OXIDATION-RESISTANT HIGH-TEMPERATURE MATERIALS

Navy missiles are becoming faster and are also able to intercept incoming targets at greater ranges. Unfortunately, increased missile speed means increased material temperatures, and some missile components are exposed to temperatures exceeding 5000°F. In the past thirty years, the Applied Physics Laboratory has participated in the development of new high-temperature materials for use in Navy missiles. This article gives a brief history of our test and analysis of various candidate materials. Free jet tests indicate that carbon/carbon infiltrated with hafnium carbide can survive surface temperatures of 4800°F for more than ten minutes.

INTRODUCTION

Rockets and ramjets are two basic types of missile propulsion systems. Rockets carry both fuel and oxidizer (such as oxygen) in the missile. Ramjets also carry fuel but no oxidizer. Rather, they have inlet scoops that capture air and burn it with the fuel in a combustion chamber. Ramjets are more complicated and require additional weight for the inlet and combustor. Rockets are an excellent form of propulsion for short-range missiles, which require that relatively small amounts of oxidizer be carried on board. But ramjets are better suited for longer-range missiles, since the added weight and complexity of the air breathing components are more than offset by the elimination of oxidizer weight and volume.

Ramjets can be classified into two subdivisions: subsonic combustion ramjets and supersonic combustion ramjets (scramjets). In the former, the incoming air is slowed from supersonic speeds in front of the inlet to subsonic speeds in the combustor. This slowing allows ample time for the fuel to mix and burn with the inlet air. At Mach numbers above 4, however, the pressure losses due to shocks and heat losses due to the high air temperatures make it more efficient to burn the fuel at supersonic speeds, which reduces shock losses in the inlet and lowers the combustor air temperature. Two problems are associated with a supersonic combustor: it is difficult to burn the fuel and air in a reasonably short combustor, and the fuel is difficult to ignite. The Laboratory has developed a scramjet missile configuration (Fig. 1) that solves these problems by inducting a small portion of the air into a subsonic combustor, which acts as a pilot for the supersonic combustor. Finding a wall material for this combustor has presented a problem, since combustor temperatures exceed 5000°F, and excess oxygen can react with the combustor wall.

Figure 1. Configuration of the supersonic combustion ramjet (Mach no. = 2, gas temperature = 4500°F, pressure = 1 atm).
Missile component steady-state temperatures increase dramatically with missile Mach number (Fig. 2). At hypersonic Mach numbers (i.e., above Mach 5), combustor temperatures can exceed 5000 °F. The design of hypersonic tactical combustors poses many severe structural problems whose solutions are limited by available materials. Several materials have been investigated as ramjet combustor insulators, including carbon/carbon (C/C) composites, pyrolytic graphite (PG), PG with a silicon carbide (SiC) coating, metal-loaded C/C composites, and C/C composites coated or impregnated with high-temperature metal oxides and metal carbides.

To characterize these materials, they must be tested under simulated flight temperatures, pressures, and gas flow shear rates. Over the past twenty years, APL has performed many thermal tests on promising new missile component materials. Recent tests show that hafnium carbide is an excellent material, with very low surface recession rates at surface temperatures as high as 4800°F. In what follows, brief descriptions of some of the material evaluation tests conducted by the Laboratory are presented.

**SILICONE ELASTOMERS**

In the early 1970s, APL conducted experimental investigations of silicone elastomers and phenolic-based ablative materials for use as insulators in advanced ramjet combustors. From that work, the commercially available silicone elastomer, DC 93-104, emerged as the most promising. Its use, however, is primarily limited to temperatures below 2000°F and in a reducing atmosphere. Therefore, it is not a good candidate material for insulating a ramjet combustor. Another of its restrictions is geometry changes caused by ablation during flight. Thus, DC 93-104 utility is confined to surfaces where geometry change is not critical; consequently, it cannot be used on leading edges or nozzle throats.

