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The Effects of Atomic Oxygen on the Thermal Emittance of High Temperature Radiator Surfaces

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THE EFFECTS OF ATOMIC OXYGEN ON THE THERMAL EMMITTANCE OF HIGH TEMPERATURE RADIATOR SURFACES

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SUMMARY

Radiator surfaces on high temperature space power systems such as the SP-100 space nuclear power system must maintain a high emittance level in order to reject waste heat effectively. One of the primary materials under consideration for the radiators is carbon-carbon composite. Since carbon is susceptible to attack by atomic oxygen in the low Earth orbital environment, it is important to determine the durability of carbon composites in this environment as well as the effect atomic oxygen has on the thermal emittance of the surface if it is to be considered for use as a radiator. Results indicate that the thermal emittance of carbon-carbon composite (as low as 0.42) can be enhanced by exposure to a directed beam of atomic oxygen to levels above 0.85 at 800 K. This emittance enhancement is due to a change in the surface morphology as a result of oxidation. High aspect ratio cones are formed on the surface which allow more efficient trapping of incident radiation. Erosion of the surface due to oxidation is similar to that for carbon; so that at altitudes less than \(~600\) km, thickness loss of the radiator could be significant (as much as 0.1 cm/year). A protective coating or oxidation barrier forming additive may be needed to prevent atomic oxygen attack after the initial high emittance surface is formed. Textured surfaces can be formed in ground based facilities or possibly in space if emittance is not sensitive to the orientation of the atomic oxygen arrival that forms the texture.

INTRODUCTION

Background

The weight of high temperature radiators for space nuclear power systems such as the SP-100 power system can represent up to 20 percent of the power system mass (fig. 1). Minimization of such a power system weight is thus greatly dependent upon the radiator design and performance. There are two techniques that can be used to reduce the weight of the radiator. One technique is to use a less dense material to construct the radiator. Table I contains a list of some typical radiator materials and their densities. The most attractive material is carbon-carbon composite with an average density of approximately 1.5 to 2.0 g/cm$^3$ which is less dense than typical refractory metal or aluminum radiator surfaces and has a high thermal conductivity.
Carbon-carbon composite materials are also stable at the operating temperature range expected for radiators for thermoelectric conversion systems (700 to 900 K) and for Stirling engine systems (525 to 650 K).

The second technique to reduce weight of the radiator is to improve its ability to transport heat which would result in a lower surface area requirement. This is accomplished by improving the thermal emittance of the surface at the operating temperature. Initially, the thermal emittance of typical metal radiators at an operating temperature of 800 K range from 0.04 for copper to 0.27 for titanium (ref. 1). Carbon-carbon composite thermal emittances at this temperature are substantially higher typically ranging from 0.46 to 0.77 depending on the manufacturing process. The desired thermal emittance for radiators for SP-100 is at least 0.85. There has been much work in the thermal emittance enhancement of metal radiator surfaces in an attempt to reach this level that have been successful (refs. 1 to 3). It would be similarly desirable to enhance the thermal emittance of carbon-carbon composite radiator surfaces to the 0.85 level to take advantage of the low density of this material and minimize the radiator surface area at the same time.

In low Earth orbit, atomic oxygen is the most predominant species from altitudes of approximately 180 to 650 km (ref. 4). It is produced by the photodissociation of molecular oxygen by photons of 243 nm wavelength from the sun (ref. 5). As a spacecraft passes through the atmosphere at these altitudes it impacts the atomic oxygen at energies between 4 and 5 eV. Atomic oxygen is a highly reactive species, and at these energies can break chemical bonds and react with many polymeric materials and some metals (ref. 4). Carbon has an erosion yield of approximately $1.2\times10^{-24}$ cm$^3$ per oxygen atom arriving at the surface. This would result in a thickness loss of roughly 50 µ at an altitude of ~400 km over a 1-year period. The desired life of a spacecraft radiator is generally about 15 years.

