuously with temperature. The type of change in bulk density with temperature was quite different from that in volume resistivity. Most of the densification took place only in the temperature range of 90 to 110° C, which is about ± 10° of T_s.

It is particularly noted that about 110° C, where the change in the bulk density eventually ceases, a steep increase in the volume resistivity was observed. Since the temperature coefficient of the specific resistivity of solid silver is only 4.1×10^{-3}, the observed increase in the volume resistivity cannot be explained by a simple temperature effect on the metallic conduction of solid silver.

As shown in Fig. 3, variation of the volume resistivity with temperature by method 1 was always U-shaped, with minimum values at about 100° C, irrespective of the composition, as long as the silver content was not very high. For all mixtures examined, the bulk density changed in the same manner and the change was smaller with larger ϕ_{Ag}. The initial and final bulk densities, i.e. the bulk densities of the hot-pressed material at 59 and 160° C, respectively, by method 1 for different mixtures, are given in Fig. 4. The calculated true density of the mixture, by adding the true densities of the two components after their composition, is also given in Fig. 4 as a dashed line. For the mixtures $\phi_{Ag} < 0.43$, the final bulk density was nearly equal to the calculated true density, indicating the existence of very few interparticle voids in those compacts.

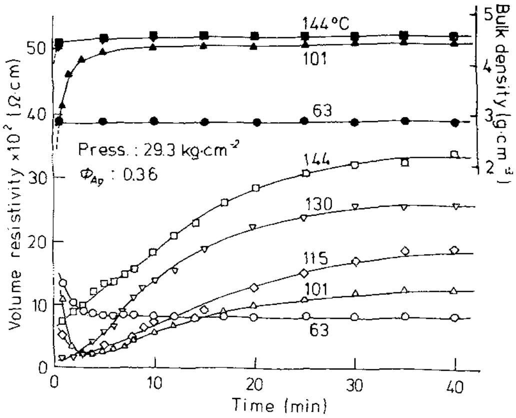


Figure 5 Variation of volume resistivity and bulk density with time on hot-pressing the mixture $\phi_{Ag} = 0.36$ with method 2.

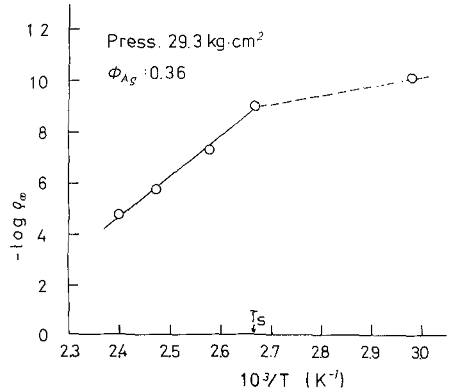


Figure 6 Relation between -log ρ_∞ and $1/T$, ρ_∞ being the final volume resistivity on hot-pressing with method 2.

3.2. Method 2

When the mixture was compressed at constant temperature and pressure, the volume resistivity decreased at the initial stage of compression due to the simple densification as shown in Fig. 5, for the mixture $\phi_{Ag} = 0.36$. This decrease in the volume resistivity appears to be the same as that observed at the beginning of the hot-pressing with method 1 at 59° C, shown in Fig. 3. Soon after the initial decrease, however, the volume resistivity increased with time at temperatures above T_s, as shown in Fig. 5. At temperatures well below T_s, e.g. at 63° C, no such increase was observed. At each temperature studied, the volume resistivity attained a constant final value, ρ_∞, within 1 h. When the logarithm of the final volume resistivity, log ρ_∞, was plotted against $1/T$, a linear relation was obtained at $T \geqslant T_s$, as shown in Fig. 6.

The volume resistivity of the compacts hot-pressed at 144° C under various pressures by method 2 is shown in Fig. 7. The final volume resistivity of the compact reached a higher final value, when a lower pressure was applied, as shown in Fig. 7, and the reciprocal of the final volume resistivity, i.e. the final volume conductivity, σ_∞, varied linearly with log P, as seen in Fig. 8. The bulk density, on the other hand, varied neither parallel to ρ_∞ nor to σ_∞ but became constant immediately after the pressure was applied.

