

Silver Particle Carbon-Matrix Composites as Thick Films for Electrical Applications

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Silver particle (3 μm) carbon-matrix composites in the form of thick films (around 100 μm thick) on alumina, as prepared from pastes comprising silver and mesophase pitch particles (14 μm), have been attained. The films on alumina were fired at 650°C in nitrogen to convert pitch to carbon. The volume electrical resistivity attained ranged from 10^{-5} Ω cm to 10^4 Ω cm, depending on the silver volume fraction. The percolation threshold was 12 vol% silver.

Key words: Composite, carbon, silver, thick film, electrical resistivity

INTRODUCTION

Electrically conductive materials in the form of thick films (i.e., coatings of thickness typically of the order of 10 μm) instead of wire or other monolithic forms are attractive for their relatively small size and consequent suitability for device miniaturization. Compared with thin films (i.e., coatings of thickness typically of the order of 0.1 μm), thick films are attractive for their relatively low cost of processing. The specific applications of the conductive materials depend on the level of conductivity. For highly conductive materials of electrical resistivity of the order of 10^{-6} Ω cm (or below), applications include electrical interconnections and electrical contacts (such as brushes). For less conductive materials, applications include electrical grounding, lightning protection, resistance (Joule) heating and electrical resistance circuit elements. In the case of resistance heating, a high level of conductivity would require the use of a very long length of the conductor (such as a coiled wire or a thick film with a tortuous pattern) in order to attain the substantial resistance that is needed to provide sufficient heat (I^2R) output. As a result, a moderate level of conductivity is desirable for resistive heating.

Thick films are made by the application of a paste onto a substrate. Depending on the composition of

the paste, various degrees of heating may be needed after paste application in order to attain a film of sufficient conductivity and stability. The paste comprises a conductive component (such as metal particles) and a binder.

Binders that have been used include glasses (which undergo viscous flow at an elevated temperature) and polymers (which become viscous, melt or cure at an elevated temperature).¹ However, these binders suffer from their being non-conductive. Owing to the insulating nature of the binder, percolation (i.e., attaining a continuous electrical conduction path through the touching of adjacent conductive particles) is essential for the composite to be conductive; without percolation, the composite remains non-conductive. The conductive component is commonly silver, due to its high conductivity. Silver is an expensive material. Thus, the use of a non-conductive binder tends to be associated with the need for a high volume fraction of the conductive component, and, consequently, high cost. A high volume fraction of the conductive component also means a low volume fraction of the binder, which results in less mechanical integrity in the thick film. Therefore, it is attractive from electrical, mechanical and cost points of view to use a conductive binder.

This paper describes thick films that involve a conductive binder, though the binder is not as conductive as the conductive component (namely silver). The binder is carbon, which is conductive, with a conductivity that increases with the temperature used to prepare the carbon from its precursor. One of the most common precursors is pitch. There are

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various types of pitch. Mesophase pitch is a type which is characterized by a high tendency to form graphite upon heating. This high tendency to crystallize stems from the liquid crystalline structure of mesophase pitch. Carbon is conductive, whereas pitch (a polymer mixture) is not. However, carbon is not an adhesive, whereas pitch is, due to its ability to flow. Therefore, this work used pitch as the binder precursor, which was a component of the thick film paste. However, carbon was the binder in the resulting thick film. In this way, this work provided silver particle carbon-matrix composites in the form of thick films. Prior work on silver particle carbon-matrix composites is limited to composites in a monolithic form.²

Metal particle carbon-matrix composites involving silver,³ iron,⁴ nickel,⁴ copper,⁴ and other particles have been previously reported in relation to applications including sliding electrical contacts.^{3,4} However, metal particle carbon-matrix composites have not been previously reported for thick film conductor applications.

The carbon-based thick films in this work are to be distinguished from carbon thin films that are made by pyrolysis of organic compounds⁵⁻¹¹ or by chemical vapor deposition.^{12,13} The carbon-based films in this work are also to be distinguished from polymer-based films that contain carbon or graphite particles.¹⁴⁻²⁰

The preparation of carbon from pitch is a process that has been studied extensively.²¹ This process involves stabilization (which is an oxidation treatment that is needed for avoiding melting and partial volatilization of the pitch during heating), followed by carbonization (which is the conversion to carbon). Graphitization is a further subsequent step that is needed, to provide crystallinity, which is associated with high electrical conductivity. Owing to the stabilization step, the process of conversion of pitch to carbon typically does not involve viscous flow. This is in contrast to the viscous flow of the glass binder during the firing of a thick film paste with a glass binder.