Emittance Enhancement of Carbon-Carbon Composites

For a diffusely reflecting surface, the hemispherical spectral emittance is in general equal to the absorptance at the same wavelength (ref. 6). Therefore, making the surface a better absorber at selected wavelengths would improve the emittance. If the roughness of a surface is greater than the wavelength of the radiation, multiple reflections on the surface will occur which results in a higher emittance level (ref. 6). Roughening of metal surfaces has been found to improve their emittance (refs. 1 to 3). It would be most desirable to roughen a C-C composite surface so that there would be finely spaced high aspect ratio cones on the surface to emit radiation at high temperatures. Application of paints to the surface would also provide emittance enhancement, however, adherence of the coating would be a concern at high temperature. By texturing the radiator surface, the emittance is enhanced by the surface morphology of the radiator, and since it is a part of the bulk material, adherence is not a great concern.

In low Earth orbit, most materials exposed to ram oriented atomic oxygen develop a surface texture (ref. 7). Carbon develops a very fine conelike structure on the surface upon exposure. Directed arrival of atomic oxygen could be used to produce a texture on the surface that would enhance the thermal emittance.
This paper discusses use of a directed atomic oxygen beam to enhance the thermal emittance of carbon-carbon composites, and the surface loss resulting from exposure of these composites to atomic oxygen.

EXPERIMENTAL APPARATUS AND PROCEDURE

Carbon-Carbon Composites

Carbon-carbon composites from five different manufacturers were used for evaluation. Generally, these were comprised of pan or pitch based carbon fibers woven into a cloth, then impregnated with phenolic resin, formed under heat and pressure, carbonized, densified with pitch and graphitized. Two-dimensional weave carbon-carbon composites were supplied by Rohr Industries, Kaiser Aerotech, and Rocketdyne. In addition to the two-dimensional C-C composite (C773-1), Rocketdyne supplied a harness weave C-C composite with carbon chemically vapor deposited on the surface (Panel-8); two-dimensional weave C-C composite with an SAIC-2A (Si, B, and Zr) oxidation inhibitor (C741C); and a two-dimensional weave C-C composite with 2.9 at % tantalum as an oxidation inhibitor (C536B). Fiber Materials Inc. supplied a four-dimensional weave C-C composite and a composite made with isostatically pressed chopped fibers. General Electric supplied a three-dimensional C-C composite with silicon carbide on the surface formed by deposited silicon that was flame melted into the composite. Pyrolytic graphite manufactured by Union Carbide was included for comparison and as a flux calibration for the atomic oxygen beam. Samples were weighed on a Sartorius balance after dehydrating in vacuum until no mass loss was observed in order to minimize errors in the mass loss measurement due to absorbed water. This generally required >48 hr of vacuum dehydration. Measurements of mass were repeated after each atomic oxygen exposure within 5 min of removal from vacuum.

Atomic Oxygen Exposure Source

Directed atomic oxygen exposure was performed with an oxygen ion source (end Hall gridless source) from Commonwealth Scientific. Samples were located 25 cm downstream of the source anode face on a water cooled sample holder where they were exposed to a 90 eV directed beam of a mixture of O$_2^+$ and O$. Pressure in the vacuum chamber was 10^{-4}$ torr during source operation and 10^{-6} torr background with the source off. A water cooled shield between the sample holder and the source was used to reduce the amount of heat radiating on the samples from the cathode filament and to prevent any filament material from depositing on the samples. A more complete description of the source is given in reference 8.

Emittance Measurement

The spectral hemispherical emittance was determined from two instruments. A Perkin Elmer Lambda-9 UV-VIS-NIR spectrophotometer was used to measure the spectral hemispherical reflectance over wavelength ranges of 250 to 2500 nm and the Hohlraum Reflectometer was used over the 1500 to 15 000 nm wavelength range. By overlapping the results from the two, the reflectance as a function of wavelength was obtained for each sample. Since the samples are not transmissive, the spectral hemispherical emittance which is equivalent to the
spectral hemispherical absorptance for these samples could be obtained by subtracting the reflectance values at each wavelength from unity. The total hemispherical emittance at each temperature was obtained by integrating the emittance versus wavelength curve with respect to the blackbody curve at the temperature of interest by using the equation below (ref. 6).

\[
\varepsilon(T_A) = \int_0^{\infty} \frac{\varepsilon_{\lambda}(\lambda, T_A) - \varepsilon_{\lambda b}(\lambda, T_A)}{\sigma T_A^4} \, d\lambda
\]

where
- \( \varepsilon_{\lambda} \) emittance at a wavelength \( \lambda \)
- \( \varepsilon_{\lambda b} \) blackbody emittance at a wavelength \( \lambda \)
- \( \sigma \) Stefan Boltzmann constant
- \( T_A \) temperature of interest

The hohlraum reflectometer and the integration technique are discussed in more detail in reference 3.