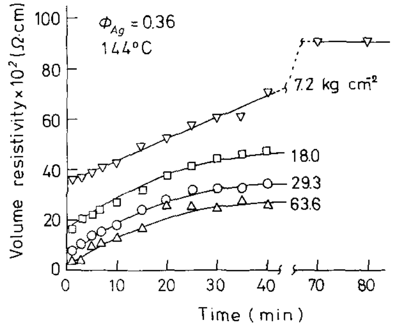


Figure 7 Variation of volume resistivity with time on hot-pressing the mixture $\phi_{Ag} = 0.36$ at various pressures with method 2.

3.3. Method 3

The results of method 3 are shown in the middle part of Fig. 9, between 60 and 78 min. The other parts of Fig. 9, are substantially the same as for method 2, since in these regions, samples were hot-pressed isothermally under constant pressure. The volume resistivity always decreased with increasing pressure, accompanied by an increas in the bulk density.

4. Discussion

4.1. Variation of the volume resistivity with time

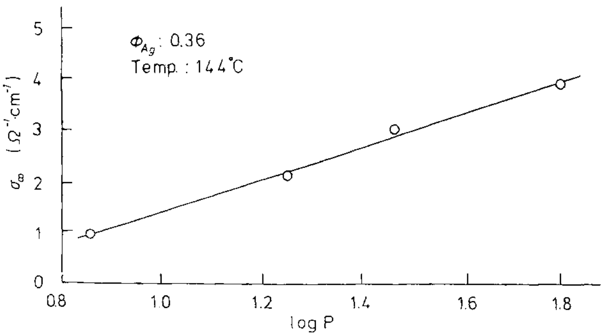
At temperatures above T_s, an increase in the volume resistivity after the initial rapid decrease was always observed, as shown in Fig. 5. The initial decrease, observed particularly at lower temperatures, is attributed to the better contact between the silver particles, due to rearrangement and/or reorientation, since the plastic deformation of polystyrene at lower temperatures is still very sluggish, as seen from the density curve in Fig. 5. At higher temperatures, on the other hand, polystyrene is soft enough for the densification to take place very rapidly when the external pressure was applied. Therefore, the initial decrease in the volume resistivity at 130 and 144° C could not be recognized.

Because the later increase in resistivity with time occurs only at $T \geqslant T_s$, it must be associated with the softening of polystyrene. The linear relation between log ρ_∞ and $1/T$ at $T \geqslant T_s$, shown in Fig. 6, might also suggest that the volume resistivity in this temperature range is associated with the flow properties of the polymer component.

4.2. Relation between the volume resistivity and the bulk density

A considerable degree of correlation between $1/\rho_a$ and the bulk density was observed for method 3, as shown in Fig. 10. In this case, however, the pressure was increased continuously and the measured volume resistivity is an instantaneous one. On the other hand, the volume resistivity for

Figure 8 Relation between σ_∞ and log P, where σ_∞ is the final volume conductivity, i.e. $1/\rho_\infty$, and P the applied pressure in method 2.



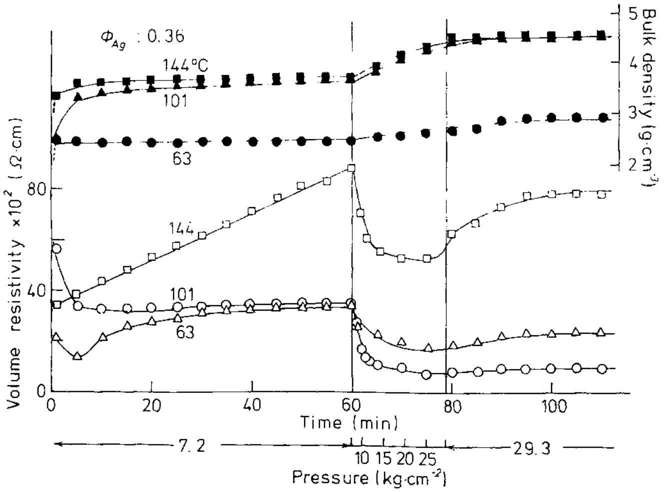


Figure 9 Variation of volume resistivity and bulk density with time and/or pressure on hot-pressing the mixture $\phi_{Ag} = 0.36$ with method 3.

