"MICROTHERSPARATION", SELF-CONTAINED PROTECTION FROM TRANSIENT ENVIRONMENTS ABOVE 6000°F

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Abstract

A self-contained, thermally protective mechanism is described and discussed. The mechanism is activated by a catalyst which operates within a composite material composed of a refractory metal matrix and an internally ablating oxide. Physicochemical conversion of the oxide from the solid to the vapor state involves several energy absorption processes. The effusing gases resulting from these processes provide a protective film on the exposed surfaces. The potential of the mechanism, results of full-scale testing of tungsten-base composites with current solid propellants, and future applications are discussed.

Introduction

The advancing technology of rockets, missiles, and space vehicles has succeeded in bringing to the fore the importance of materials engineering. More and more frequently new applications cannot be made successful without matching the time-temperature capabilities of materials with the operational time-temperature requirements. Typical applications requiring this type of matching are: nose cones, leading edges, combustion chambers, and nozzle throats. Steurer (1), Pellini and Harris (2), and King (3), among others, have reported on the basic materials and types of protection systems with the greatest potential for a given application.

For exposures of a few minutes and environmental temperatures in the 5000-6000°F range, heat sink systems with or without film cooling protection are adequate for homogeneous materials such as tungsten. At increased transient heat fluxes (up to four minutes at 1000-10,000 Btu/ft²·sec) the environmental temperatures may exceed the melting points of all known materials (2) and protective systems which absorb thermal energy by
Ablation, sublimation, or transpiration must be utilized. These mechanisms make use of the heats of change of state for energy absorption. Ablation systems utilize the state changes involved while carrying materials from the solid, through the liquid, to the gaseous state. Subliming systems involve materials which will pass directly from the solid to the gaseous state. Transpiring systems utilize the heat absorption of a second phase passing through a skeleton matrix. A significant problem which arises while attempting to carry materials through several changes of state is that of retaining the liquid phase until vaporization has occurred and its heat absorption potential fully utilized. Fillers are added to ablative systems in an attempt to accomplish this end. Sublimation does not present a problem since the liquid state does not exist. A well devised transpiration system can minimize this problem due to the capillary forces within the channels whereby the skeleton retains the liquid phase.

Transpiration, as it is currently interpreted, presents several potential drawbacks to versatile operation. First, the extremely small passages or capillaries which are needed to distribute the transpirant throughout the structure must be kept open at all times. This is necessary to prevent loss of cooling effects and resultant hot spots which lead to melting. Secondly, transpirant flow should be programmed to match the heat flux. If this is not done, the transpiration systems cannot be considered self-adjusting for a variety of conditions.

The above problems have been largely surmounted by a recent discovery at Bendix Products Division of a mechanism which is termed "Microtranspiration." This mechanism, operating in a tungsten composite, occurs in microscopic channels throughout the material. The presence of a catalyst within the material provides a means to open these channels during the exposure to high heat flux and to trigger the physicochemical energy absorption processes, which include reactions and state-changes of a transpirant material. The rate of gas production within the structure is determined primarily by the heat flux to the structure. Therefore, it may be said, that the Microtranspiration mechanism is self-controlling. The workability of this mechanism has been demonstrated by numerous no-erosion, sub-scale, and full-scale firings of solid propellant rocket motors utilizing these composites in the nozzle throat.

Development of the Hypothesis

Microtranspiration effects were discovered during a materials development program at Bendix which was initiated in 1958 and was designed to improve the strength-weight ratio and increase the operating temperature limitation of rocket nozzle inserts. Composites formed from tungsten and refractory oxides
were evaluated in sub-scale liquid and solid motors and found to be superior to pure tungsten. Early in 1960, full-scale firings of a second-stage Minuteman motor were successfully completed with zero erosion of a tungsten-beryllium oxide throat insert in a Bendix-designed nozzle.