The temperature is low for stabilization (e.g., 350°C); the temperature is higher for carbonization (e.g., 1,000°C); the temperature is even higher for graphitization (e.g., 2,700°C). Owing to the high temperature, graphitization is expensive and may not be feasible, due to the limited temperature resistance of the substrate (e.g., alumina) of the thick film. Therefore, graphitization was not included in the process used in this work. Further, the heat treatment temperature used in the carbonization step in this work was relatively low (e.g., 650°C), due to the need to minimize volatilization of the resulting carbon. The volatilization is due to the reaction of carbon with oxygen to form gases such as CO₂. It tends to occur to a certain extent even during purging by nitrogen, due to the tendency for imperfect purging. It is more detrimental to thick films than monolithic materials, due to the geometry.

The objectives of this work were (I) the development of conductive thick films involving a conduc-

Table I. Properties of Pitch

| Property | Description |
|------------------------------|--------------------------------|
| Appearance | Pellets (black) at 77°F (25°C) |
| Particle Size | 14 μm |
| Specific Gravity | 1.23 at 77°F (25°C) |
| Vapor Pressure (mm Hg) | Nil |
| Initial Boiling Point | Decomposes |
| Solubility in Water | Insoluble |
| Bulk Density | 0.7 ± 0.3 g/cm ³ |
| Glass Transition Temperature | 203°C |
| Softening Point | 285 ± 5°C |

Table II. Properties of Silver Particles

| Property | Description |
|------------------------|----------------------|
| Appearance | White metallic solid |
| Particle Size | 3 μm |
| Specific Gravity | 10.49 |
| Vapor Pressure (mm Hg) | Nil |
| Solubility in Water | Insoluble |
| Boiling Point | 2,200°C |
| Melting Point | 966°C |

tive binder, (ii) the preparation and testing of silver particle carbon-matrix composites in the form of thick films, and (iii) the development of conductive thick films that exhibited a range of electrical conductivity, as needed for various applications.

EXPERIMENTAL METHODS

Mitsubishi Gas Chemical Company, Inc. (Japan) AR-grade mesophase pitch* was used as the binder precursor. The physical and chemical properties of this pitch are shown in Table I. This pitch is obtained by polymerization of naphthalene with a super-acid catalyst. It is characterized by a very low softening point and low viscosity at a molten stage while retaining a high coking value and 100% mesophase. The conductive component was silver particles produced by the Ames Goldsmith Corporation, with the properties shown in Table II. The liquid vehicle used in the paste was di(ethylene glycol) butyl ether (from Aldrich Chemical Co., Inc., Milwaukee, WI, USA). The weight ratio of ether to pitch ranged from 1:1 to 8:1; the higher the silver content, the greater was the proportion of ether. The volume fraction of silver was systematically varied from 8.1% to 69.3%. The silver particles, pitch particles and ether were mixed manually with a glass rod to form a workable paste, which was then applied manually with a glass rod (followed by leveling of the top surface of the film with a razor blade) onto a 25 mm × 5 mm region (defined by

*<http://www.mgc-a.com/newProducts/media/ARBrochure.pdf>

masking the remaining part of the substrate by adhesive tape, which was removed immediately after paste application) of an alumina substrate (25 mm × 25 mm × 0.61 mm, 96% Al₂O₃, 3M Corp.).

The process of stabilization and carbonization used in this work is described below.

- (a) Put the specimen in a box furnace and heat to 200°C in air at a heating rate of 1°C/min. This is the stabilization step.
- (b) Remove the specimen from the furnace and allow the specimen to cool to room temperature.
- (c) Put the specimen back into the furnace and purge the furnace chamber with nitrogen gas.
- (d) Heat the furnace from 71°C to 200°C at 5°C/min, then from 200°C to 300°C at 2°C/min, and then from 300°C to 650°C at 4°C/min. Finally, hold at 650°C for 30 min for the purpose of carbonization.

The stabilization temperature of 200°C was chosen because it is below the glass transition temperature of 203°C and the oxidation rate decreases sharply above the glass transition temperature.²²

The DC sheet resistance and DC volume resistivity of the resulting thick films were measured by either the two-probe method or the four-probe method. The four-probe method involves four electrical contacts. The outer contacts are for passing current, whereas the inner contacts are for voltage measurement. In contrast, the two-probe method involves two electrical contacts, each of which is both for passing current and for voltage measure-

ment. The four-probe method is more reliable, as the two-probe method includes the contact resistance in the measured resistance. However, in cases where the specimen resistance is large, the contact resistance is small compared to the specimen resistance, and the two-probe resistance result is reliable. In this work, the two-probe method was used only for specimens that exhibited very high resistance values (10⁶ Ω or above), such as specimens that contained no silver.

