Ablation Thermal Protection Systems

Suitability of ablation systems to thermal protection depends on complex physical and chemical processes.

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Many modern aerospace systems encounter temperatures in excess of those at which the usual structural materials can be expected to function properly. For example, high-speed flight and propulsion systems require active cooling of their primary structures at certain crucial times during their use. One of the methods by which this necessary active cooling is achieved is by use of an ablating system, that is, a system where the cooling is provided by a material that undergoes phase changes or chemical changes, with concomitant removal of the products of the change.

Systems Requirements and Thermal Protection

A vehicle flying at a high velocity compresses the air in front of it in the region of the leading edge of the vehicle. At supersonic speeds, the compression region is bounded by the vehicle surface and a shock wave. As a result of the compression, the air between the shock wave and the vehicle's surface is heated and its pressure is increased. The temperatures achieved in the air behind the shock wave by stagnation of the air relative to the vehicle at the specified flight conditions (Fig. 1) are called stagnation temperatures. The pressure achieved by the stagnation process is also shown. For example, at an altitude of 30 kilometers, a vehicle flying at 6 kilometers per second (about 13,500 miles per hour) will heat the air ahead of it to about 7000°K and pressurize it to about 10 atmospheres. This condition might be associated with an unmanned reentry vehicle. High stagnation temperatures associated with the high-speed flight region produce appreciable dissociation and some ionization of the air. The energies associated with the dissociation and ionization reactions of the air are appreciable and significantly increase the heat transfer to the surface of the flight vehicle.

The high rate of heat transfer in high-speed flight can be roughly related to the properties of the materials used and the radiation-equilibrium temperature (that which would be achieved by an ideal nonconducting structure which received heat at heating rate of the stagnation point, and radiated it back into space). The high-temperature layer of heated gas between the flight vehicle and the shock wave is considered to be transparent and nonradiating in the calculation of heat transfer. In relation to the problem of reentry materials, this assumption is reasonable at velocities usually achieved on ballistic flight or orbital reentry (about 6 to 7 km/sec) but is incorrect at reentry velocities associated with direct lunar and planetary return (about 10 km/sec). Figure 2 shows the radiation-equilibrium temperatures for vehicles with nose radii of 2.5 and 30 centimeters. If a velocity of 6 km/sec is maintained at an altitude of 30 km, the surface temperature exceeds 4000°K for the 2.5-cm nose. Severity of environment increases as velocity is increased or altitude is decreased, or both. Since the laminar stagnation point heating rate depends inversely on the square root of nose radius, the radiation-equilibrium temperatures are higher for the 2.5-cm radius. The calculation was based on an assumed surface emissivity of 0.9. The magnitude of the heating rates can be deduced from the lines of constant values of the product of heating rate and the square root of nose radius shown in Fig. 2. The high radiation-equilibrium temperatures shown for hypersonic flight in Fig. 2 imply a need for active cooling. In turn, the magnitude of the required cooling rate is roughly implied by the heating rates.

The difficulty of the materials problem is compounded by the severity of the oxidation that can occur and the mechanical stresses resulting from severe thermal gradients within the materials. Several methods are available for cooling an exterior structure to temperatures below the radiation-equilibrium temperature. The simplest cooling method relies entirely on heat conduction to the interior of the vehicle. With this method, sufficient mass must be provided to allow storage of the heat input while the interior temperature of the vehicle remains within reasonable limits. This simple "heat-sink" approach was applied to the design of some early reentry vehicles. A variation on this simple heat-sink approach would utilize channels behind the exposed surface in which a coolant is flowed. Depending upon the specific design, the attainable cooling rate would be limited by the heat conduction in the structure, the heat-transfer coefficient between the coolant and channel walls, the allowable coolant temperature rise, or the initial coolant temperature. After it passes through the cooling channels, the coolant must be stored hot or discarded from the vehicle. Recirculation would require a large refrigeration system to return the coolant to the proper initial temperature.