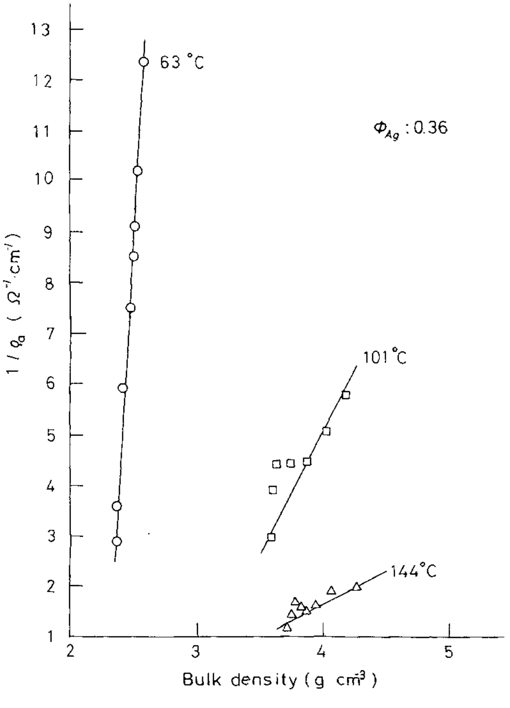


Figure 10 Relationship between $1/\rho_a$ and the bulk density on hot-pressing the mixture $\phi_{Ag} = 0.36$ with method 3.

methods 1 and 2 are those after prolonged compression at a constant pressure. This implies that the variation of the volume resistivity can be explained by the change in the contact area between silver particles, due to the bulk densification, as long as the volume resistivity is measured either soon after the compact is compressed or under conditions of increasing pressure with a sufficient rate of increase. The simple relation between the volume resistivity and the bulk density at the beginning of compression also might have been observed for method 2, if it had been possible to measure the initial values of volume resistivity and the bulk density, or extrapolated these values reasonably to time zero, as one can surmise from the volume resistivity–time curve in Fig. 7.

When the powder mixture is compressed under constant pressure for a prolonged time, as in methods of 1 and 2, the relation between the bulk density and the volume resistivity is no longer simple. Final bulk densities of the compacts from methods 1 and 2 were nearly equal to the calculated values shown in Fig. 4 by the dashed line, indicating that no appreciable interparticle void