Electrical contacts used for electrical resistance measurement were in the form of silver paint in conjunction with copper wires. Each contact was applied along the full width (5 mm) of the thick film strip. The thick film strip painted on the 1 × 1 in. (25 mm × 25 mm) alumina substrate was 5 mm in width and 1 in. (25 mm) in length. In the case of the four-probe method, the outer contacts were 20 mm apart and the inner contacts were 10 mm apart. In the two-probe method, the contacts were 15 mm apart.

We obtained the sheet resistance by dividing the measured resistance by the ratio of the distance between the inner contacts to the width of the thick film strip. The volume resistivity ρ was obtained from the equation

$$\rho = R \frac{wt}{\ell} \quad (1)$$

where w is the width, t is the thickness, λ is the distance between the voltage contacts, and R is the

Table III. Sheet Resistance, Volume Resistivity and Thickness of Carbon-Matrix Thick Films with Various Silver Volume Fractions

| Silver volume fraction | Resistance (Ω) | Volume Resistivity (Ω cm) | Sheet Resistance (Ω/sq.) | Thickness (μm) |
|------------------------|--|--|--|----------------------|
| 0* | 58 × 10 ⁶ 35.5 × 10 ⁶ | (8.1 ± 7.3) × 10 ⁴ (5.0 ± 4.4) × 10 ⁴ | (2.92 ± 0.44) × 10 ⁷ (1.78 ± 0.27) × 10 ⁷ | 28 ± 25 28 ± 25 |
| 8.13%* | 2.27 × 10 ⁶ 2.66 × 10 ⁶ | (1.7 ± 0.2) × 10 ⁴ (1.4 ± 0.2) × 10 ⁴ | (7.60 ± 1.00) × 10 ⁵ (8.91 ± 1.18) × 10 ⁵ | 229 ± 25 152 ± 25 |
| 10.0%* | 2.30 × 10 ⁶ 1.64 × 10 ⁶ | (2.1 ± 0.3) × 10 ⁴ (1.9 ± 0.2) × 10 ⁴ | (1.16 ± 0.17) × 10 ⁶ (8.26 ± 1.23) × 10 ⁵ | 178 ± 25 229 ± 25 |
| 12.5%† | 5.620 1.417 | (3.2 ± 0.7) × 10 ⁻² (7.2 ± 1.8) × 10 ⁻³ | 2.83 ± 0.42 0.71 ± 0.11 | 114 ± 25 102 ± 25 |
| 15.0%† | 0.810 1.253 | (6.2 ± 1.0) × 10 ⁻³ (8.0 ± 1.6) × 10 ⁻³ | 0.41 ± 0.06 0.63 ± 0.09 | 152 ± 25 127 ± 25 |
| 20.9%† | 0.0661 0.0678 | (4.2 ± 0.8) × 10 ⁻⁴ (3.4 ± 0.8) × 10 ⁻⁴ | (3.33 ± 0.50) × 10 ⁻² (3.42 ± 0.51) × 10 ⁻² | 127 ± 25 102 ± 25 |
| 30.0%† | 0.0360 0.0327 | (3.4 ± 0.5) × 10 ⁻⁴ (1.9 ± 0.4) × 10 ⁻⁴ | (1.81 ± 0.27) × 10 ⁻² (1.65 ± 0.25) × 10 ⁻² | 191 ± 25 114 ± 25 |
| 40.0%† | 0.0134 0.0119 | (6.8 ± 1.7) × 10 ⁻⁵ (9.1 ± 1.5) × 10 ⁻⁵ | (6.75 ± 1.01) × 10 ⁻³ (5.99 ± 0.90) × 10 ⁻³ | 102 ± 25 152 ± 25 |
| 50.0%† | 0.00402 0.00399 | (3.8 ± 0.5) × 10 ⁻⁵ (3.0 ± 0.5) × 10 ⁻⁵ | (2.03 ± 0.30) × 10 ⁻³ (2.01 ± 0.30) × 10 ⁻³ | 191 ± 25 152 ± 25 |
| 60.0%† | 0.00669 0.00774 | (3.8 ± 0.8) × 10 ⁻⁵ (3.4 ± 1.0) × 10 ⁻⁵ | (3.37 ± 0.50) × 10 ⁻³ (3.90 ± 0.59) × 10 ⁻³ | 114 ± 25 89 ± 25 |
| 69.3%† | 0.00478 0.00373 | (2.7 ± 0.6) × 10 ⁻⁵ (2.1 ± 0.5) × 10 ⁻⁵ | (2.41 ± 0.36) × 10 ⁻³ (1.88 ± 0.28) × 10 ⁻³ | 114 ± 25 114 ± 25 |

*Two-probe method.

