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# Low-Earth-Orbit Exposure of Carbon-Based Materials Aboard Shuttle Flight STS-46

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**Six different types of carbon and carbon–boron nitride composites were exposed to low Earth orbit (LEO) aboard Space Shuttle flight STS-46. The samples received a nominal atomic-oxygen fluence of 2.2 × $10^{20}$ atoms/cm$^2$ in 42 h of exposure. Pyrolytic graphite and highly oriented pyrolytic graphite showed significant degradation, and the measured erosion yield was within a factor of 2 of published values. The erosion yield of pyrolytic boron nitride was found to be 2.6 × $10^{-26}$ cm$^3$/atom in plasma asher exposure, over 42 times lower than that of pyrolytic graphite. This low erosion yield makes graphite–boron nitride mixtures quite resistant to LEO exposure. Evidence suggests that the graphitic component was preferentially etched, leaving the surface boron nitride rich. Atomic-oxygen resistance increases with boron nitride composition. Carbon-fiber–carbon composites eroded in LEO, and the carbon pitch binder was found to etch more easily than the graphite fibers, which have much higher atomic-oxygen resistance.**

## Nomenclature

| | |
|---|---|
| $A$ | = area |
| $F$ | = fluence |
| $\Delta M$ | = change in mass |
| $\varepsilon$ | = erosion yield |
| $\rho$ | = density |

## Introduction

HIGH-TEMPERATURE radiators are necessary for rejection of waste heat generated aboard orbiting spacecraft.[1,2] Radiator materials must be able to operate at temperatures up to 900 K. Other materials requirements for space radiators are high thermal conductivity and surface emittance. Furthermore, conductivity and emittance must not change with exposure to the corrosive low Earth orbit (LEO) space environment.

Atomic oxygen (AO) is the primary reactive species present in LEO.[3] Oxygen atoms strike spacecraft surfaces with an average kinetic energy of 4.5 eV due primarily to the orbital speed of the spacecraft. The AO attack is directional along the spacecraft's velocity vector, since the spacecraft is moving into the oxygen atoms. Ultraviolet light from the sun is also present, and synergistic degradation effects are suspected.

Ion beams have been extensively used to modify the surface morphology of many materials, resulting in a carpetlike surface texturing.[4] Surface modification of this type can significantly alter the surface emittance of a waste-heat radiator.

Bulk basal-plane pyrolytic graphite and vapor-grown carbon fibers show the highest thermal conductivity of all materials.[5] Also, graphite can withstand temperatures up to 2800 K and has found extensive use in high-temperature applications. These properties make graphite an excellent choice for radiator applications. However, it has been shown in both laboratory simulations and actual LEO exposure that graphite is readily etched by AO.[6]

This paper considers the stability of carbon–boron nitride mixtures (C–BN), carbon–carbon-fiber (C–C) composites, highly oriented pyrolytic graphite (HOPG), and pyrolytic graphite (PG) in an AO environment. Their usefulness as space radiator materials has been evaluated through exposure to LEO aboard Space Shuttle flight STS-46 in July 1992.

## Experiment

Six different types of materials were prepared in bulk form. Two different types of graphite were chosen, namely PG and HOPG.[5] Two C–BN samples with 40% and 60% PG were also flown. The 40% C–BN sample was hot-pressed, whereas the 60% C–BN was as deposited.[7] It will be shown that the presence of boron nitride in the mixture serves to greatly decrease erosion. Boron nitride is not as good a thermal conductor as graphite, so the thermal conductivity of C–BN materials is less than that of pure graphite, but it should still be quite acceptable for space radiator applications.

The remaining two samples were composites of vapor-grown carbon fibers embedded in a graphite (pitch) matrix. These C/C composites were made by either liquid or gas infiltration of the graphite precursor into the fiber weave.

Sample characterization consisted of accurate measurements of mass and dimensions. Mass was measured using an ultramicrobalance with a resolution of $10^{-7}$ g, and the physical dimensions were measured using a vernier caliper with a resolution of 25 $\mu$m. Dimension and mass measurements allow for measurement of erosion yield.[6]

Scanning electron microscopy (SEM) and atomic-force microscopy (AFM) were employed to measure topographic changes and quantify surface roughness. AFM is a contact method that gives extremely fine-scale measurements of surface roughness over small areas, on the order of 100 $\mu$m or less.