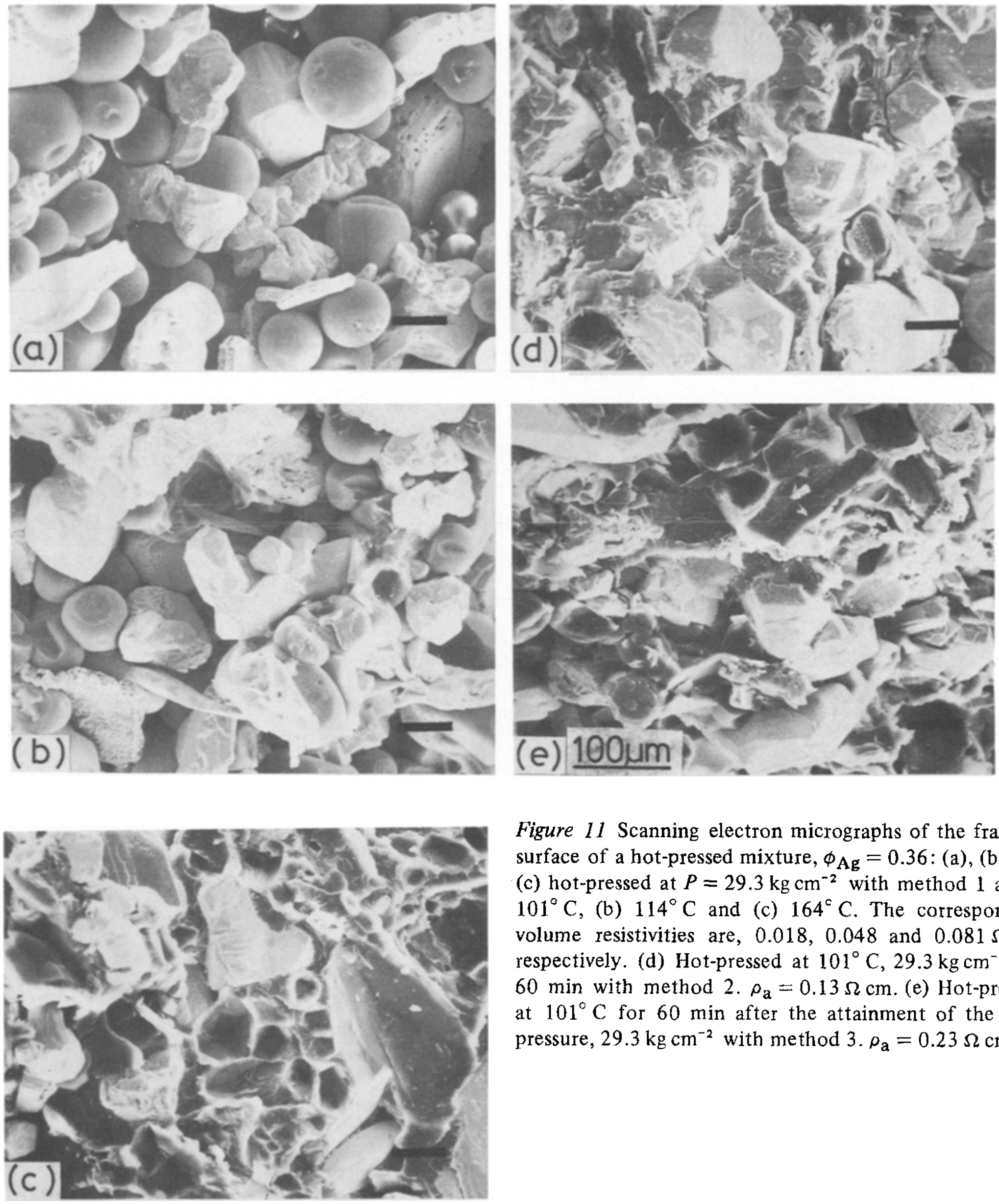


Figure 11 Scanning electron micrographs of the fracture surface of a hot-pressed mixture, $\phi_{\mathrm{Ag}} = 0.36$: (a), (b) and (c) hot-pressed at $P = 29.3\ \mathrm{kg\,cm^{-2}}$ with method 1 at (a) 101° C, (b) 114° C and (c) 164° C. The corresponding volume resistivities are, 0.018, 0.048 and 0.081 Ω cm, respectively. (d) Hot-pressed at 101° C, 29.3 kg cm^{-2} for 60 min with method 2. $\rho_a = 0.13$ Ω cm. (e) Hot-pressed at 101° C for 60 min after the attainment of the final pressure, 29.3 kg cm^{-2} with method 3. $\rho_a = 0.23$ Ω cm.

space was remaining at the later stage of hot-pressing, where gradual increase in the volume resistivity still persisted. Since no bulk flow of polystyrene is expected at this stage, the silver network structure must be detached locally in the vicinity of the contact point during the prolonged compression.

