

EFFECT OF EXFOLIATION ON THE ELECTRICAL RESISTIVITY OF INTERCALATED GRAPHITE

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ABSTRACT

Exfoliation of graphite-bromine was found to increase the a-axis electrical resistivity (ρ_a) by a factor of 230 and decrease the c-axis electrical resistivity (ρ_c) by a factor of 20, so that the anisotropy in the electrical resistivity (ρ_c/ρ_a) decreased by a factor of 5×10^4 . During heating of graphite-bromine, ρ_c first increased slightly and then decreased abruptly upon exfoliation. During subsequent cooling, ρ_c increased abruptly upon collapse of the exfoliated structure. The c-axis electrical resistance did not vary much with temperature upon exfoliation or collapse.

INTRODUCTION

The low electrical resistivity of intercalated graphite along the in-plane directions has been of scientific and technological interest. Upon heating past a critical temperature, intercalated graphite exfoliates [1,2], expanding by dozens to hundreds of times along the c-axis (unless the expansion is constrained mechanically [3]). When the heating occurs in a controlled manner, the expansion can be reversible; when the heating is excessive, the expansion is irreversible. The effect of reversible and irreversible exfoliation on the electrical resistivity of intercalated graphite is of concern to the application of intercalated graphite as an electrical conductor. It is therefore the subject of this paper.

Miyauchi et al. [4] reported that the a-axis electrical resistivity of graphite-bromine (based on artificial graphite heat-treated at 3000°C) was increased by 22-25% upon heating past about 200°C. Upon cooling, the a-axis electrical resistivity decreased back to the value before heating, such that the decrease started at about 320°C during cooling. This effect was attributed to exfoliation.

In the present work, we have investigated the effect of irreversible exfoliation on the a-axis and c-axis electrical resistivity of graphite-bromine based on highly oriented pyrolytic graphite (HOPG). In addition, the effect of reversible exfoliation on the c-axis electrical resistivity was studied.

EXPERIMENTAL

Sample preparation

Highly oriented pyrolytic graphite (HOPG), which was kindly provided by Union Carbide Corporation, was intercalated with bromine to stage 2 by exposure to bromine vapor at room temperature. Subsequently it was allowed to desorb in air at room temperature to an intercalate concentration of about 40 wt. % bromine.

Exfoliation of the intercalated graphite was carried out by furnace heating.

Experimental technique

The electrical resistivity was measured by using the four-probe method. Silver conducting paint was used to attach the copper contact wires to the sample. For measuring the c-axis resistivity, two electrical contacts were made on each of two opposite surfaces (perpendicular to the c-axis) of the sample; a contact on each surface served as a current probe, while the other contact on each surface served as a voltage probe. For measuring the a-axis resistivity, four contacts were made on the same surface of the sample; the two inner contacts served as voltage probes, while the two outer contacts served as current probes. A 24 V, 12 A DC variable power supply was connected to the current probes.

To study the effect of reversible exfoliation on the c-axis electrical resistivity, the c-axis electrical resistivity and the expansion along the c-axis were measured simultaneously while the graphite-bromine sample was heated in air by a small resistance heater coil, which surrounded the sample. The expansion was measured by using a probe which touched the top surface (perpendicular to the c-axis) of the sample and was connected to a linear variable differential transducer (LVDT). The sample temperature was measured by a chromel-alumel thermocouple which was inside the probe such that it almost touched the top surface of the sample. The probe weighed 28 g. The dimensions of the sample (perpendicular to the c-axis) were 0.136 X 0.100 in. The initial thickness of the sample was 0.006 in. The voltage across the sample along the c-axis, the current along the c-axis, the temperature and the expansion were simultaneously measured and recorded by using chart recorders, while the sample was repeatedly heated and cooled.

Experimental resultsEffect of irreversible exfoliation

The effects intercalation and exfoliation on the a-axis and c-axis electrical resistivity of HOPG are shown in Table 1.

Also included in the table are the published values for ZYX graphite, Graphite Foam and Grafoil [5], which are commercially available from Union Carbide Corporation. ZYX is exfoliated HOPG; Grafoil is exfoliated natural crystals rolled into a sheet; Graphite Foam is like Grafoil except for a less severe compression.

Intercalation greatly decreased the a-axis electrical resistivity but had little effect on the c-axis resistivity. After intercalation, exfoliation increased the a-axis electrical

Table I. Electrical Resistivities (in $\Omega \cdot \text{cm}$) at Room Temperature.