The bulk samples were cut into circular geometries to fit into the provided sample holder. In order to isolate the effects of the AO, the back sides of the samples were used as a control surfaces.

All samples were part of the exposure-3 payload for limited-duration space-environment candidate materials aboard STS-46. The samples were exposed to the space environment throughout the entire shuttle flight. However, the samples received direct

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ram exposure to AO for only 42 h during the 8-day mission, and the oxygen fluence received during this exposure was nominally $2.2 \times 10^{20}$ atoms/cm$^2$. The oxygen fluence was determined both by atmospheric modeling using the MSIS-86 thermospheric model[8] and by a mass spectrometer flown aboard STS-46 on the EOIM-3 payload. Kapton mass loss measurements[9] showed the oxygen fluence to be $2.3 \times 10^{20}$ atoms/cm$^2$.

## Results and Discussion

Figure 1 shows the visible surface roughening of the PG, HOPG, and C/C composites. The C–BN samples showed no visible degradation except for a slight darkening of the 60% C–BN sample.

SEM results for the PG, HOPG, and C/C composite made by gas infiltration showed uniform degradation. The C/C composite made by liquid infiltration showed preferential etching of the graphite pitch surrounding the carbon fibers as shown in Fig. 2. The 40% C–BN sample showed no changes in the SEM photographs.

The hot-pressed 40% C–BN sample is composed of microscopic domains of pure pyrolytic boron nitride and boronated PG; the size of the domains was found by SEM to slightly exceed 0.1 $\mu$m. Evidence on the as-deposited 60% C–BN was inconclusive as to whether the material is a single-phase mixture of C, B, and N or a two-phase mixture of pyrolytic boron nitride domains and boronated PG domains.[7] Figure 3 shows an unexposed and an exposed AFM picture of the surface of the 60% C–BN sample. The figure appears to show the preferential etching of either PG or pyrolytic boron nitride domains. A preliminary study of pyrolytic boron nitride using oxygen plasma ashers showed the erosion yield to be $2.6 \times 10^{-26}$ cm$^3$/atom. This is over 42 times lower than the published $1.1 \times 10^{-24}$-cm$^3$/atom erosion yield of PG.[6] This suggests that the PG is being preferentially etched, leaving pyrolytic boron nitride domains. This behavior was observed in both the as-deposited and hot-pressed materials.

Table 1 shows the surface roughness data for the 40% and 60% C–BN samples taken for three scan sizes with the AFM. The 1-$\mu$m scan has the greatest percentage change between the unexposed and exposed samples; namely, 59% for the 40% C–BN, and 238% for the 60% C–BN samples. The percentage change for the 100-$\mu$m scan was only 29% for the 40% C–BN and 36% for the 60% C–BN. This indicates the surface roughened on a submicrometer scale, for which the small scans were more sensitive. From these data it can be seen that the 40% C–BN sample was more stable in LEO than the 60% C–BN sample; this is to be expected, since pyrolytic boron nitride has a lower erosion yield than PG.

**Table 1 Rms surface roughness of 40% and 60% C–BN**

| Sample | Roughness, nm | | |
|---|---|---|---|
| | 1-$\mu$m scan | 10-$\mu$m scan | 100-$\mu$m scan |
| Unexposed 40% C–BN | 9.88 | 56.714 | 108.500 |
| Exposed 40% C–BN | 15.713 | 70.460 | 139.600 |
| Unexposed 60% C–BN | 9.343 | 15.619 | 133.137 |
| Exposed 60% C–BN | 31.586 | 37.377 | 181.667 |

