The Electrical Conductivity of Graphite Filaments and Their Alkali-metal Intercalation Compounds

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A bundle of carbon filaments, each about 20 cm in length and 7 μm in diameter, could be grown from purified graphitic material in argon plasma generated in a d.c. arc. The filaments were converted into softer filaments on heat-treatment to 3000—3400 °C. The filaments formed intercalation compounds of potassium, rubidium, and caesium. The electrical resistivities were found to be 1300, 610—660, 23—25, and 28—30 μΩ cm at 300 K for the original filament, the heat-treated filament, and the first stage golden and the second stage dark-blue intercalation compounds of the heat-treated filament, respectively.

Filamentary growth of carbons has been reported to occur when a carbon-rich gas such as carbon monoxide,[1] methane,[2] heptane,[3] and benzene[4] is pyrolyzed in the presence of some solid material, and also when carbons such as graphite[5] and carbon black[6] are heat-treated to temperatures higher than 3000 °C. Haanstra *et al.*[1] have obtained pencil-like carbon columns, 3—6 μm in diameter and about 1 mm long, by pyrolysis of carbon monoxide on a β-SiC crystal. The columns were found to have a conehelical structure; they are stacked from parallel layers of carbon atoms, bent into a cone mantle with a top-angle of about 141°.

Koyama[4] has obtained carbon fibers of a cylindrical scroll structure by pyrolyzing a mixture of benzene and hydrogen on a graphite block abraded with an emery paper. Bacon[5] grew graphite whiskers from a graphite-rod electrode in a d.c. arc under a pressure of 92 atm of argon at 3900 K. They consist of one or more concentric tubes, each in the form of a scroll or rolled-up sheet of graphite layers.

We could grow a bundle of "carbon filaments," each about 20 cm long and 7 μm in diameter, by heating purified graphitic material in argon plasma. Each filament was found to have a smooth surface and a cylindrical shape with circular cross-section of nearly constant diameter over its entire length. Each was composed of three parts: the outer sheath, the inner sheath, and the core.[7] The outher sheath, about 0.7 μm thick, consists mainly of circumferentially oriented graphitic layers; the inner sheath, about 1.4 μm thick, consists mainly of radially oriented graphitic layers. The core, about 2.8 μm in diameter, probably consists of randomly distributed minute crystallites or amorphous material, because it did not show any electron diffraction pattern. The carbon filaments were converted into softer filaments on heat-treatment to 3000—3400 °C.

In this paper we will report the electrical conductivities of these newly obtained carbonaceous filaments as well as of their alkali-metal intercalation compounds. We will discuss the conductivities in relation to their fine crystalline structures inferred not only from the X-ray and electron diffractions but also from the Raman scattering and the magnetoresistance.

Experimental

A piece of grafoil GTA (Union Carbide Co.) was immersed in hot aqua regia for a day and then purified by heating repeatedly to 800 °C for 10 min in a stream of wet chlorine. These processes reduced the concentration of impurities, for example iron, from 80 to less than 8 ppm. Carbon filaments could not be grown from unpurified grafoil. The purified grafoil, supported by a graphite rod between two graphite-rod electrodes, was heated with argon plasma generated in a d.c. arc. When the temperature of plasma exceeded 5000 °C, a bundle of carbon filaments started to grow at the rate of about 1 cm min^{-1} under the nearly atmospheric pressure of argon.

The carbon filaments thus obtained were converted into softer filaments on graphite-resistance heating at 3000 °C, or on high-frequency heating at 3400 °C. The former will be referred to as graphite 30 and the latter as graphite 34 filaments. The diameter of an individual filament was measured by means of scanning electron microscopy.

The intercalation compounds of the filaments with K, Rb, and Cs were prepared by vapor phase reaction in a dual furnace.[8] Their electrical resistivity was measured in the range from 4.2 to 300 K by a four-probe d.c. method in the same way as reported previously.[9] The four-probe contacts with the intercalation compounds were pressure-fixed before the vapor phase reaction.

Graphite 30 and 34 filaments formed lst stage compounds of brilliant golden luster and 2nd stage compounds of dark-blue luster. The X-ray diffraction from the golden compound formed between a graphite filament and Cs, for example, gave sharp spots lying perpendicular to the filament axis and diffuse spots on the axial line. The interlayer distance was determined to be 5.96 Å from the former spots, and the Cs–Cs distance to be 4.92 Å from the latter spots. These values are coincident with those reported for the compound prepared from highly-oriented pyrolytic graphite (abbreviated to HOPG) and Cs.[10] The carbon filaments as grown, on the other hand, did not change their appearance, though their resistivity was reduced by introduction of alkali-metals.