	Material	ρ_a	ρ_c	ρ_c/ρ_a
This work	Pristine HOPG	1.6×10^{-4}	6.8×10^{-1}	4.4×10^3
	Intercalated(Br)HOPG	2.4×10^{-6}	6.3×10^{-1}	2.6×10^5
	Exfoliated(Br)HOPG	5.4×10^{-4}	3.0×10^{-2}	5.5×10^1
From Ref. 5	ZYX graphite	8×10^{-4}	/	/
	Graphite Foam	6×10^{-3}	5.5×10^{-2}	9
	Grafoil	1.1×10^{-3}	1.1×10^{-1}	1.0×10^2

resistivity by a factor of 230 and decreased the c-axis resistivity by a factor of 20, so that the anisotropy in the electrical resistivity (ρ_c/ρ_a) decreased by a factor of 5×10^4 . After exfoliation, the a-axis resistivity is even higher than that of pristine graphite.

Our value for ρ_a of exfoliated graphite is comparable to that of ZYX graphite [5]. Our value for ρ_c of exfoliated graphite is lower than that of Graphite Foam [5], which is in turn lower than that of Grafoil [5]; this implies that rolling increases ρ_c , probably due to the cracking perpendicular to the c-axis.

Effect of reversible exfoliation

Figure 1 shows the variation of the c-axis electrical resistivity (ρ_c) and the fractional expansion (change in thickness/initial thickness along the c-axis) with temperature during heating and cooling in Cycle No. 1. The c-axis resistivity began decreasing at 140°C during heating, whereas the expansion began at 160°C during heating. During cooling, the resistivity began increasing at 140°C , while the collapse of the sample began also at 140°C .

Figure 2 shows the variation of the c-axis electrical resistivity and the fractional expansion along the c-axis with temperature during heating and cooling in Cycle No. 2. The resistivity began decreasing at 110°C during heating, while the expansion began also at 110°C during heating. During cooling, the resistivity began increasing appreciably at 130°C , while the collapse began also at 130°C . In both cycles, the resistivity increased upon heating before the large decrease.

In both cycles, the expansion was reversible. However, the resistivity showed an irreversible decrease after going through Cycle No. 1. In Cycle No. 2, the resistivity change was more reversible than that in Cycle No. 1.

Although the c-axis electrical resistivity changed by a factor of 40 in Cycle No. 1 and by a factor of 20 in Cycle No. 2, the c-axis electrical resistance did not show any appreciable dependence on temperature.

DISCUSSION

The resistivity changes for reversible (Figs. 1 and 2) and irreversible exfoliation (Table 1) are consistent with one another.

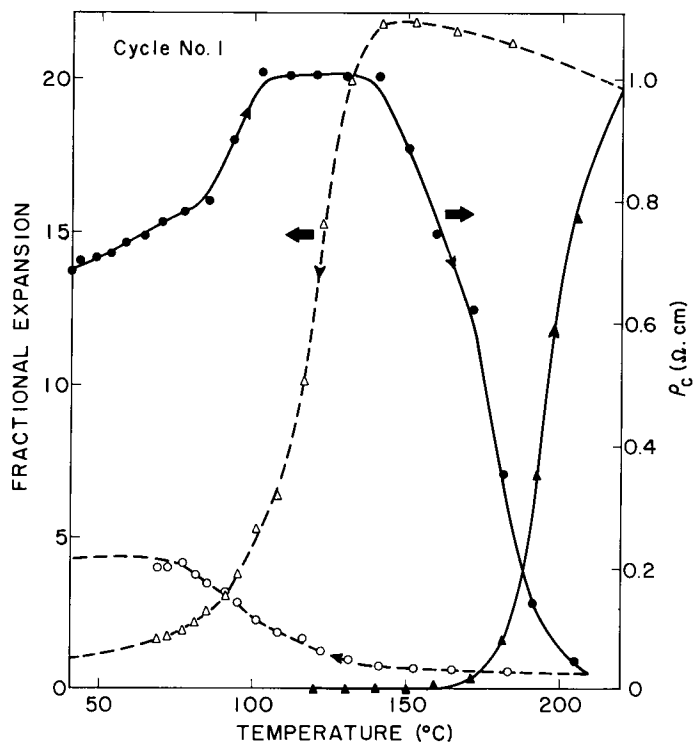


Fig. 1. Variation of the c-axis electrical resistivity (ρ) [circles] and the fractional expansion (change in thickness/initial thickness along the c-axis) [triangles] with temperature during heating (full lines and solid symbols) and cooling (dashed lines and open symbols) in Cycle No. 1.

