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Measurement of Thermal Stress in Graphite Intercalated with Bromine[1]

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The thermal stress of graphite intercalated with bromine was found to increase from zero at about 100°C to about 1.3 MPa at 200°C. The effect was reversible with hysteresis. The thermal stress increase had a sharp temperature dependence due to its association with the exfoliation phase transition.

KEY WORDS: bromine; exfoliation; graphite; intercalation; phase transition; stress; temperature; thermal stress.

1. INTRODUCTION

A thermal stress is an extrinsic stress produced by a material upon heating. It is to be distinguished from the intrinsic stress due to material defects. Due to the nearly reversible nature of a thermal stress, a thermal stress is to be measured at an elevated temperature or as a function of temperature, whereas the intrinsic stress can be measured at room temperature.

The thermal stress is a useful technological parameter because it is necessary for the mechanical design of systems which use the material at an elevated temperature. Moreover, the thermal stress is a physical quantity that is closely related to the thermal expansion. In fact, thermal stress measurement complements thermal expansion measurement. In thermal stress measurement, the stress generated by a sample upon heating is measured as a function of temperature while the sample dimension is not allowed to change. In contrast, thermal expansion measurement involves

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measuring the dimensional change as a function of temperature while the stress experienced by the sample is not allowed to change.

Graphite intercalation compounds are layered compounds which contain graphite layers and intercalate layers. The number of graphite layers between the nearest intercalate layers is known as the stage of the compound. The intercalate can act as an electron acceptor or an electron donor, thereby doping the graphite and greatly increasing the in-plane electrical conductivity of the graphite. Dozens of chemicals can function as intercalates. Bromine is one of the most well-known acceptor intercalates and graphite–bromine is the only graphite intercalation compound of which the thermal stress had been previously measured [1]. Based on six data points, the thermal stress along the c axis of pyrolytic graphite (not highly oriented) intercalated with bromine had been reported to increase linearly from zero at about 100°C to about 0.4 MPa at 200°C [1]. In this work, a much more sophisticated thermal stress measurement was undertaken on highly oriented pyrolytic graphite (HOPG) intercalated with bromine. The dependence of the thermal stress on temperature was found to be nonlinear with hysteresis, such that the stress increased from zero at about 100°C to about 1.3 MPa at 200°C.

2. EXPERIMENTAL

The thermal stress measurement was performed by using a mechanical testing system (Instron Model 1125, 22,000-lb load frame, machine stiffness of 1×10^6 lb/in.) operating in the compression mode with the crosshead held fixed. In other words, the mechanical testing system automatically applied a controlled amount of compressive stress which was just enough to counteract the tensile stress generated by the sample upon heating. For a typical maximum load of 5 kg, the strain (fractional expansion) in the sample was 0.05%.

High-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. At the time of the data collection, desorption had occurred for about 6 h, so that, at the start of the measurement, the intercalate concentration was about 75 wt% bromine and the stage was mixed (2 and 3). The sample thickness (along the c axis) was 0.071 cm. The cross-sectional area of the sample was 0.3427 cm^2.

The graphite–bromine sample was placed between the ends of two glass (Pyrex) rods. The other end of each of the glass rods had been fixed to one of the steel compression plates of the Instron mechanical testing system mentioned above. A chromel–alumel thermocouple was placed beside the sample, such that it almost touched the sample. The sample and parts of the glass rods were surrounded by a small resistance heater coil, which extended about 2.5 cm both above and below the sample. The temperature detected by the thermocouple was controlled by a TECCO temperature programmer. The temperature was increased and then decreased in steps.

The stress contributed by the thermal expansion of the glass rods as a function of the temperature during heating and cooling was measured by having no sample between the rods and allowing the rods to touch one another. It was found that the thermal expansion of the glass rods contributed a stress ranging from 0.02 MPA at 60°C to 0.19 MPa at 225°C. This correction had been made in the stress data reported here.

The thermal stress measurement was also carried out on a pristine HOPG sample. The measured stress as a function of temperature was

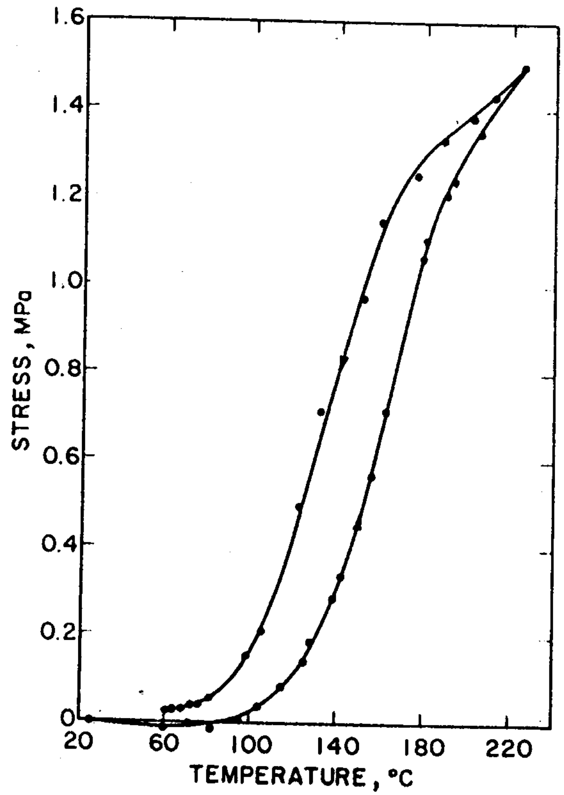

Fig. 1. Variation of stress with temperature during heating and cooling in Cycle 7.

approximately the same as that obtained with the glass rods touching one another. This means that the thermal expansion of pristine HOPG contributed negligible stress.

Figure 1 shows the stress measured as a function of temperature in Cycle 7. The stress began to increase at about 100°C, and the increase became rapid at about 125°C. Hysteresis was observed during cooling. The change in stress was almost completely reversible. The stress after cooling was slightly higher than that before heating. There was little variation of the thermal stress with cycle number.

3. DISCUSSION

The increase in the thermal stress of graphite–bromine with increasing temperature was observed by Martin and Brocklehurst [1] and in this work. As indicated by Martin and Brocklehurst [1], this effect is associated with exfoliation, which is a phase transition in which the intercalate vaporizes in the graphite, forms gas pockets, and causes the sample to expand along the *c* axis. By using HOPG, which has a more well-defined *c* axis than the pyrolytic graphite used by Martin and Brocklehurst, we found that the thermal stress is about three times that reported by Martin and Brocklehurst and that the stress increases sharply at the exfoliation temperature in a nonlinear fashion, in contrast to the linear (more gradual) stress increase observed by Martin and Brocklehurst.

The large thermal stress and its sharp temperature dependence observed in this work suggest the use of graphite–bromine in a thermomechanical device which is temperature sensitive.

REFERENCES

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