THE ROOM-TEMPERATURE MECHANICAL PROPERTIES OF BORON-DOPED GRAPHITE

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1. Introduction

From earlier studies on boron-doping, it is well-known that boron can have a significant effect on the physical properties of graphite. For example, Soule and Nezbeda [1] showed that the dynamic basal-shear modulus $C_{44}$ increases at room temperature from 0.45 GN/m$^2$ to 4.5 GN/m$^2$ as the boron level in natural single crystals increases from 7 to 1500 ppm. This 10-fold increase was attributed to dislocation pinning by boron atoms. Wagner and Dickinson [2] investigated the influence of boron on physical properties such as electrical resistivity, thermal conductivity and dynamic Young's modulus for polycrystalline graphite. All showed important changes for boron concentrations up to 0.8 wt %, but the room-temperature modulus only showed a 19% increase from 16.4 GN/m$^2$ to 19.5 GN/m$^2$; this, again, was attributed to dislocation pinning. The boron in the polycrystalline case was added to the green mix during the manufacturing process. In the light of their own and earlier evidence, Wagner and Dickinson concluded that up to about 0.16 wt %, boron enters the graphite lattice substitutionally, and between this level and 0.8 wt %, some occupies interstitial sites but without carbide formation.

The aim of the present work is to investigate the effect of boron addition on mechanical properties such as the dynamic modulus and the form of the stress-strain curve of an isotropic, polycrystalline graphite. This note presents preliminary results on the room-temperature properties.

2. Material and doping procedure

The material used was a Gilso carbon, nuclear-grade graphite supplied by the UKAEA, Springfields Laboratory. The density was 1.75 gms/cc. Specimens for compression testing were machined in the form of cylinders 10 mm long and 4 mm diameter, and specimens for the dynamic modulus determination were 20 mm long and 4 mm diameter. The compression tests were carried out on an Instron machine at a cross-head speed of 0.2 mm/min. They included tests to fracture and load-unload tests to measure hysteresis loss below the fracture stress. The dynamic modulus was measured by the resonance technique.

Boron was diffused into the specimens by heating them in the presence of boron powder in an argon atmosphere at 2900°C for one hour. The boron content of some specimens was subsequently determined by chemical analysis at Springfields. A good indication of the presence of boron in the graphite lattice is the effect it has on the thermal conductivity [2]. The variation of the conductivity with boron concentration in the material used here is shown in Fig.1. The change is quite consistent with that reported by Wagner and Dickinson [2] and is evidence of the success of the diffusion technique employed.

In order to ensure that any changes in properties due to further graphitization of the specimens at 2900°C would not influence conclusions on the effects of boron, a group of 'control' specimens were given the same heat treatment in the absence of boron, and changes in properties can therefore be measured relative to these specimens. The effect of heat treatment on the thermal conductivity was negligible, as indicated by the filled circle in Fig.1.

3. Results

The dynamic Young's modulus of all specimens was measured before ($E_0$) and after ($E$) the heat treatment and addition of boron, and the change ($E-E_0$) produced is shown as a function of boron concentration in Fig.2. Each data point is the mean of eight values, and the bars indicate the standard deviation. The mean values for the control specimens before and after heat treatment were 10.19 and 9.23 GN/m$^2$ respectively.

The effect of boron on the static modulus measured in the compression tests is shown in Fig.3. Six specimens were tested at each boron level, but the scatter in the data is much larger than for the dynamic case since the modulus was not measured before the diffusion treatment. Nevertheless, the trends clearly follow those observed in Fig.2. The variations of fracture stress and strain to fracture with boron concentration are shown in Fig.4. It can be seen that the trends in these data are similar to that of the modulus. No systematic change in hysteretic energy loss at a given amplitude with boron level was observed.

4. Discussion

Perhaps the most surprising feature of the data given in the preceding section is that the changes in the mechanical properties are so small. For example, the changes in the dynamic modulus $E$, which are similar to those reported by Wagner and Dickinson [2], are two orders of magnitude smaller in percentage terms than those produced in the single-crystal modulus $C_{44}$. The latter are very much in line with those found by Seldin and Nezbeda [3] in single-crystal and pyrolytic samples after neutron irradiation. Since the changes in $C_{44}$ are almost certainly due to dislocation pinning, the small changes reported here could be considered to throw doubt on the role dislocations play in determining the elastic and yielding mechanisms of polycrystalline graphite. However, it is more likely that the fact that $E$ does change by approximately 10% is an indication of the contribution $C_{44}$, and hence dislocations, make to the polycrystalline properties. For example, it is well-known (see [4] for review) that the elastic properties of a polycrystal fall
between the two extremes of the uniform-strain model of Voigt and the uniform-stress model of Reuss. If it is assumed that $C_{14}$ is the only single-crystal constant significantly affected by addition of boron, then a 10-fold increase in $C_{14}$ would make an insignificant change to the Voigt modulus and an almost 10-fold change to the Reuss modulus. The present results suggest that the true modulus is more heavily weighted to the Reuss form than is, say, the arithmetic mean of the two extremes.

The assumption that $C_{14}$ is the only constant changed by boron doping has not yet been tested by experiment. It is the only constant changed significantly by neutron irradiation [3], and we are currently repeating the mechanical property measurements on neutron-irradiated specimens. The results of this investigation and further analysis and work on the boron doping will be reported at a later date.

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References