4.3. Impedance of the electrical conductivity by softened polystyrene

With the aid of scanning electron microscopy, the processes of deformation and penetration of polystyrene were directly observed on the fracture surface of the hot-pressed tablet. As shown in Fig. 11, polystyrene gradually loses its spherical shape as densification proceeds at $T \geqslant T_s$, and forms thin "sheaths" around the polyhedral silver particles, as shown in Fig. 11c. As expected, the compacts with the largest number of sheaths and thickest sheaths correspond to the highest volume resistivity. By comparing Fig. 11a, d and e, it is clear that although the final hot-pressing temperature (101° C) and pressure (29.3 kg cm^{-2}) in these cases are the same, the structure of the compacts is very different when heating and compressing conditions vary.

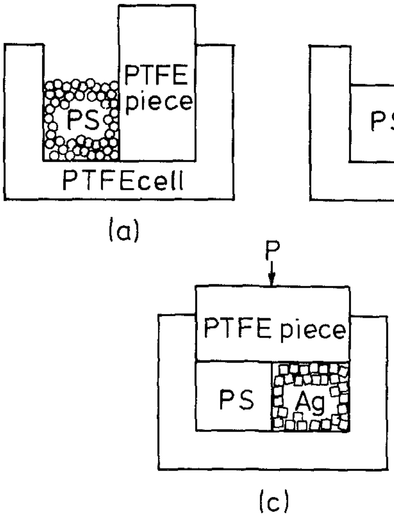


Figure 12 Schematic illustration of the model experiment to examine whether polystyrene penetrates into the silver powder bed.

From direct measurement under atmospheric pressure [9], it was established that a number of softened polymeric substances wet inorganic and metallic substrates. However, the contact angle reaches its equilibrium value only very slowly because of its extremely high viscosity [9]. The sluggish increase in the volume resistivity at $T \geqslant T_s$ could thus be explained by a mechanism where the contiguity of silver particles is slowly impeded due to the penetration of polystyrene between the silver particles as the wetting spreads. Neverthless, it may not be easy to conceive that a film of the softened polymer develops in such a way that it breaks the contact of the metallic particles, which are cramped together under the external compressive force. A model experiment was therefore carried out to determine whether such a penetration of polystyrene takes place spontaneously.

In the model experiment, polystyrene was placed in the left part of a small cubic cell made of polytetrafluoroethylene (PTFE) as shown in Fig. 12a. By heating the cell at 180° C for several hours under atmospheric pressure, polystyrene was sintered to form an almost continuous body. After the cell was cooled and the PTFE piece removed, silver powder was placed in the right hand side of the cell to a level just as high as the polystyrene (Fig. 12b). Using another piece of PTFE, polystyrene and silver were compressed together with the aid of a laboratory clamp. After heating at 144° C for 24 h, the whole material was taken out of the cell and observed under the SEM. As shown in Fig. 13, wettting of polystyrene on silver was observed, particularly in the vicinity of the original contact interface. As a result, polystyrene penetrated into the silver layer (from left to right in Fig. 13). Therefore, it must be possible that on hot-pressing the binary powder mixture, the contiguity of the silver network is locally impeded by the development of the penetrating membrane around and between the silver particles. By assuming that the meniscus of flowing polystyrene between silver particles changed from convex to concave with time, which is, according to Schonhorn *et al.* [9], very likely in the case of a softened polymer, the negagtive capillary pressure could then force the neighbouring silver particles