Results and Discussion

The longitudinal resistivities were found to be 1300, 660, and 610 μΩ cm for carbon, graphite 30, and graphite 34 filaments, respectively, at 300 K; these increase monotonously with decreasing temperature down to 4.2 K, as shown in Fig. 1, a—c. The re-

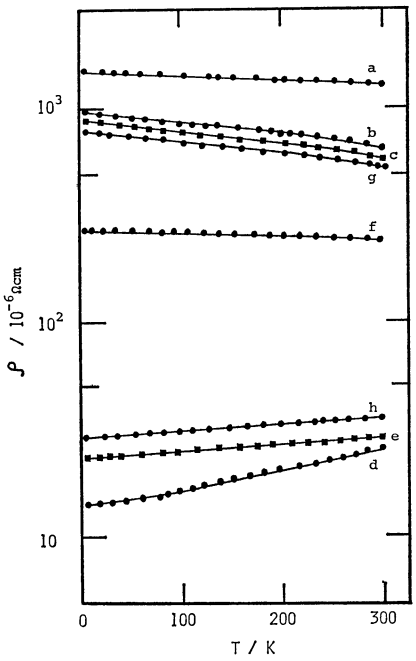

Fig. 1. Temperature dependence of resistivity for filaments.
a: Carbon, b: graphite 30, c: graphite 34, d: K-intercalated graphite (1st), e: K-intercalated graphite (2nd), f: K-intercalated carbon (1st), g: K-intercalated carbon (2nd), and h: K-intercalated graphite (1st) with hydrogen.

sistivity of the graphite filament was found to be lower than that of the carbon filament, but no great difference was found in resistivity between the graphite 30 and 34 filaments. The lower resistivity of the graphite filaments, which were obtained on heat-treatment to 3000—3400 °C, can be ascribed to the preferred alignment of the graphite-type crystallites along the filament axis.

Raman scattering induced by argon-ion laser radiation (488 nm), though it only probed an optical skin depth (<0.1 μm), gave a spectrum of a sharp and intense peak at 1582 cm^{-1} and a tiny and broad peak at 1360 cm^{-1} for the graphite filament. The Raman spectrum for the carbon filament, on the other hand, showed two broad peaks, around 1590 and 1370 cm^{-1}. The former spectrum is quite similar to that found for crudely pulverized natural graphite or for grafoil, and the latter to that of carbon black.[11]

The graphite filament exhibited sharper X-ray diffraction spots and greater intensity contrast between the dark-field (002) or (100) electron-micrograph of the outer sheath and that of the inner sheath, compared with those found for the carbon filament. These results indicate a higher degree of preferred orientation of crystallites in the graphite filament.

The resistivity of HOPG along the basal plane ρ_a has been reported to be 40 μΩ cm at 300 K,[12,13] and to show a slight rise with decreasing temperature down to around 77 K, followed by a rapid descent to 4.2 K. The resistivity along the c-axis, ρ_c has been reported to be about 0.1 Ω cm at 300 K,[12] and to increase with decreasing temperature.[14] The temperature dependence of resistivity observed for the graphite filament is different from that for HOPG, but rather similar to that found for bulk polycrystalline graphite such as grafoil[9] and that of the c-axis resistivity for pyrolytic graphite.[14]

The graphite filament was obtained on heating the carbon filament at a high temperature region where three-dimensional ordering of the layers characteristic to the graphite structure is expected to develop, but some loose aggregates of misoriented crystallites still seem to remain among graphite-type crystallites. The graphite-type crystallites which form the outer and inner sheaths of a filament are preferentially aligned with their basal planes parallel to the filament axis, so charge carriers are expected to move along the basal plane in the direction of the filament axis in each crystallite, the higher basal plane conductivity providing a lower resistivity path along that direction. Hence, the misoriented crystallites and crystalline boundaries seem to determine the value of longitudinal resistivity and to characterize the temperature dependence.

Presumably, some thermally activated process may be included in the conduction through the misoriented crystallites. Indeed, the resistivity exhibited an exponential change with reciprocal temperature in the temperature region above 150 K, and the activation energy was determined to be 0.01 eV for the graphite filament, though it still remains unknown whether this activation energy is related to the semiconducting energy gap or to some hopping process of charge carriers. Graphite whiskers[5] and graphitized carbon fibers[15] have been reported to show an HOPG-like temperature dependence of resistivity.