**GRAPHITE MATERIALS**

During the 1970s, new graphite materials were developed with less ablation and higher temperature capabilities than DC 93-104. These materials were made from solid graphitized carbon and C/C laminates. To use these materials in flight, one must be able to accurately predict erosion rate so that an optimum balance can be achieved for weight, missile performance, and cost. The Laboratory undertook an experimental program to determine surface recession rates as functions of surface temperature, pressure, gas flow rate, and gas composition.¹

The resulting database was obtained using an experimental test apparatus (Fig. 3) developed at APL. It consists of an electrically heated graphite electrode that can

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heat material samples up to 4500°F. Specimens of Union Carbide’s ATJ graphite, about 3.3 mm in diameter and 1.8 mm thick, are placed in a shallow cylindrical recess at the tip of the heater. Since ablation is a function of the gases in the environment, one must simulate the flight environment gases flowing over the sample. This simulation was done by injecting gases normal to the surface through a nozzle. Tests were run at flow rates between 12 and 22 m/s using air, oxygen, carbon dioxide, and carbon monoxide. Tests were also run with a mixture of nitrogen, oxygen, carbon dioxide, and carbon monoxide, which simulates the combustion products of Shelldyne-H fuel burned with the optimal amount of oxygen (i.e., equivalence ratio = 1.0) and with less than the optimal amount of oxygen (i.e., equivalence ratio = 0.3). Specimen surface temperatures ranged from about 2000°F to 4500°F. Figure 4 presents a summary of results. As expected, the recession rate increased with temperature. The test extended the results of Matsui et al. from 2700°F to temperatures approaching 4500°F. The development of this test apparatus gives us a quick, relatively inexpensive means of evaluating high-temperature materials.

CARBON/CARBON COMPOSITES

Carbon/carbon composite materials are particularly attractive for supersonic combustor applications since they possess the strength necessary to withstand the high pressures of a combustor. But they also have rather high surface recession rates, because at high temperatures carbon reacts with oxygen to form CO and CO₂. Consequently, relatively thick-walled combustors are required to ensure adequate strength at the end of flight. These thick walls are heavy and occupy space that could be used for additional fuel. Two experimental programs were initiated to reduce the surface recession rate of C/C composites.

Metal-Loaded C/C Composites

The first test program consisted of loading C/C materials with high-melting-point zirconium and hafnium metal whiskers. Loaded C/C composite samples were exposed to two simulated scramjet engine combustor environments typical of a long-range, high-altitude flight and a sea-level flight. Tests were conducted in the McDonnell Douglas High Impact Pressure (HIP) arc heater test facility. Secondary gases and water were added to the stream to simulate combustion gas products.

In addition to the metalized materials, the following reference materials were used: virgin C/C, PG-coated C/C, PG/SiC-coated ATJ graphite, and ATJ graphite. Test samples 1.25 × 1.25 × 4.03 cm long were placed at various angles from 10° to 25° to the flow. Surface temperatures of 4500°F were obtained.

Average recession rates for each material type were determined from pre- and post-test sample weight measurements. The results indicated no benefit from the metal additives. In fact, the limited data suggested that metal additives increased recession rates. Although most of the metalized samples had lower recession rates than the ATJ graphite samples, they had a greater total recession than the other reference materials. The PG and PG/SiC materials clearly showed superior performance over the metal-loaded C/C materials. Movies of the samples taken during testing showed some mechanical material removal for the C/C materials. Apparently, metal impregnation reduces the shear strength capabilities of C/C and increases its surface recession rate slightly.

Oxidation-Resistance Coatings on C/C Composites

Although loading C/C materials with metal whiskers proved to be ineffective, we felt that C/C composites could be protected from the oxidizing atmosphere with a thin layer of high-temperature metal oxide. Candidate protective materials are listed in Table 1. In general, carbides have the highest melting temperatures. A test program using the HIP facility (sponsored by the Naval Surface Warfare Center) was initiated to determine which material could be used in the supersonic combustor environment. Compounds of hafnium, zirconium, and thorium were developed as coatings and/or were impregnated into the surface of two- and three-dimensional C/C composites. The C/C matrix materials were coated with HfC, HfC/SiC, HfC/HfB₂, HfB₂, HfTaB₂, and iridium/thorium. In addition, Refractory Composites, Inc., developed a method allowing for the chemical vapor infiltration (CVI) of HfC into the carbon weave.