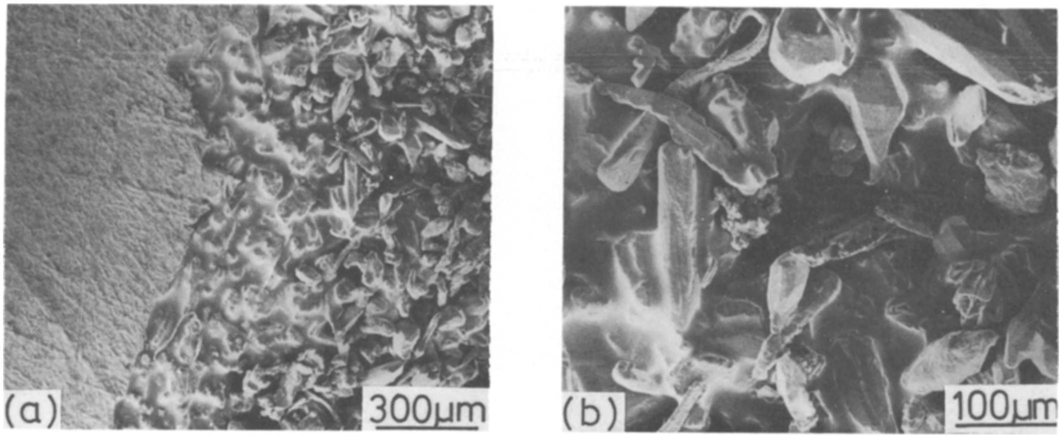


Figure 13 Scanning electron micrographs of the specimen obtained from the model experiment shown in Fig. 12. Part of (a) is magnified in (b). Wetting of polystyrene on the surface of silver and the resulting penetration of polystyrene between the silver particles are apparently observed.

apart, which in turn enables penetration of the softened polymer between silver particles. According to this speculative mechanism, it is easy to explain the result shown in Fig. 8, where the final volume resistivity is larger when a smaller pressure was applied.

It is to be noted, that penetration of the polymeric component must be considerably slow in most cases, because the spread of wetting is always opposed by the very high viscosity of the softened polymer. Therefore, on continuously increasing the pressure, as in the case of method 3, where the contact area of the metallic component increases relatively rapidly, the effect of the spread of wetting on the volume resistivity is not appreciable, as already shown in Fig. 10, unless the rate of pressure increase is sufficiently low.

5. Conclusions

Electrical volume resistivity of a hot-pressed metal–polymer binary powder mixture does not always vary in a simple manner with bulk density, if the polymer component tends to flow and to wet the surface of the conducting component, as shown in the present experiment on the silver–polystyrene binary system. Volume resistivity decreased with increasing pressure at all temperatures studied (59 to 164° C). Above the softening temperature of polystyrene, $T_s = 101^\circ$ C, volume resistivity under constant pressure increased with time even after the bulk density of the compact became constant, and reached a final value, ρ_∞. A linear relationship was observed between $\log \rho_\infty$ and $1/T$, in the region $T \geqslant T_s$. The relation between $1/\rho_\infty$ and $\log P$ was also linear.

Judging from the scanning electron micrographs, contiguity of silver particles seems to be gradually impeded due to the penetration of thin films of polystyrene between the silver particles after the onset of softening of polystyrene.

A new method of preparing plastic-based composites with a desired electrical resistivity is thus possible through an appropriate hot-pressing of a metal–polymer powder mixture.

References

1. P. L. MURRAY, D. LIVEY and J. WILLIAMS, "Ceramic Fabrication Process" (Wiley, New York, 1958) p. 147.
2. R. L. COBLE, *J. Appl. Phys.* **41** (12) (1970) 4798.
3. H. K. PALMER and R. C. ROWE, *Powder Technol.* **10** (1974) 225.
4. H. SEKITO and H. KUNO, *J. Jap. Soc. Powder Met.* to be published.
5. I. J. BEAR and V. BARDAY, *Powder Met. Int.* 7 (3) (1975) 121.
6. J. GURLAND, *Trans. Met. Soc. AIME* **236** (1966) 642.
7. A. MALLIARIS and D. T. TURNER, *J. Appl. Phys.* **42** (1971) 614.
8. H. KUNO, T. YAMAGUCHI and T. YASHIRO, *J. Soc. Mat. Sci. Japan* **16** (164) (1967) 347.
9. H. SCHONHORN, H. L. FRISCH and T. K. KWEI, *J. Appl. Phys.* **37** (1966) 4967.

Received 31 May and accepted 7 July 1976.