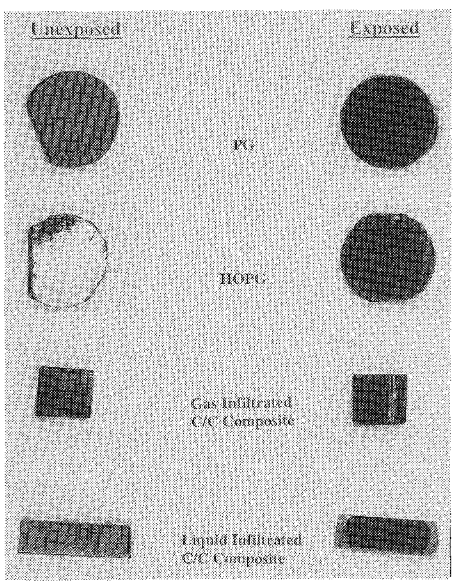
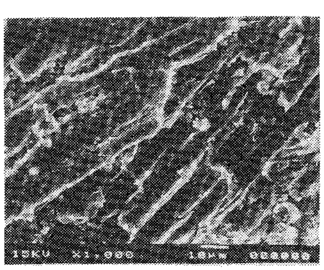


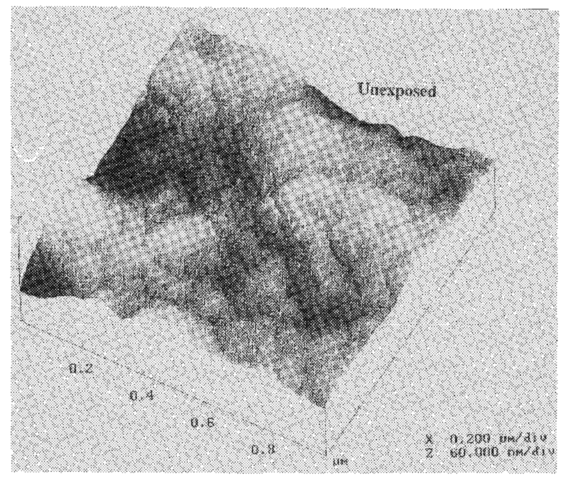

**Fig. 1 Visible degradation of samples after LEO exposure.**



**Unexposed**

**Exposed**

**Fig. 2 SEM images showing preferential etching of graphite binder in the liquid-infiltrated C/C composite.**



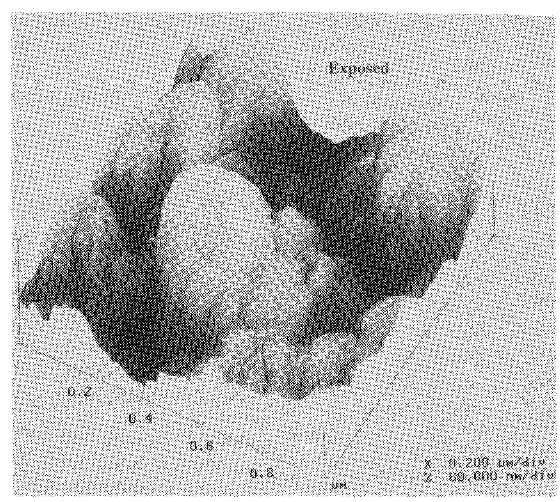




**Fig. 3 AFM data showing preferential etching of graphite domains in 60% C–BN.**

**Table 2 Measured density, mass loss, and calculated erosion yield for all samples**

| Material | $\rho$, g/cm$^3$ | $\Delta M$, mg | $\varepsilon$, cm$^3$/atom |
|---|---|---|---|
| PG | 2.171 | 0.62 | $0.538 \times 10^{-24}$ |
| HOPG | 2.096 | 0.77 | $0.692 \times 10^{-24}$ |
| 40% C–BN | 2.134 | 0.08 | $0.071 \times 10^{-24}$ |
| 60% C–BN | 1.782 | 0.21 | $0.222 \times 10^{-24}$ |
| C/C, liquid infiltration | 1.403 | 0.22 | $1.093 \times 10^{-24}$ |
| C/C, gas infiltration | 1.517 | 11.5398 | — |

