

# PREPARATION AND ELECTRICAL PROPERTIES OF GRAPHITE FIBER NITRATE

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The intercalation compounds of graphite have relatively high electrical conductivity. The intercalation compounds of cellulose precursor carbon fiber with potassium (1) and nitric acid (2) have been reported. After intercalation with potassium, the electrical conductivity of the fiber was increased by a factor of about 20. But the temperature dependence of the conductivity between room and liquid helium temperatures was the same as the starting fiber's one, even after saturation with potassium, viz., they showed negative temperature coefficient of resistivity. The absorption of the agent did not destroy the fiber structure. By nitration of the fiber the conductivity also increased, and the mechanical properties were changed. The carbon fibers obtained by pyrolysing benzene have been indicated to be one of the most graphitizable carbon (3) - (6).

The present paper deals with the preparation and electrical properties of graphite fiber nitrate, being so-called as a residue compound, by using the carbon fibers through benzene decomposition. They have high electrical conductivity and do not show any lowering of mechanical strength.

The original graphite fibers were prepared by heat treatment of carbon fibers at 3000°C, which were grown on a substrate at 1100°C by pyrolysing benzene diluted with hydrogen. The graphite fibers consisted of concentric graphite layers around the fiber axis like the annual rings of a tree. These fibers were cut into 1 - 2 cm length, and had a constant diameter of 10 - 80  $\mu\text{m}$ . The fiber samples were immersed in fuming nitric acid kept at 20°C. After 24 hrs. of immersion they were taken out into the air and kept in the container with sodium carbonate for more than 24 hrs. By these procedures the intercalated fibers, so-called as a residue compound, were formed (hereafter denoted as GFN).

The electrical resistivity is decreased rapidly to 7% of starting value after 10 min. of immersion in nitric acid, indicating the formation of an intercalation compound. Subsequently the resistivity decreases much gradually and remains almost unchanged after 24 hrs. of nitration. The fiber thus formed seems to be a stage II intercalation compound. It could indicate that nitrate diffuses into fiber through the surface. When the fiber is taken out into the air and kept in the container, the resistivity increases gradually. After several hours it becomes stable, at which the value is about 15% of the starting fiber's one. The resistivity changes that occurred during the procedure are shown in Table 1. The fiber nitrate (GFN) thus obtained showed no appreciable resistivity change in the air over long periods of time (Fig.1).

Though the fiber's diameter increases slightly after nitration, the fiber structure is not destroyed. The cross-section morphology of the annual ring structure is still retained in GFN.

In Fig.2, the electrical resistivity of GFN is

shown as a function of ambient temperature in comparison with original graphite fiber. The fiber nitrate exhibits a metallic characteristic, which might be attributed to a mechanism of the scattering of the charge carriers by thermal phonons. The temperature coefficient of the resistivity is about  $2.28 \times 10^{-3}/^\circ\text{C}$  at 273K. The variation in resistivity is almost unchanged at temperatures below 40K. This trend is nearly the same in different samples, and might be the result of impurities and defective lattice. When the ambient temperature is increased by the rate slower than 4K/hr, an anomaly in resistivity is observed, which may correspond to the order-disorder transition of graphite-nitrate (7). At temperatures above 330K, the resistivity increases significantly because of the decomposition of the compound.

Magnetoresistance effect, measured by applying the magnetic field perpendicular to the fiber axis, is shown in Fig.3. They show a positive effect throughout the temperatures examined. The magnetoresistance anisotropy, measured by changing the angle between the fiber axis and the magnetic field, is also retained. These results suggest the existence of the graphitic layers unaffected by nitrate.

The variation of thermoelectric power with temperature is shown in Fig.4, in comparison with original graphite fiber. The thermoelectric power changes to a positive sign after nitration, and increases monotonically with increasing the temperature. The phonon-drag effect observed in graphite fiber disappears, presumably because of a disturbance of the crystal lattice and shortening of the mean free path of carriers.

In summary, by nitration the fibers with metallic p-conductivity are obtained from the graphite fibers. Their mechanical strength is almost the same as the original fiber's one. They could afford promise of being used as electrical conductor.