RESULTS AND DISCUSSION

The carbon-carbon composites were exposed in two separate batches to the directed atomic oxygen beam due to the available space on the sample holder. Samples were removed from the vacuum chamber for emittance and mass measurements. Figure 2 contains the results from these exposures on the total thermal emittance at 500 and 800 K for both batches of radiator surfaces. All plots show an increase or no change in emittance with exposure time (which is directly proportional to the total amount of atomic oxygen arriving at the surface). The arrival rate in this case is assumed to be constant. The equivalent atomic oxygen fluence is calculated based on the loss rate of the pyrolytic graphite that was used as a control in all exposures and the erosion yield of carbon in space (1.2x10^{-24} cm^3/atom) (ref. 8). One interesting thing to note is that no matter what the initial composite total thermal emittance is, all appear to approach approximately the same end value after a fluence of approximately 4x10^{20} atoms/cm^2. At 800 K this value is between 0.85 and 0.90 which is higher than the desired value for radiator thermal emittance for space missions. The value at 500 K is slightly smaller. The three-dimensional carbon-carbon composites in general started out with the highest values of emittance, but after exposure to directed atomic oxygen, reach the same limiting emittance values as the two-dimensional weave composites. Weave pattern appears to play a minor role in thermal emittance once the surface has developed a full texture due to atomic oxygen exposure. Figure 3 illustrates the alteration in surface morphology for each composite upon exposure to atomic oxygen. Scanning electron photomicrographs show development of a cone structure on all surfaces of between 3 and 5 \( \mu \) in height except for the General Electric three-dimensional C-C composite which had SiC on the surface. This sample did not show the characteristic texture on the surface and appeared to develop a protective coating. Etch pits occur where the coating is not completely covering the surface. The Rocketdyne samples containing the oxidation inhibitor did not appear to form a protective covering on the surface although the braid pattern overall on these samples is more visible after exposure (fig. 4). These samples also appeared to have slightly smaller
cone heights overall than samples which did not contain any inhibitor. The amount of oxidation inhibitor in these samples was very small (<3 at %).

Figure 5 contains the total thermal emittance versus temperature plots for each of the composites that were exposed in order to provide a better feel for the total emittance of a radiator composed of this composite over a range of operating temperatures. In general, atomic oxygen exposure of a small amount produced the greatest effect on high temperature thermal emittance which would make sense since high temperature is the shortest wavelength radiation and this would be affected more easily with a small amount of texture. As cone height increases, the thermal emittance at lower operating temperatures also improves. The General Electric C-C composite is the only one which showed an almost negligible change in emittance with exposure.

Figure 6 contains the mass loss for each composite as a function of equivalent atomic oxygen fluence. All of the composites, including those with oxidation inhibitors exhibited approximately the same mass loss rate. This was even true for the General Electric C-C composite which appeared to develop an oxidation resistant coating on the surface. If such a coating is developing, the mass loss rate should decline with exposure. If the coating is not protecting, the surface should develop a texture similar to that of the other composites. The mass loss rate can be an important issue to consider depending on the altitude at which the spacecraft will operate. Figure 7 illustrates the thickness loss of C-C that can be expected in 1-year at various altitudes. If operation is above ~700 km in altitude, a 15-year exposure should result in the removal of <11 μm from the surface. For most radiators, this would be an insignificant loss. At lower altitudes, the loss can become significant. At lower altitudes, an atomic oxygen resistant coating or self developing barrier is needed in order to prevent further removal of C-C once the radiator is textured. For higher altitude applications and for radiators that develop their own atomic oxygen resistant barrier upon exposure, it may be possible to orient the radiator into the ram atomic oxygen in low Earth orbit and allow the environment to texture the radiator prior to proceeding to the operating altitude. Orientation in this case may be critical and more difficult to achieve than texturing in a ground based system. A textured surface subjected to a sweeping atomic oxygen arrival may remove the texture thereby reducing the thermal emittance. Figure 8 illustrates the amount of time in orbit at various altitudes needed to texture a ram oriented flat surface.