†Four-probe method.

measured resistance. The thickness was measured with a micrometer. Owing to the error in the thickness measurement, the sheet resistance is more accurate than the volume resistivity. The conductivity is the reciprocal of the volume resistivity. At least two specimens of each composition were tested.

RESULTS AND DISCUSSION

Table III and Figs. 1 and 2 show the electrical resistance results as a function of silver volume fraction. In the absence of silver, the volume resistivity was about $7 \times 10^4 \Omega \text{ cm}$. In the presence of silver up to 10.0 vol%, the volume resistivity remained high (around $2 \times 10^4 \Omega \text{ cm}$). Between silver contents of 10.0 and 12.5 vol%, the volume resistivity decreased by six orders of magnitude, due to percolation. Beyond a silver content of 12.5 vol%, the volume resistivity continued to decrease, though less abruptly. The lowest resistivity attained was $2 \times 10^{-5} \Omega \text{ cm}$, the value for the highest silver content (69.3 vol%) investigated. However, the resistivity was only slightly higher than this when the silver content was 40.0 vol%. A similar trend was obtained for the variation of the sheet resistance with silver volume fraction, as shown in Fig. 1.

Reference 2 reported that the volume electrical conductivity of silver particle carbon-matrix composites in monolithic form was $10^5 \Omega^{-1} \text{ cm}^{-1}$ at a silver content of 40 vol%. The value obtained in this work at the same silver content was $10^4 \Omega^{-1} \text{ cm}^{-1}$ (i.e., a resistivity of $8 \times 10^{-5} \Omega \text{ cm}$). Thus, the conductivity values for the monolithic and thick film forms are quite close at 40 vol% silver. However, in the regime of low silver content (e.g., 8 vol%) and the regime of high silver content (e.g., 60 vol%), the conductivity in Ref. 2 is substantially higher than that of this work. This difference between Ref. 2 and this work is due to the difference in the shape of the curve of conductivity (log) as a function of silver volume fraction. In Ref. 2 the conductivity (log) increases linearly with the silver volume fraction, hence showing no percolation effect. In contrast, percolation is clearly observed in this work at 12 vol% (Figs. 1 and 2).

The absence of percolation in Ref. 2, in contrast to the presence of percolation in this work, is probably due to the difference in processing method and raw materials between Ref. 2 and this work. However, details on the processing method and raw materials are not given in Ref. 2.

In addition to the experimental data, Fig. 2 shows a calculated curve based on the general effective

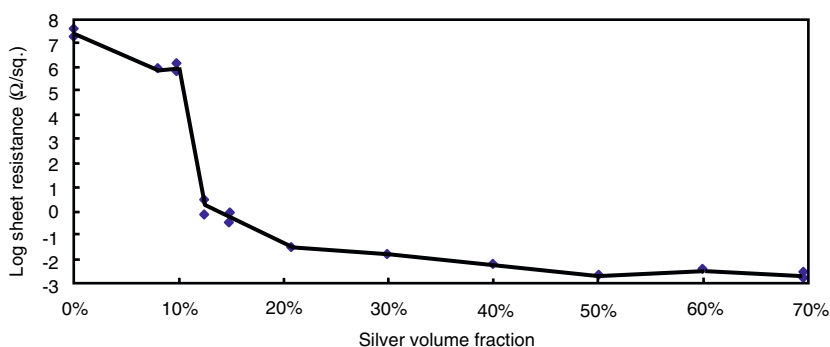


Fig. 1. Variation of the sheet resistance (log) with silver volume fraction.

