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Intercalated graphite as a smart material for high-stress, high-strain, low-electric-field electromechanical switching

D D L Chung

Composite Materials Research Laboratory, Furnas Hall, State University of New York at Buffalo, Buffalo, NY 14260, USA

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Abstract. This paper describes a new smart material system using intercalated graphite as the material and using exfoliation as the phase transition that gives rise to the electromechanical switching action. In this action, a stress of up to 3 MPa (400 psi) or a strain of up to 4500% results reversibly from an applied electric field of only 7 V cm^{-1}. This high-stress, high-strain, low-electric-field type of electromechanical switching is in sharp contrast to the electromechanical switching provided by piezoelectric materials. The exfoliation is a phase transition involving the vaporization of the intercalate between the graphite layers to form bubbles. For bromine as the intercalate, the bubbles remain mostly closed and exfoliation is reversible. The resulting stress or strain is along the *c* axis of the graphite, so highly oriented pyrolytic graphite and graphite flakes are both possible for achieving electromechanical switching. Applications of this new smart material include electrically activated thermal contacts, electrical contacts and micromanipulations.

1. Introduction

In spite of the growing importance of smart materials and structures, the phenomena that render 'smartness' to materials have been mostly limited to the shape memory effect, piezoelectricity, ferroelectricity, electrostriction and magnetostriction. This limited range of phenomena restricts the variety and versatility of smart materials. This paper focuses on a novel phenomenon which makes possible a new class of smart materials. This phenomenon is a reversible phase transition, namely exfoliation, which occurs in intercalated graphite and can be activated by an applied electric field along the *c* axis of the graphite. The consequence of exfoliation is a stress of up to 3 MPa (400 psi) or a strain of up to 4500%. The electric field required for exfoliation is merely 7 V cm^{-1}. This high-stress, high-strain, low-electric-field electromechanical switching was first reported by this author in 1986 [1]. In contrast, for $BaTiO_3$ (a piezoelectric material), an electric field of 4000 V cm^{-1} is required to provide a stress of the same magnitude (400 psi), if linear behaviour applies.

2. The phenomenon

Intercalated graphite is graphite containing foreign species (called the intercalate) in the form of layers (usually monolayers) between the graphite layers. It is a layered compound in which the intercalate acts either as an electron acceptor or as an electron donor. The exfoliation of intercalated graphite [2] is a phase transition involving the vaporization of the intercalate in the graphite. During the vaporization, the intercalate islands change into bubbles made possible by the shear of the graphite layers. For certain intercalates (e.g., HNO_3, $FeCl_3$), the decomposition of the intercalate into smaller molecules causes the bubbles to blow up, resulting in irreversible exfoliation. For some other intercalates (e.g., Br_2), no such decomposition occurs and the bubbles remain closed, resulting in reversible exfoliation [3]. It is reversible exfoliation that is useful for rendering 'smartness' to intercalated graphite.

Exfoliation is a phase transition that is activated by heat. It occurs reversibly at 100 °C in the case of graphite intercalated with bromine (graphite–bromine) after the first exfoliation–collapse cycle. In the first cycle, the exfoliation temperature is higher. The plot of the fractional expansion versus temperature is shown in figure 1 for graphite–bromine in the first two cycles. Note that the fractional expansion reaches values above 40, which means a strain of more than 4000%. The plot of expansion versus temperature is the same for all cycles after the first cycle.

The stress associated with exfoliation can be measured by determining the amount of stress needed to

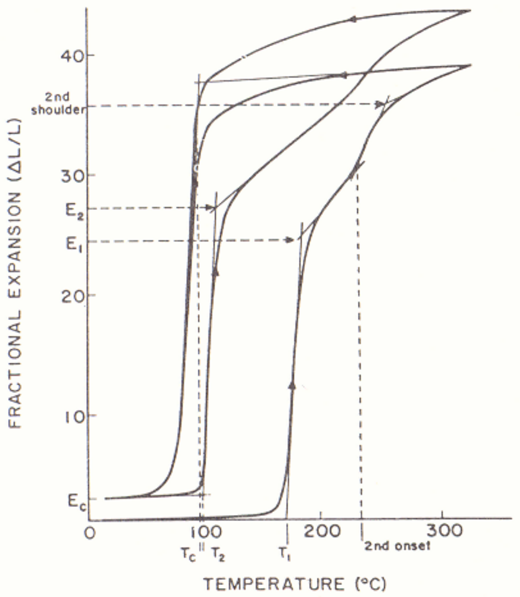

Figure 1. Fractional expansion versus temperature during the first two exfoliation–collapse cycles for graphite–Br_2 (HOPG) which had been desorbed from 3.2 mol% Br_2 to 1.3 mol% Br_2, then reintercalated to 6.3 mol% Br_2 and desorbed to 1.6 mol% Br_2 prior to heating.