A post-firing evaluation of the second-stage insert revealed micropores on the front-face surface which had been exposed to the hot combustion gases. The left portion of Figure 1 shows a bisected throat insert. The black dots are representative of micropores found on the curved front-face surface of tungsten composites after each firing. A rectangular portion of the insert cross-section was mounted in plastic and then deeply etched. The microstructure is shown on the right. Note the retention of the front-face structural integrity. This retained structure is responsible for zero-erosion firings. Adjacent to the front face is a permeable zone which extends in a rather uniform manner to a maximum depth of 0.150 in. Backing this up is the original composite structure which continues to the back face. Magnification of the enlargement in Figure 1 is indicated by the 0.150 in. line below the photomicrograph.

Discovery of the loss of the oxide from only the front face of the composite gave rise to conjecture that a self-contained transpiration mechanism was operative. Since the loss from the composite occurred only from the microcells of ceramic in the material microstructure, and escape of this ceramic was through micropores on the front-face surface, this proposed mechanism was termed "Microtranspiration".

To further study the oxide loss, a throat insert was infiltrated after firing with molten copper. It was then sectioned and its microstructure examined. Figure 2 compares the results of attempted infiltration of a throat insert before and after firing. The white matrix is tungsten, the grey-black areas ceramic, and the hatched constituent is copper. It can be seen that before firing no infiltration of copper occurs. After firing, the copper occupies many of the areas previously occupied by the oxide. This oxide loss occurs to a rather uniform depth along the surfaces exposed to the hot gases. Linear analysis of many microstructures of inserts, infiltrated after firing, revealed that the tungsten volume constituent remains nearly constant from the front face through the permeable zone to the back face. The ceramic constituent decreases in volume near the front face and then abruptly returns to the normal composition. This indicates that the oxide release occurs in a relatively narrow band at any given instant during firing.

A review of nozzle firings and experimental work revealed several important points: (a) The micropores were never found after firing on homogeneous materials such as tungsten but were always found on tungsten composites, (b) the loss of oxide is relatively uniform for a fixed insert composition fired in the
Figure 1. Sectional View of Throat Insert.
Figure 2. Oxide Loss from a Tungsten Composite.
same motor, (c) reports from several full-scale firings indicated that the Bendix tungsten composites showed less interface carbide formation than did pure tungsten, when both were in contact with a graphite back-up material. Laboratory tests have shown that the depth of this carbide formation is dependent upon temperature and this smaller depth of carbide is interpreted as resulting from lower back-face temperature. This indication of a lower temperature was supported by measurements made during firings, (d) a tungsten-aluminum oxide composite showed evidence of oxide loss from the surface of the material when heated in a furnace at 4000°F. On the colder walls of the furnace, a few inches from the heated specimen, whiskers of Al₂O₃ were found, indicating that vapor species were released. These data further supported our hypothesis that the transpirant was effusing as a gas through the front-face surface, absorbing energy en route, and providing a protective film.

The means by which the tungsten composite provides the mechanical retention of the molten material during vaporization is seen in Figure 3. This figure compares the ablation characteristics of an externally ablating material and an internally ablating material. In the homogeneous material shown on the left (4), the metal or ceramic begins to melt on the surface and the exhaust gas stream sweeps away a portion of liquid particles before the heat of vaporization is completely utilized. For applications such as rocket nozzle throats, where zero erosion is desirable, the mechanism provided by the microtranspiring composite shown on the right, provides for retention of the original surface and allows for complete utilization of the transpirant heat capacity.

The early work in the Bendix composite development program was done with tungsten-beryllium oxide composites. The beryllium oxide was considered desirable because of its high melting point, high specific heat, and relatively high conductivity. The hypothesis of Microtranspiration, however, indicated that the melting point should be of secondary importance to the capacity of the transpirant to absorb heat during phase changes and dissociation. Aluminum oxide then qualified as a potential transpirant because of its high heat of dissociation even though its melting point is about 1000°F lower than that of beryllium oxide. Rocket firing tests using tungsten-aluminum oxide composites supported the hypothesis.