These samples were tested under simulated combustor conditions. In general, the coated materials performed well for short periods. In time, however, hot gases penetrated into the C/C substrate, eroding it and undermining the coating. The HfC coating remained very resistant to the flow and stayed on the surface until the undermining became too great and the coating spalled off.
Program goal

Oxidation-Resistant High-Temperature Materials

Figure 5. Combustor condition screening results from the McDonnell Douglas high-impact pressure arc heater facility. (Nominal surface temperature = 5000°F, nominal surface pressure = 20 psia, test duration = 30 s.) The following were tested: black, chemical vapor infiltration; green, coatings on graphite; blue, graphite; amber, composite; red, coated/glazed C/SiC composite.

Table 1. Candidate combustor protective compounds.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Melt or decomposition temperature (°F)</th>
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<tbody>
<tr>
<td>Carbides (TaC, HfC, NbC, ZrC, TiC)</td>
<td>7200-5500</td>
</tr>
<tr>
<td>Borides (HfB₂, TaB₂, ZrB₂, NbB₂, TiB₂)</td>
<td>6100-5500</td>
</tr>
<tr>
<td>Nitrides (HfN, TaN, ZrN, TiN)</td>
<td>6000-5300</td>
</tr>
<tr>
<td>Oxides (ThO₂, HfO₂, MgO, ZrO₂)</td>
<td>5800-5000</td>
</tr>
<tr>
<td>Metals (W, Re, Os, Ta)</td>
<td>6200-5400</td>
</tr>
<tr>
<td>Nonmetals (C)</td>
<td>6800</td>
</tr>
</tbody>
</table>

With cvT, HfC samples performed better (Fig. 5). They were tested for up to 10 min and showed very little mass loss. Samples tested for 5 min were not visually different from those tested for 10 min (Fig. 6, samples 10 and 11). The ability of HfC-infiltrated materials to withstand temperature cycling was tested to a limited degree, by applying two thermal exposures to a single sample (sample 9, Fig. 6). The sample was heated the first time for 2 min, then cooled to room temperature for 3 h and heated again for 3 min. There was a slight spallation of the coating during the initial heating and no discernible change during the second heating. After the test, the sample had the same visual appearance as samples heated for single cycles of 5 and 10 min (Fig. 6).

CONCLUSIONS

The Laboratory has participated in the development of several oxidation-resistant materials for supersonic combustors. Wind tunnel tests indicated that DC 93-104 is adequate when used in a nonoxidizing atmosphere at temperatures below 2000°F. An apparatus was developed to test graphite and C/C materials in an oxidizing atmosphere at high temperatures. The best materials from these screening tests were evaluated in the HIP free jet test facility. We found that HfC-infiltrated C/C composites had the lowest recession rates and could survive exposure to a 5000°F oxidizing flow for periods exceeding 10 min. The results indicate that HfC-infiltrated C/C should make a good supersonic combustor material. Additional tests are required to evaluate HfC at times greater than 10 min.
REFERENCES


THE AUTHOR

ROBB W. NEWMAN received his B.S. degree in mechanical engineering from Cornell University in 1965 and his master’s degrees in space technology, administrative science, and computer science from The Johns Hopkins University. He joined APL in 1966 and has been involved in programs in transpiration cooling, laser heating, and high-temperature materials testing. He has served as co-chair of the Standard Missile, BLK IV Airframe Structure Coordinating Committee. Mr. Newman is currently interested in intelligent systems and is supervisor of the Applied Intelligent Systems Section of the BumbleBee Engineering Group.