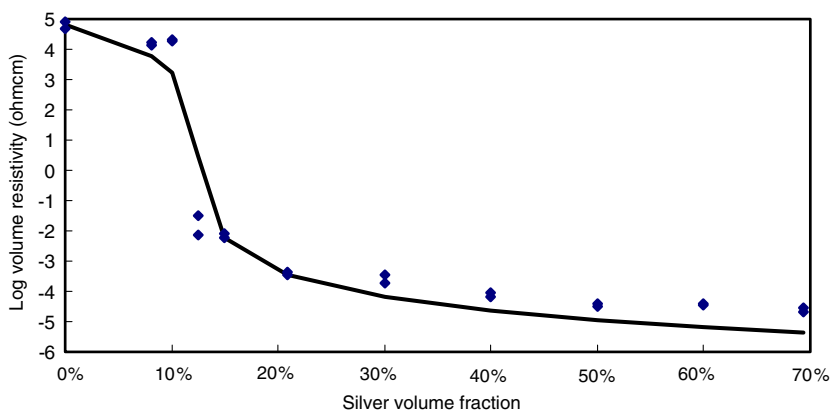


Fig. 2. Variation of the volume resistivity (log) with silver volume fraction. The data points are experimental. The curve is theoretical.

media (GEM) model.²³ The equation used to calculate the volume resistivity ρ_m of the composite is

$$\frac{(1 - \phi)(\rho_m^{1/t} - \rho_h^{1/t})}{\rho_m^{1/t} + \left(\frac{1 - \phi_c}{\phi_c}\right)\rho_h^{1/t}} + \frac{\phi(\rho_m^{1/t} - \rho_l^{1/t})}{\rho_m^{1/t} + \left(\frac{1 - \phi_c}{\phi_c}\right)\rho_l^{1/t}} = 0, \quad (2)$$

where ρ_h is the resistivity of the component with high resistivity, ρ_l is the resistivity of the component with low resistivity, ϕ is the volume fraction of the component with low resistivity, ϕ_c is the percolation threshold, which was found experimentally to be 12.5%, and t is the critical exponent, which was found by fitting to be 2.3 in this work. The calculated curve and the experimental data fit quite well, thus providing support for the occurrence of percolation in the composite system studied.

The calculated resistivity above the percolation threshold is lower than the experimental values, due to porosity, which was observed by scanning electron microscopy of the film surface. The pore size was typically around 5–10 μm .

The lowest resistivity attained in this work is $3 \times 10^{-5} \Omega \text{ cm}$, which is much lower than the value of $1 \times 10^{-3} \Omega \text{ cm}$ for silver paint.²⁴ and silver epoxy.²⁵ This is due to the conductive nature of carbon, compared to the nonconductive nature of epoxy or other organic vehicles. However, the value attained in this work is higher than the value of $4 \times 10^{-6} \Omega \text{ cm}$ for silver glass,¹ in spite of the nonconductive nature of glass. This is because of the high temperature (e.g., 900°C) associated with the firing of silver glass and the consequent sintering of the silver particles to form a network.

The silver volume fraction of the thick film composition (just above the percolation threshold of 12 vol%) of this work was low compared to that of silver glass. Since silver is much more expensive than glass or pitch, a low silver volume fraction results in cost reduction.

The highest resistivity attained in this work was $8 \times 10^4 \Omega \text{ cm}$ (for 0 vol% silver). The second highest value is $2 \times 10^4 \Omega \text{ cm}$ (for 8–10 vol% silver). Owing to the conductive nature of carbon, a silver content below the percolation threshold still causes the resistivity to decrease relative to the case without silver. These high values of the order of $10^4 \Omega \text{ cm}$ are not provided by silver epoxy, silver paint, or silver glass. They are attractive for providing thick film resistors, which are needed for resistance heating, electrical circuits and other applications. The composition without silver is attractive also in that it gives films that are thinner (30 μm) than those containing silver (100–200 μm). The absence of silver makes the paste more workable, thereby resulting in a film that is thinner and more uniform.

CONCLUSION

Silver particle carbon-matrix composite thick films, along with their silver-pitch-ether paste precursor, were developed. The pitch (mesophase) was converted to carbon by heating in nitrogen at 650°C for 30 min. This carbonization step was preceded by stabilization at 200°C in air. The resulting films on alumina were of thickness ranging from 90 to 230 μm , silver volume fraction ranging from 8% to 69%, volume electrical resistivity ranging from 10^{-5} to $10^4 \Omega \text{ cm}$, and sheet resistance ranging from 10^{-3} to $10^6 \Omega/\text{square}$. The percolation threshold was 12 vol% silver, as shown by an abrupt drop in volume resistivity by seven orders of magnitude. The resistivity above the percolation threshold was above the calculated volume, due to porosity.

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