Potential of the Mechanism

For a theoretical evaluation of the quantitative capacities of the composites to absorb heat, the end products of the reactions which occur during firing must be known. From this information, along with the heats of state-change, dissociation,
Figure 3. Ablation Characteristics of Homogeneous and Microtranspiring Composite Materials.
and reaction, the heat absorption capacities of the composites can be calculated. The work done by Inghram and Drowart (5) and Drowart, et al (6) indicated that aluminum oxide in a tungsten Knudsen cell heated to 4300°F yielded numerous molecular species which could be identified with a mass spectrometer. These data, extrapolated to 5500°F and shown in Figure 4, give the relationship between the high temperature vapor species in the tungsten-aluminum oxide system. At 4000°F the mole percentages of the two major vapor species are reported (6) as follows: Al-49 and O-35.

The total pressures of all species, even at 5500°F, is not sufficient to allow them to effuse against the high pressure existing along the front face, so the pressure of the vapor species must somehow be increased. This increase is accomplished by the presence of a catalyst which triggers the release of these gases and provides sufficient total internal pressure for the gases to effuse. Without the catalyst no Microtranspiration occurs. For proprietary reasons, it is not possible at this time to divulge the exact nature of the catalyst material. This requirement for a specific combination of high heat flux with a two-phase composite containing the necessary catalyst, is probably why this mechanism has not been reported previously.

Based on the vapor species indicated in Figure 4, a comparison of the heat absorption capacity of tungsten with three tungsten composites is shown in Figure 5. The solid lines compare the composites of 20 volume percent transpirant and the dashed lines represent the potential with 40 percent transpirant. Both types of oxide composites have been made, but full-scale testing to date has been confined to 20 percent oxide composites. It can readily be seen that potential heat absorption capacities of greater than 400 percent that of tungsten are indicated when these oxide composites are heated from room temperature to 6150°F, (melting point of tungsten).

The tungsten-copper composite is fabricated by infiltrating a porous tungsten body with a copper alloy. One problem is that the maximum volume percent copper to yield a usable part was found to be about 20 percent. Another problem with the tungsten-copper composite is the low melting point and high fluidity of the copper which results in loss of liquid transpirant before heat of vaporization is completely utilized. Because of the limited potential of the tungsten-copper composite, it was discarded in favor of the tungsten-oxide materials. Other advantages gained through the use of oxide transpirants are: (a) that the physicochemical changes associated with these oxides occur at higher temperatures, thereby making greater use of the matrix heat sink potential before internal ablation begins, and (b) the higher internal operating temperatures achieved with oxide transpirants reduces the heat flux to the throat.
Figure 4. High Temperature Vapor Species in the W-Al₂O₃ System.
Figure 5. Comparison of Heat Absorption Capacity from 70° to 6150°F.
insert, extending operating time. Therefore, the material operates in that desirable temperature range in which it retains adequate physical properties and yet utilizes much of its inherent heat sink capacity.

Based on heat absorption capacities, computations were made comparing the front-face temperatures of a tungsten-aluminum oxide composite with tungsten in the throat of a nozzle. As shown in Figure 6, the hypothetical extreme environment to which the 0.800 inch thick throat section was exposed, consisted of a gas temperature of 7000°F and a heat transfer coefficient of 2000 Btu/ft² hr °F. Within 14 seconds, the front-face surface of tungsten would have reached its melting point of 6150°F. The 40 volume percent aluminum oxide composite would have a front-face surface temperature of only 4700°F at 14 seconds, and 64 seconds would be required for the surface to reach 6150°F. The ΔT of 1500°F shown on Figure 6 indicates the potential of the Microtranspiration mechanism in a tungsten-oxide composite to provide thermal protection against 7000°F propellants.

The experimental results of Vassallo, et al (7) and Lapple, et al (8) using model systems have demonstrated the feasibility of internal ablation as a means of thermal protection. It is felt that Microtranspiration verifies in practice the experimental work performed by these investigators.

