THERMAL DIFFUSIVITY BEHAVIOR IN CARBON FILMS FOLLOWING A SHORT PERIOD OF OXIDATION

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Introduction

Increasing interest in carbon-carbon composites for thermal management systems has resulted in several investigations into thermal conductivity [1]. The relationship between thermal conductivity and carbon structure is so strong that thermal conductivity measurement has been employed by several researchers to characterize the carbon material quality [2]. Few studies have been dedicated to determining the mean free path and the thermal behavior of carbon subjected to oxidizing environments. In this paper, we investigate the thermal property changes at the surface when oxidation occurred.

Experimental

Optical beam deflection (OBD) is a non-contact method of determining the thermal diffusivities of materials. The experimental arrangement has been described elsewhere [3], so only a brief summary will be given here. Figure 1 shows the experimental configuration. An intensity-modulated beam of light is sent through a microscope and focused on the sample. This beam generates a thermal wave in the sample that travels outward from the heated region. The thermal waves that propagate near the surface of the sample periodically warm the air layer adjacent to the sample. A time-variant gradient in the index of refraction of the air results. A laser beam propagating parallel to and very near the sample surface is periodically deflected as it passes through the heated air. A position-sensitive detector monitors the deflections of the laser beam. A lock-in amplifier detects the time of travel of the thermal wave from the phase of the signal generated by the deflected beam relative to that of the heating beam. The phase of the signal as a function of the position of the probe beam is recorded. The diffusivity α can be determined from a knowledge of the chopping frequency f and the gradient of the phase, $\Delta\phi/\Delta x$:

$$\alpha = \frac{(180^\circ)^2 f}{\left(\frac{\Delta\phi}{\Delta x}\right)^2 \pi}.$$

A description of the temperature field has been given in three dimensions by Jackson [4], and a detailed calculation of the laser beam deflection has been performed by Kuo [5]. The linearity of the phase with the position of the probe beam has also been shown [6].

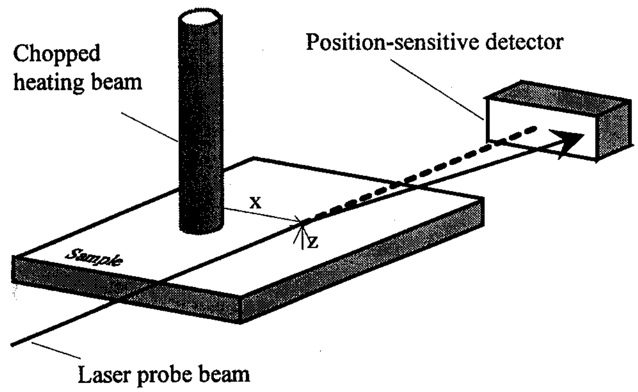

Figure 1. Arrangement of OBD experiment.

Results and Discussion

Earlier results [3] show the behavior of the thermal diffusivity of carbon materials as a function of the temperature of heat treatment. Polyimide carbon films 30 μm and 120 μm thick were studied in that experiment. The films were made at 1000 °C and heat treated in an inert atmosphere at five temperatures between 1800 °C and 2600 °C. After each heat treatment the thermal diffusivity was measured at room temperature. The thermal diffusivities as a function of heat treatment temperature for anisotropic CVD carbon and the polyimide carbon films are shown in Figure 2. For the films, the OBD results show the same dependence on the temperature of heat treatment as anisotropic CVD carbon. As the temperature approached 2600 °C, the thermal diffusivities increased significantly compared to those at lower temperatures.

The two polyimide carbon films which had been heat treated at five temperatures up to 2600 °C were oxidized at 800 °C in an oxygen atmosphere for a matter of minutes. Their thermal diffusivities were then measured using OBD. Table 1 shows that the thermal diffusivities of both films decreased by approximately a factor of five relative to the unoxidized films.

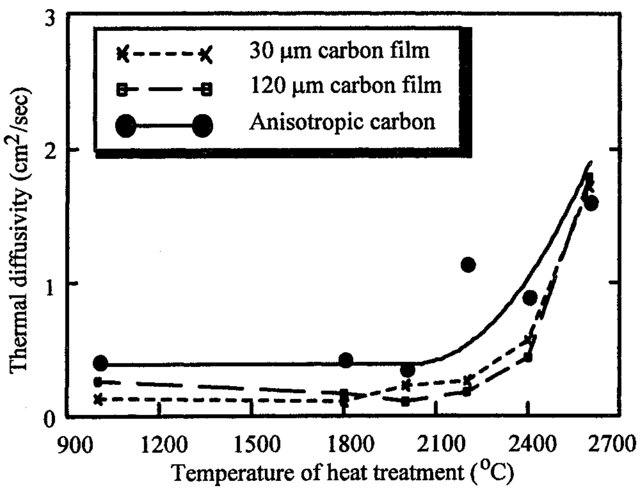

Figure 2. Plots of thermal diffusivities of polyimide carbon films and anisotropic carbon as a function of the temperature of heat treatment.

Table 1. The Thermal Diffusivities (cm^2/sec) of Polyimide Carbon Films before and after Oxidation.

Thickness	Unoxidized	Oxidized
30 μm	1.714	.350
120 μm	1.776	.245

As shown in Figure 2, the thermal diffusivities of the polyimide carbon films behave like those of anisotropic CVD carbons when subjected to heat treatment. Heat treatment in an inert atmosphere at increasingly higher temperatures causes a significant ordering of the carbon network to occur which leads to the graphite structure. In anisotropic carbon materials the grain size is larger than in isotropic CVD carbon. In fact the anisotropic CVD carbon is highly graphitizable and leads to an increase in the thermal diffusivity.

When the films are oxidized at 800 °C in the presence of oxygen, some of the carbon atoms at the grain boundaries and on the edges are oxidized. The oxidation process essentially interrupts the carbon ordering on the surface by creating pits or microholes on the surface. These sites serve as insulating barriers for heat propagating along the carbon film's surface. The mean free path is thus reduced and the thermal diffusivity declines.

OBD is successful for studying this change in polyimide carbon films because it is able to measure the thermal diffusivity at the surface of the material. The heat detected by the probe beam propagates along the surface of the sample. Other experimental methods, such as the flash lamp method, require that the heat propagates from one surface to the opposite surface. These methods measure an average thermal diffusivity for all the material encountered by the heat. They are not sensitive to changes occurring at the surface involving a small fraction of the material in the sample.

Conclusions

Heat treatment of polyimide carbon films in an inert atmosphere at temperatures nearing 2600 °C graphitizes grains of carbon. The alignment of these grains and the distance between the planes of carbon atoms within them determines the thermal diffusivity of the film.

Subsequent oxidization of these films at 800 °C in the presence of oxygen burns some carbon atoms at grain boundaries and at film edges with a corresponding drop in the thermal diffusivity.

Because heat detected by the probe beam in OBD has propagated along the surface of the material, this method is well-suited to detect surface changes in samples, such as the oxidation of polyimide carbon films observed here.

Carbon materials oxidized in the presence of oxygen form an insulating surface layer. In this regard Heat generated at the surface of the material will not be conducted into the material at the rate predicted by calculations based on the properties of the bulk material alone.

The present results could have particular significance in applications such as carbon-carbon composite (C/C) aircraft brakes where the carbon surfaces are always subjected to high temperatures in an oxidizing atmosphere. It appears that the thermal diffusivity of the rubbing surfaces is highly reduced after only a few stops and the material chosen for heat transfer to dissipate heat energy reacts in a way opposite to that expected. This reduction in thermal diffusivity would make the C/C brake more degradable.

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