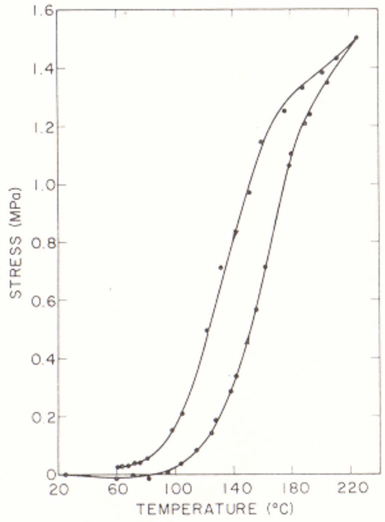

Figure 2. Variation of stress with temperature during heating and cooling in cycle no 7 of the thermomechanical measurements.

avoid exfoliation. A plot of stress versus temperature in cycle no 7 of graphite–bromine is shown in figure 2. A stress of 1.5 MPa was reached in this case.

The heat required for exfoliation can be provided by passing an electric current through the intercalated graphite. Because the *c* axis electrical resistivity is much higher than the *a* axis resistivity, Joule heating is more effective by passing the current through the *c* axis. Figure 3 shows a plot of the stress versus electric power (with the current along the *c* axis) in cycle no 10 of graphite–bromine. The increase in stress occurred in two steps. The first step started at a power of 2 W and reached a stress of about 1 MPa. The second step started at a power of 9.9 W and reached a stress of more than 2 MPa. During a subsequent decrease of the power, the second step was smoothed out, but the stress returned to zero. Figure 3 demonstrates the feasibility of using about 10 W of electric power to generate reversibly a stress of about 2 MPa.

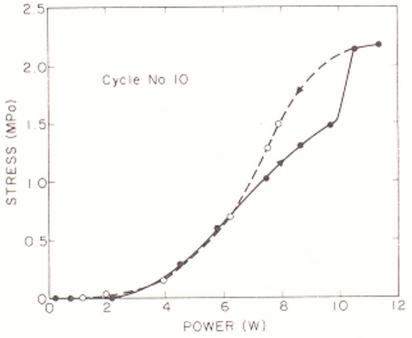

Figure 3. Variation of stress with the electric power as the power was increased (full curve and full circles) and decreased (broken curve and open circles) during cycle no 10.

The feasibility of electromechanical switching using the exfoliation phenomenon is shown in figure 4 for cycle no 17 of graphite–bromine. The current was instantaneously increased from 0–12 A, held at 12 A for 23 s, and then instantaneously decreased from 12–0 A. The instantaneous current increase caused the stress to rise from 0–2.28 MPa (maximum) in 9 s, and caused the temperature to rise from 28–116 °C (maximum) in 15 s. The instantaneous current decrease caused the stress to drop from 2.28–0.05 MPa in 4.8 s, and caused the temperature to drop from 116–30 °C in 25 s. Hence, although the rise and fall of the stress are closely related to those of the temperature, the rise time and fall time for the stress are considerably smaller than those for the temperature. Figure 4 also shows that the voltage increased sharply from 0–0.94 V in the first 0.1 s, but subsequently decayed, reaching 0.38 V at 15 s, when the temperature had reached a steady state of 116 °C. Upon switching off the current at 23 s, the voltage instantaneously fell to zero. The behaviour shown in figure 4 was observed in all cycles (cycle no 17–40) in which the current was instantaneously turned on (to 12 A) and off. With the sample (highly oriented pyrolytic graphite (HOPG)) of thickness 0.058 cm along the *c* axis, the voltage of 0.4 V corresponded to an electric field of 6.9 V cm^{-1}. Thus, a stress of 2.28 MPa was produced reversibly by an electric field of only 6.9 V cm^{-1}!

Figure 4 demonstrates the capability of the intercalated graphite to serve as an electromechanical switch. The lifetime of the electromechanical switch was found to be limited by the lifetime of the contact wires, which burned out due to the heating. For the copper wires used (0.014 in diameter), the lifetime was 40 cycles. For copper wires of diameter 0.035 in, the lifetime exceeded 58 cycles, at the end of which no sign of failure was observed. Hence, by using thick contact wires (or contact foils in a practical device), the lifetime is expected to be sufficient such that practical use of the electromechanical switch is possible.