As the gases are formed internally and effused through the structure, they pass into the boundary layer which exists between the main stream of combustion gases and the throat insert face. The effused gases enter into this boundary layer in its lowest velocity region and thus relatively small mass effusion rates are required to produce significant thickening. The existence of the effused gases in the boundary layer will create two effects: (a) an effective thermal shielding of the surface of the insert, and (b) a chemistry change of the gas film immediately adjacent to the insert. Past studies by Gross, et al (9) and current investigations by Vassallo, et al (7) and Maloof (10) have indicated the potential thermal shielding effect of gases transpired into the boundary layer. While a quantitative value for the heat flux shielding of the effused gas in this system is not now available, it is felt that this factor is contributing significantly to the success of the Microtranspiration mechanism. The alteration of the boundary film chemistry effect can be described primarily as a dilution and shielding effect whereby potentially corrosive elements in the combustion gases may be prevented from reaching the surface of the insert, thereby reducing oxidation, corrosion, etc. Current studies are underway to evaluate this portion of the mechanism.

The gas evolution and cooling film protection of Microtranspiration are self-controlling in that at high heat flux
Figure 6. Throat Materials Comparison in Hypothetical Extreme Environment.
rates more gases are released, giving rise to more cooling and film protection thereby reducing surface temperatures. The cooling is statically performed so that no auxiliary pumping systems are required. This assures maximum reliability for the protective system.

While pure tungsten appears generally satisfactory for current propellant temperatures, other materials such as the tungsten-oxide composites will be required for operation at 7000°-8000°F. Microtranspiring tungsten composites have been successfully fired with many currently known solid propellants. A summary of the firings is shown in Table 1. While zero erosion has been found in all cases, some problems have been encountered in certain designs. Care must be exercised to take into account properties such as the thermal shock resistance of the composite materials. Some insert designs have successfully overcome this problem.

Future Applications

The mechanism is applicable to materials other than tungsten-base composites and should extend the range of usefulness for many materials to above the melting point of any constituent. The self-cooled nature of this class of materials means that composites can be used in transient environments of high temperatures since the structure itself will not reach these high temperatures. This assures that strength properties available in the moderate temperature range can be retained at elevated temperatures for limited periods. The composites, therefore, should be more resistant to mechanical erosion than pure tungsten because the wall operating temperatures are lower.

It is felt that Microtranspiration provides the key for material systems operating in the 7000-8000°F range of transient conditions. Studies are continuing at Bendix Products Division to obtain more information on this mechanism and its application for transient high heat flux environments.

Conclusions

Based upon information obtained to date regarding the mechanism of Microtranspiration and its effects, some conclusions may be drawn.

a. A material has been developed which exhibits an internal ablation mechanism proposed by theoretical studies of other investigators.

b. The mechanism, operating within a tungsten-oxide composite material, has been successfully tested in several, full-scale rocket nozzles exposed to current solid propellants.
Table 1. Solid Propellant Firings of Tungsten Composites

<table>
<thead>
<tr>
<th>MOTOR</th>
<th>TEST SOURCE</th>
<th>EROSION RATES</th>
</tr>
</thead>
<tbody>
<tr>
<td>MATERIAL EVALUATION</td>
<td>BENDIX, THIOLKOI, HERCULES (MINUTE-MAN PROPELLANT)</td>
<td>ZERO</td>
</tr>
<tr>
<td>PROPELLANT CHECK</td>
<td>GRAND CENTRAL, ROHM&amp;HAAS (UP TO 900 PSI - 6200°F)</td>
<td>ZERO</td>
</tr>
<tr>
<td>MINUTEMAN (FULL SCALE)</td>
<td></td>
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<tr>
<td>1st STAGE</td>
<td>THIOLKOI</td>
<td>ZERO</td>
</tr>
<tr>
<td>2nd STAGE</td>
<td>AEROJET&amp;THIOLKOI</td>
<td>ZERO</td>
</tr>
<tr>
<td>3rd STAGE</td>
<td>HERCULES</td>
<td>ZERO</td>
</tr>
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c. The mechanism is not limited to refractory metal composite systems, but can, by judicious choice of materials and fabrication methods, be extended to other matrix-transpirant systems.

d. The increased energy absorption potential, without increase in weight (with regard to pure tungsten), of the current tungsten-oxide composite should make it applicable for use in transient environments in the 8000°F range.

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References


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