CONCLUSIONS

Exposure to a directed beam of atomic oxygen alters the surface morphology of a carbon-carbon composite surface such that it develops high aspect ratio finely spaced cones on the surface that improves the ability of the surface to emit radiation. Emittance in general has been shown to improve by texturing to almost a factor of two for some composites. Values of emittance at 800 K for textured composites is greater than 0.85 which is the desired emittance for most space based radiator systems. These values are achieved after exposure to a fluence of ~4x10^20 atoms/cm^2. Mass loss for all composites is similar to that for carbon. In low Earth orbit, thickness loss may be significant at altitudes <700 km, therefore a protective coating or surface which develops a protective barrier on exposure may be needed for these applications. Textured high emittance surfaces can be formed by ground based exposure to atomic oxygen or possible exposure in space at low
altitudes. The latter may not be as practical if emittance is sensitive to
the orientation of the atomic oxygen arriving on the surface.

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<table>
<thead>
<tr>
<th>Material</th>
<th>Density, g/cm³</th>
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<tbody>
<tr>
<td>Copper</td>
<td>8.9</td>
</tr>
<tr>
<td>Niobium - 1 percent Zirconium</td>
<td>8.6</td>
</tr>
<tr>
<td>304 Stainless steel</td>
<td>8.0</td>
</tr>
<tr>
<td>Titanium</td>
<td>4.5</td>
</tr>
<tr>
<td>Titanium - 6 percent Aluminum</td>
<td>4.5</td>
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<tr>
<td>Aluminum - 4 percent Vanadium</td>
<td>4.5</td>
</tr>
<tr>
<td>Aluminum alloys</td>
<td>2.8</td>
</tr>
<tr>
<td>Carbon-Carbon composite</td>
<td>1.5 to 2.0</td>
</tr>
</tbody>
</table>


(Values for C-C Composite obtained from C-C composite suppliers)
FIGURE 1. - ARTIST'S CONCEPT OF A NUCLEAR POWERED SPACECRAFT SHOWING RADIATOR PANELS COVERING MUCH OF THE OUTER SURFACE.

FIGURE 2. - TOTAL THERMAL EMITTANCE AS A FUNCTION OF THE TOTAL ATOMIC OXYGEN ARRIVAL FOR CARBON-CARBON COMPOSITES THAT WERE EXPOSED.
(a) ROHR C-C COMPOSITE.

(b) ROHR C-C COMPOSITE AFTER ATOMIC OXYGEN DIRECTED EXPOSURE AT A FLUENCE OF 4.2x10^{20} ATOMS/CM².

FIGURE 3. - SCANNING ELECTRON PHOTOMICROGRAPHS OF C-C COMPOSITES BEFORE AND AFTER ATOMIC OXYGEN EXPOSURE.
(c) KAISER A C-C COMPOSITE.

(d) KAISER A C-C COMPOSITE AFTER ATOMIC OXYGEN DIRECTED EXPOSURE AT A FLUENCE OF 4.2x10^{20} ATOMS/cm².

FIGURE 3. - CONTINUED.
(e) KAISER C-C COMPOSITE.

(f) KAISER C-C COMPOSITE AFTER ATOMIC OXYGEN DIRECTED EXPOSURE AT A FLUENCE OF $4.2 \times 10^{20}$ ATOMS/CM$^2$.

FIGURE 3 - CONTINUED.
(g) Fiber materials 4-D weave C-C composite.

(h) Fiber materials 4-D weave C-C composite after atomic oxygen directed exposure at a fluence of $4.2 \times 10^{20}$ atoms/cm$^2$.

FIGURE 3. - CONTINUED.
(i) FIBER MATERIALS ISOSTATICALLY PRESSED C-C COMPOSITE.

(j) FIBER MATERIALS ISOSTATICALLY PRESSED C-C COMPOSITE AFTER ATOMIC OXYGEN DIRECTED EXPOSURE AT A FLUENCE OF $4.2 \times 10^{20}$ ATOMS/cm$^2$.