Table 1. The electrical resistivity of fiber sample at room temperature

Original graphite fiber	$8 \times 10^{-5}$ ( $\Omega \cdot \text{cm}$ )
Nitrated fiber (in nitric acid)	$0.6 \times 10^{-5}$
Nitrated fiber (in the air, GFN)	$1.2 \times 10^{-5}$

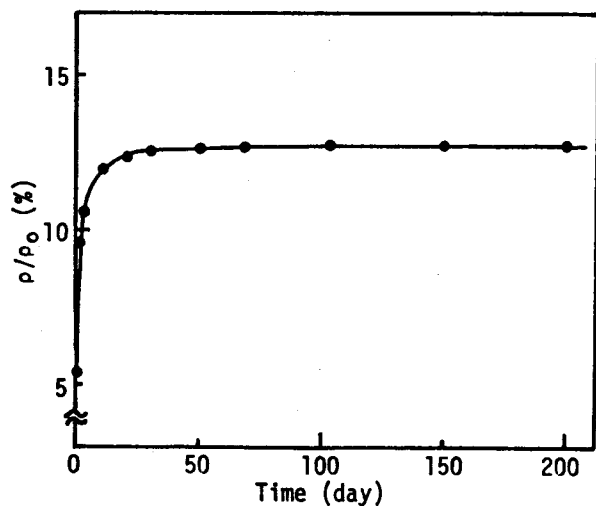


Fig. 1. Change of electrical resistivity with time at room temperature.

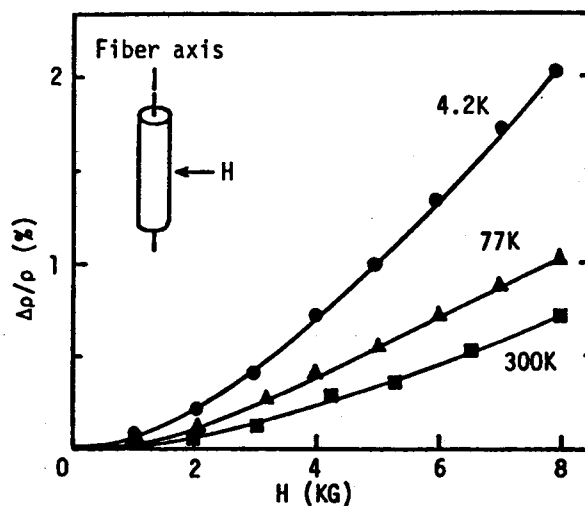


Fig. 3. Magnetoresistance effect of graphite fiber nitrate.

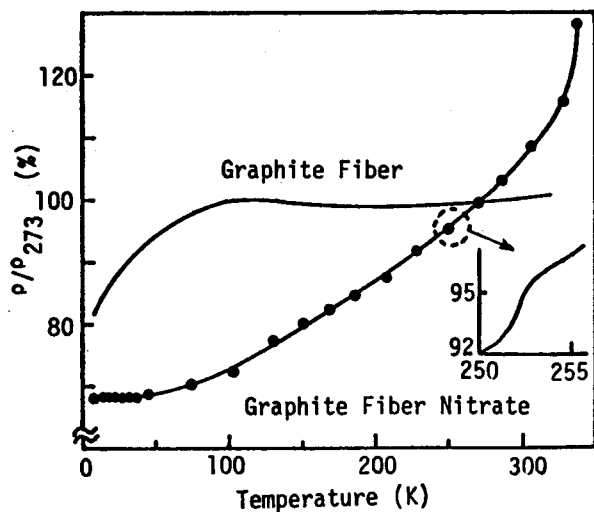


Fig. 2. Temperature dependence of electrical resistivity.

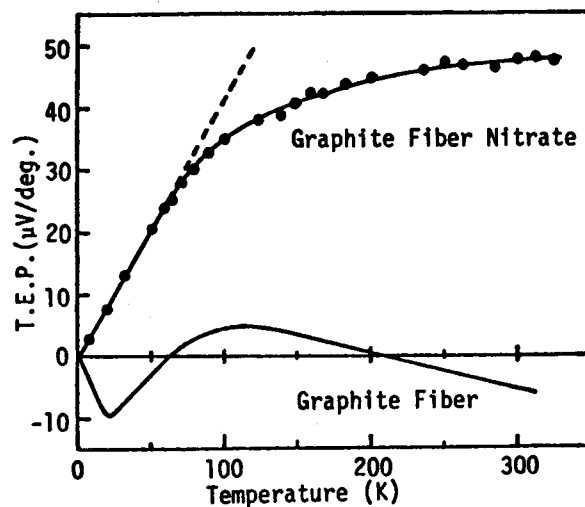


Fig. 4. Thermoelectric power of graphite fiber nitrate.

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