The increase in the a-axis electrical resistivity due to exfoliation is attributed to the bending of the graphite layers. The magnitude of the increase (a factor of 230) is much greater than that (a factor of 1.2) reported by Miyauchi et al. This difference is attributed to the poorer quality of the graphite material used by Miyauchi et al., as a more well-oriented and planar microstructure makes exfoliation easier and more extensive [1]. The high expansion onset temperature observed by Miyauchi et al. (200°C) compared to that we observed (160°C in Cycle No. 1, 110°C in Cycle No. 2) is also attributed to this reason.

The decrease in the c-axis electrical resistivity due to exfoliation is also attributed to the bending of the graphite layers. X-ray diffraction evidence for the bending had been previously reported [1].

The temperature for the onset of exfoliation expansion was higher for Cycle No. 1 than Cycle No. 2. These temperatures are consistent with those previously reported for graphite-bromine based on HOPG [2].

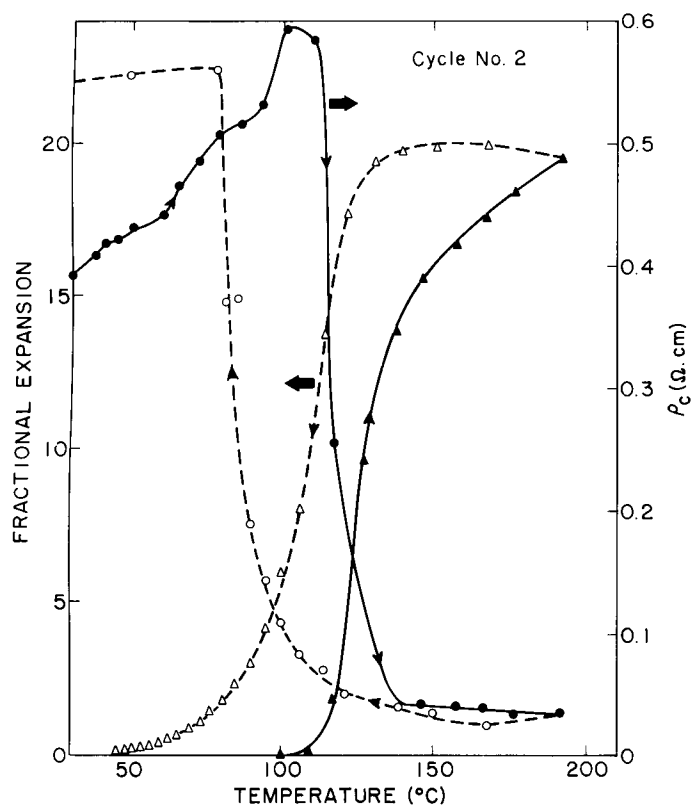


Fig. 2. Variation of the c-axis electrical resistivity (ρ_c) [circles] and the fractional expansion (change in thickness/initial thickness along the c-axis) [triangles] with temperature during heating (full lines and solid symbols) and cooling (dashed lines and open symbols) in Cycle No. 2.

In Cycle No. 1, the c-axis electrical resistivity started its large decrease upon heating at a lower temperature than the start of the expansion. This is because the resistivity is sensitive to small-scale structural changes which occur before the large-scale expansion. Such small-scale structural changes include the formation of pockets of intercalate. The buckling of these intercalate pockets occurs during the large-scale expansion.

The increase in the c-axis electrical resistivity upon heating before the large decrease is attributed to the formation of microcracks, which later evolve into the intercalate pockets.

The resistivity change observed in Cycle No. 1 was not reversible, whereas that in Cycle No. 2 was much more reversible. This is attributed to the slight irreversible bending of the graphite layers that occurred in Cycle No. 1.

Although the c-axis electrical resistivity changed abruptly and reversibly upon heating, this effect cannot be used for electrical switching. This is because the c-axis

electrical resistivity decreased while the c-axis thickness increased, so that the c-axis resistance did not vary much with temperature. On the other hand, the a-axis resistivity as well as resistance increased quite abruptly with temperature [4], so that the change of a-axis resistance with temperature may be exploited for thermally activated electrical switching.

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