A preliminary measurement of transverse magnetoresistance ($\Delta\rho/\rho_0$) was carried out on single filaments in the magnetic field up to 120 kOe,††† by using an Intermagnetics MIDIBRUTE 120 superconducting magnet. Electrical contacts of a filament were made with silver paint to four thin gold wires. The magnetoresistance was found to be positive for the carbon filament and to be negative for the graphite filament at 4.2 K in the entire range of magnetic field. Rotation of a single filament around the filament axis, which was oriented perpendicular to the magnetic field, did not change the magnetoresistance.

Soft cokes heat-treated at temperatures lower than 1100 °C have been reported to show a positive magnetoresistance and those heat-treated at 1500 °C to show a negative magnetoresistance at 4.2 K.[16] A number of suggestions have been made as to the origin of the negative magnetoresistance in a wide range of carbons: crystalline size effect,[17] localized spins,[18] a mobility edge,[19] and a dependence of carrier concentration on a magnetic field.[20] It is unknown to which origin the negative magnetoresistance property observed is attributable, but it seems fairly certain that some sort of disordered state is responsible for the property.

The average carrier mobility along the filament axis, $\bar{\mu}$ was estimated to be about 300 $cm^2 V^{-1} s^{-1}$ at 4.2 K for the carbon filament; the following equa-

††† Oe=$1000/4\pi$ A m^{-1}.

tion[14] was assumed to be applicable to the magnetoresistance observed:

$$\bar{\mu}=\sqrt{2}(\Delta\rho/\rho_0)^{1/2}\times 10^8/H. \quad (1)$$

Graphite filaments formed 1st stage alkali-metal intercalation compounds of such brilliant golden luster as that of HOPG-based compounds. Non-graphitizable carbons have been reported not to form intercalation compounds. This has been attributed to the cross-linking of the graphitic layers.[21] Hence, the graphite filaments in this study seem to have little cross-linking, though three-dimensional ordering of the layers did not develop on heating to 3000—3400 °C. This is the first example of brilliant golden intercalation filaments as far as we know.

The graphite filaments intercalated with K, Rb, or Cs were found to show a greatly reduced resistivity, in the range of 23—25 μΩ cm for the lst stage compounds, and in the range of 28—30 μΩ cm for the 2nd stage compounds, at 300 K. They were also found to be metallic in character, showing a decrease in resistivity with decreasing temperature (Fig. 1, d, e). No difference in resistivity value was found among the potassium, rubidium and caesium compounds.

The lst stage compounds prepared between HOPG and alkali-metals have been reported to possess the basal-plane resistivity in the range of 10—14 μΩ cm at room temperature[22,23] and to show a decreasing resistivity with decreasing temperature. The grafoil-based alkali-metal intercalation compounds showed resistivity values in the same range and a similar temperature dependence.[9]

When the lst stage golden potassium-intercalated filament was heated in a dual furnace under the conditions in which the 4th stage intercalation compound was expected to be prepared,[8] the filament turned black and showed an increase in resistivity. In general, the resistivity was found to decrease monotonously with intercalant concentration.

The carbon filament, on the other hand, provided alkali-metal intercalation compounds of the resistivity of about 240 and 550 μΩ cm at 300 K, when prepared under the same conditions of preparation as those for the lst and the 2nd stage HOPG-based compounds, respectively. The resistivity of these intercalated carbon filaments was found to increase with decreasing temperature (Fig. 1, f, g).

From these observations, it is inferred that an introduction of alkali-metal atoms not only increases the number of conducting carriers in the graphitic layers, but also eliminates some of imperfections present in the pristine graphite filaments. Certainly, the X-ray diffraction from the intercalated graphite filament gave much sharper spots than that from the pristine filament did. The electric anisotropy, ρ_c/ρ_a has been reported to be reduced from 2500 for HOPG to 34 for the intercalated compound,[22] so misorientation of crystallites seems to have less influence on resistivity value after they are intercalated with alkali-metals. The intercalated filaments were unstable in air, so they could not be taken out from a sealed glass tube. Because of the technical difficulties encountered in these reactive filaments, their magnetoresistance have not been measured yet.

A golden potassium-intercalated graphite filament turned blue and its resistivity reached 36 from 25 μΩ cm at 300 K, when hydrogen purified through a heated Pd–Ag thimble was introduced to the intercalated filament. This change is quite similar to that observed for the grafoil-based potassium intercalation compound,[9,24] and can be explained in terms of the formation of a ternary compound.[25]

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