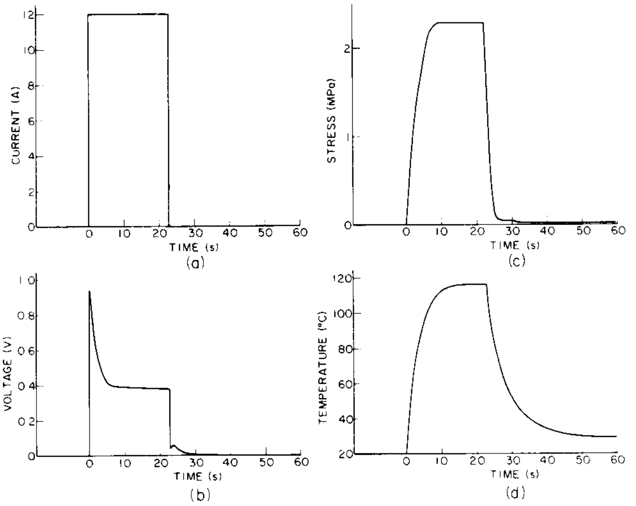

Figure 4. The effect of current switching on the stress, temperature and voltage as a function of time for cycle no 17.

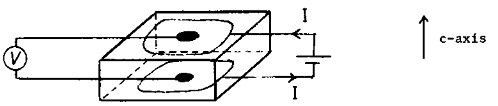

Figure 5. Laboratory contact design.

Because the applied electric field serves to heat the intercalated graphite, the sign of the field does not matter. In other words, the stress is independent of the sign of the electric field. This is in contrast to the case of a piezoelectric material. Therefore, both DC and AC electric fields are effective for generating stress along the *c* axis of intercalated graphite.

The amount of intercalate desorption occurring during exfoliation can be minimized by allowing the intercalate graphite to desorb at room temperature for a week of more before exfoliation. Most of the desorption during exfoliation occurs during the first two cycles. Thus, desorption during exfoliation can be further minimised by allowing a few cycles of exfoliation to take place beforehand.

The data described above were all obtained by using highly oriented pyrolytic graphite (HOPG). Exfoliation similarly occurs in graphite flakes [4], though the small size of graphite flakes compared with that of HOPG make the application of electrical contacts more tedious. On the other hand, graphite flakes are much less expensive than HOPG.

Because exfoliation of graphite–bromine occurs reversibly at 100 °C, the amount of electric power needed for exfoliation is expected to decrease with increasing ambient temperature. The ambient temperature must be below 100 °C in order for the electromechanical switching phenomenon to take place. For the case of a piezoelectric material such as $BaTiO_3$, the Curie temperature (120 °C for $BaTiO_3$) is the maximum ambient temperature.

Intercalated graphite does not have an inherent electric field. In contrast, a piezoelectric material such as $BaTiO_3$ does and this inherent electric field may interfere with neighbouring electronic devices.

Table 1. Advantages and disadvantages of intercalated graphite compared to piezoelectric materials.

Advantages

- Strain up to 4500% and stress up to 3 MPa (400 psi) at an electric field of only 7 V cm^{-1}
- DC or AC electric field
- sign of applied electric field does not matter
- no inherent electric field
- optomechanical switching possible
- low density
- thermally conductive
- electrically conductive

Disadvantages

- converts electrical energy to mechanical energy, but not vice versa
- stress response time = 5–9 s (expected to decrease in the future)
- ambient temperature < 100 °C
- tendency to shear

The electromechanical switching of intercalated graphite allows the conversion of electrical energy to mechanical energy, but not vice versa. In contrast, a piezoelectric material allows both electrical to mechanical and mechanical to electrical energy changes.

Exfoliation can alternatively be achieved by using a laser, which provides heat. Thus, instead of electromechanical switching, optomechanical switching is possible. However, we will deal only with electromechanical switching here.

Table 1 summarises the advantages and disadvantages of intercalated graphite compared to a piezoelectric material as a smart material for electromechanical switching.

3. Electrical contact design

The electrical contact design for laboratory testing is different from that for practical use. In both cases, copper electrical contacts are attached to the graphite by using silver paint.

For laboratory testing, four electrical contacts (two for applying the current and two for measuring the voltage) are applied to each sample on opposite faces perpendicular to the *c* axis. The current contact is in the form of a ring, whereas the voltage contact is in the form of a dot. Each of the two opposite faces of a sample has a current contact surrounding a voltage contact, as illustrated in figure 5. The use of four contacts allows accurate measurement of the voltage between the two faces of the sample, as was shown in [1].