FIGURE 3. - CONTINUED.
(K) GENERAL ELECTRIC C-C COMPOSITE.

(1) GENERAL ELECTRIC C-C COMPOSITE AFTER ATOMIC OXYGEN DIRECTED EXPOSURE AT A FLUENCE OF 5.8x10^{20} ATOMS/CM^2.

FIGURE 3. - CONTINUED.
(m) ROCKETDyne PANEL-8 C-C COMPOSITE.

(n) ROCKETDyne PANEL-8 C-C COMPOSITE AFTER ATOMIC OXYGEN DIRECTED EXPOSURE AT A FLUXECE OF $5.8 \times 10^{20}$ ATOMS/cm$^2$.

FIGURE 8. - CONTINUED.
ROCKETDYNE C536-B C-C COMPOSITE.

ROCKETDYNE C536-B C-C COMPOSITE AFTER ATOMIC OXYGEN DIRECTED EXPOSURE AT A FLUENCE OF $5.8 \times 10^{20}$ ATOMS/CM$^2$.

FIGURE 3. - CONTINUED.

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ROCKEIDYNE C773-1 C-C COMPOSITE.

ROCKEIDYNE C773-1 C-C COMPOSITE AFTER ATOMIC OXYGEN DIRECTED EXPOSURE AT A FLUENCE OF $5.8 \times 10^{11}$ ATOMS/cm$^2$.

FIGURE 3. - CONTINUED.
ROCKETDyne C741C C-C Composite.

ROCKETDyne C741C C-C Composite after atomic oxygen directed exposure at a fluence of $5.8 \times 10^{20}$ atoms/cm$^2$.

Figure 3. - Concluded.
(b) C-C composites from batch 1 as received (top) and after texturing with atomic oxygen (bottom). Left to right, Rohr, Kaiser A, Kaiser C, Fiber Materias 4-D weave, and Fiber Materias isostatically pressed.

FIGURE 4. - C-C composites unexposed and exposed to directed atomic oxygen (fluence levels identical to those in Figure 3).
FIGURE 5. - TOTAL THERMAL EMITTANCE AT VARIOUS EQUIVALENT FLUENCE LEVELS AS A FUNCTION OF OPERATING TEMPERATURE.
ATOMIC OXYGEN FLUENCE, ATOMS/cm²

- 0
- $1.90 \times 10^{20}$
- $3.66 \times 10^{20}$

**Figure 5.** CONTINUED.
Figure 5. - Concluded.

Figure 6. - Mass loss as a function of equivalent atomic oxygen fluence.
FIGURE 7. - THICKNESS LOSS EXPECTED FOR A CARBON-CARBON COMPOSITE EXPOSED ONE YEAR AT A FIXED ALTITUDE.

FIGURE 8. - TIME TO OBTAIN DESIRED EMITTANCE AT A FIXED ALTITUDE IN LOW EARTH ORBIT FOR A RAM ORIENTED, FLAT, CARBON-CARBON COMPOSITE SURFACE.
Radiator surfaces on high temperature space power systems such as the SP-100 space nuclear power system must maintain a high emittance level in order to reject waste heat effectively. One of the primary materials under consideration for the radiators is carbon-carbon composite. Since carbon is susceptible to attack by atomic oxygen in the low earth orbital environment, it is important to determine the durability of carbon composites in this environment as well as the effect atomic oxygen has on the thermal emittance of the surface if it is to be considered for use as a radiator. Results indicate that the thermal emittance of carbon-carbon composite (as low as 0.42) can be enhanced by exposure to a directed beam of atomic oxygen to levels above 0.85 at 800 K. This emittance enhancement is due to a change in the surface morphology as a result of oxidation. High aspect ratio cones are formed on the surface which allow more efficient trapping of incident radiation. Erosion of the surface due to oxidation is similar to that for carbon, so that at altitudes less than approximately 600 km, thickness loss of the radiator could be significant (as much as 0.1 cm/year). A protective coating or oxidation barrier forming additive may be needed to prevent atomic oxygen attack after the initial high emittance surface is formed. Textured surfaces can be formed in ground based facilities or possibly in space if emittance is not sensitive to the orientation of the atomic oxygen arrival that forms the texture.