The densities of the samples were determined from the physical dimensions and mass. The mass loss of each sample was the preflight mass minus the postflight mass. The AO fluence was nominally $2.2 \times 10^{20}$ atoms/cm$^2$. The erosion yield was calculated by

$$\varepsilon = \frac{\Delta M}{\rho A F} \tag{1}$$

The mass loss, density, and erosion yield for all samples are shown in Table 2. The densities and erosion yields of the PG and HOPG samples were within a factor of 2 of published data.[6] The C/C composites and C–BN samples were new materials in space, so there were no published data for comparison. The erosion yields for the C–BN samples were an order of magnitude lower than either the PG or the HOPG. The gas-infiltrated C/C composite lost mass because of mishandling, making the data unusable.

The degradation observed on pure graphite samples and the pitch in C/C composites indicate that these materials are not stable in LEO and will require protective coatings if deployed. The AO resistance of C–BN mixtures is very encouraging. These materials show promise as radiator materials without the need for protective overcoats, owing to the presence of boron nitride. The sample containing 40% carbon outperformed that containing 60% carbon. Much more work could be done in studying the effectiveness of bulk mixtures of carbon and boron nitride, as well as graphite fiber composites containing boron nitride in the binding matrix. Fiber composites of this type would be advantageous in that the thermal conductivity would be dominated by the graphite fibers and the AO resistance would be enhanced by the presence of boron nitride.

## Conclusions

Six different carbon-based materials were exposed to 42 h of LEO aboard Space Shuttle flight STS-46. The PG, HOPG, and C/C composites were degraded by AO exposure, making them less desirable for space-radiator applications. Measured erosion yields agreed well with published results. Samples of C–BN showed a strong resistance to AO erosion. This resistance increased as the percentage of carbon decreased, since the erosion yield of pyrolytic boron nitride is lower than that of PG by a factor of 42. In these C–BN mixtures, AO preferentially etches the graphitic component of the material at the surface, leaving the surface boron nitride rich. C/C composites degraded easily when exposed to LEO. The graphite binder eroded similarly to bulk pyrolytic graphite; however, graphite fibers in the C/C composites were found to erode much more slowly than the surrounding pitch binder.

## Acknowledgment

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## References

[1]Mirtich, M. J., and Kussmaul, M. T., "Enhanced Thermal Emittance of Space Radiators by Ion-Discharge Chamber Texturing," NASA TM-100137, March 1987.

[2]Rutledge, S. K., Banks, B. A., and Mirtich, M. J., "High Temperature Radiator Materials for Applications in the Low Earth Orbital Environment," NASA TM-100190, April 1987.

[3]"U.S. Standard Atmosphere 1976," NASA TM-X-74335, U.S. Government Printing Office, 1976.

[4]Banks, B. A., "Ion Beam Applications Research—A 1981 Summary of Lewis Research Center Programs," NASA TM-81721, April 1981.

[5]Moore, A. W., "Highly Oriented Pyrolytic Graphite," *Physics and Chemistry of Carbon*, Vol. 11, edited by P. L. Walker, Jr., and P. A. Thrower, Marcel Dekker, New York, 1973, pp. 69–185.

[6]Banks, B. A., Rutledge, S. K., and Brady, J. A., "The NASA Atomic Oxygen Effects Test Program," *Proceedings of the 15th Space Simulation Conference* (Williamsburg, VA), Oct. 1988.

[7]Moore, A. W., Strong, S. L., Doll, G. L., Dresselhaus, M. S., Spain, I. L., Bowers, C. W., Issi, J. P., and Piraux, L., "Properties and Characterization of Codeposited Boron Nitride and Carbon Materials," *Journal of Applied Physics*, Vol. 65, No. 12, 1989, pp. 5109–5118.

[8]Hedin, A. E., "MSIS-86 Thermospheric Model," *Journal of Geophysical Research*, Vol. 92, No. A5, 1987, pp. 4649–4662.

[9]Rutledge, S. K., Banks, B. A., DiFilippo, F., Brady, J., Dever, T., and Hotes, D., "An Evaluation of Candidate Oxidation Resistant Materials for Space Applications in LEO," NASA TM-100122, Nov. 1986.

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