For practical use, two contacts per sample are sufficient, i.e. on contact on each face of the sample for passing the current, as illustrated in figure 6(*a*). To increase the force resulting from the electromechanical effect in practical use, the two contacts can be in the form of two copper foils sandwiching more than one piece of graphite of about the same thickness, as illustrated in figure 6(*b*). To increase the stress resulting

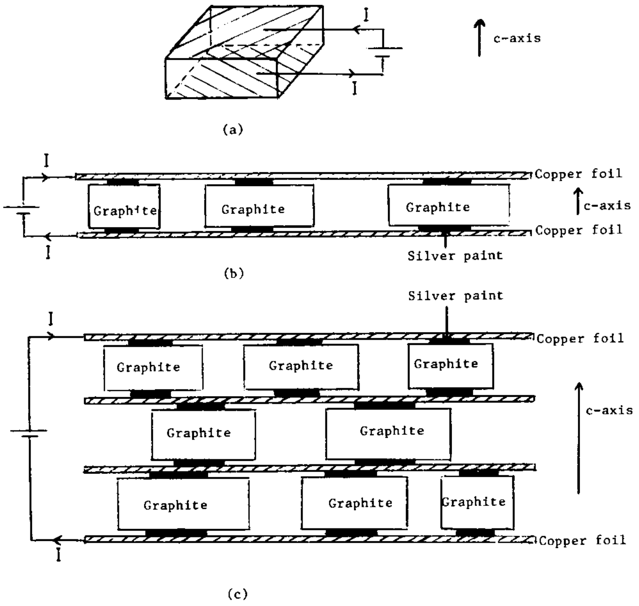

Figure 6. Practical contact designs.

from the electromechanical effect, multiple layers of the sandwich can be used, as illustrated in figure 6(*c*).

The use of multiple pieces of graphite rather than a single large piece is necessitated by: (i) the difficulty of uniformly intercalating a large piece of graphite (exceeding 2 cm in width), (ii) the tendency for a large piece of intercalated graphite to have defects that cause nonuniform exfoliation, (iii) the possibly longer response time associated with a large piece of graphite, (iv) the tendency for a thick (along the *c* axis) piece of graphite to cleave perpendicular to the *c* axis, and (v) the high cost of large pieces of HOPG.

The use of copper foils instead of copper wires for electrical contacts for practical use is adopted because of: (i) the greater durability (against heat and the effects of bromine) of copper of a larger dimension, and (ii) the greater convenience of applying contacts in the form of foils.

4. Applications

The applications of the new smart material of this paper include: (i) electrically activated thermal contacts for the transfer of heat, (ii) electrically activated electrical contacts for the transfer of electrical signals, and (iii) electrically activated movement for moving one component relative to another. These applications are illustrated in figure 7.

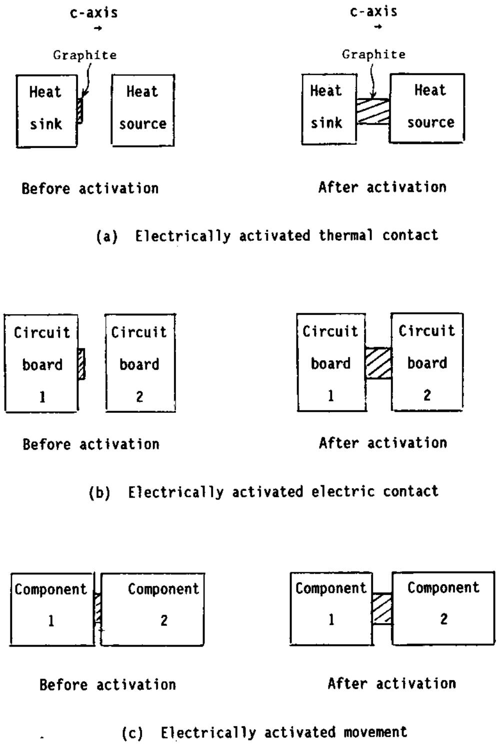

Figure 7. Applications of intercalated graphite as a smart material.

The *c* axis electrical resistivity of exfoliated HOPG graphite–bromine is 3.0×10^{-2} Ω cm, as compared to the value of 6.3×10^{-1} Ω cm prior to exfoliation [5]. The corresponding *a* axis resistivity is 5.4×10^{-4} Ω cm, as compared to the value of 2.4×10^{-6} Ω cm prior to exfoliation [5]. Hence, exfoliation decreases the *c* axis resistivity due to the *c* axis conduction path made possible by the bending of the graphite layers, while it increases the *a* axis resistivity due to the bending of the graphite layers. The decrease in the *c* axis resistivity after exfoliation makes the application of the intercalated graphite as an electrically activated electrical contact even more attractive.

Because of the close relationship between electrical and thermal conductivities, the *c* axis thermal conductivity of intercalated graphite is expected to increase after exfoliation, thus making the application of intercalated graphite as an electrically activated thermal contact even more attractive.

The compressive strength is limited by the shear between the graphite layers, which means that the intercalated graphite is incapable of serving as the load-bearing component of a structure.

Acknowledgments

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