If the coolant is discarded at the heated surface, then additional advantages can be achieved. First, there is no need for plumbing to carry the coolant away from the heated region. Second, the coolant can be heated to near the stagnation temperatures shown in Fig. 1. This allows some advantage to be taken of phase-change and chemical-reaction energies. Third, certain aerodynamic effects of introducing the coolant into the boundary layer can be beneficial in significantly reducing the net heat transfer.

The transpiration cooling system described above is, in the true sense, an ablation system in that a small quantity of material is sacrificed to achieve necessary cooling of the structure. However, the system would require pipes, valves, and pumps to transport coolant to the surface. For a reentry vehicle, it would either be very inefficient or it would also have to be regulated to match the cooling rate to the time-varying heat flux. Then, by taking advantage of phase changes in materials, the coolant can be brought to the heat-

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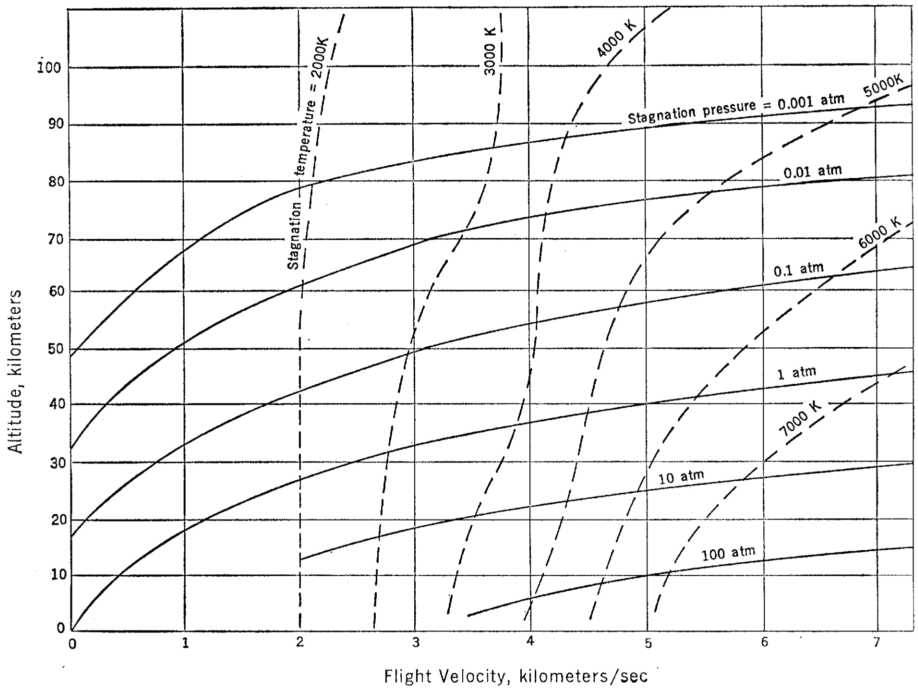


Fig. 1. Map of stagnation conditions for high-speed flight for real air based on data in (*1*).

ed surface. Such phase changes can be simple or can depend on a complex chemical reaction. The ablating materials are then exposed directly to the severe environment. Their efficiency is measured by the reduction of heat input to the vehicle per unit weight of material ablated. Since the rate of phase change is proportional to the heat input, the rate of coolant flow can be properly self-modulated.

Although the above discussion is based on the high-speed flight application, it is pertinent to other applications. For example, Fig. 3 is based on Coulbert's (*2*) analysis which showed regions of minimum weight designs for oxygen-hydrogen rocket motors to be used in space. The long-time, low-thrust application generally requires low chamber pressure and, consequently, produces lower heat transfer rates than the high-thrust application. The graphite heat sink corresponds to the simple heat sink described earlier. Regenerative cooling is an example of the use of a pumped coolant. In this case, the coolant is a propellant which is discarded into the motor chamber. Radiation cooling basically represents operation at the radiation-equilibrium temperature—although in the rocket motor application, it is also a backwall cooling system. Finally, there is a region of moderate-to-high thrust, where ablation systems yield optimum designs.

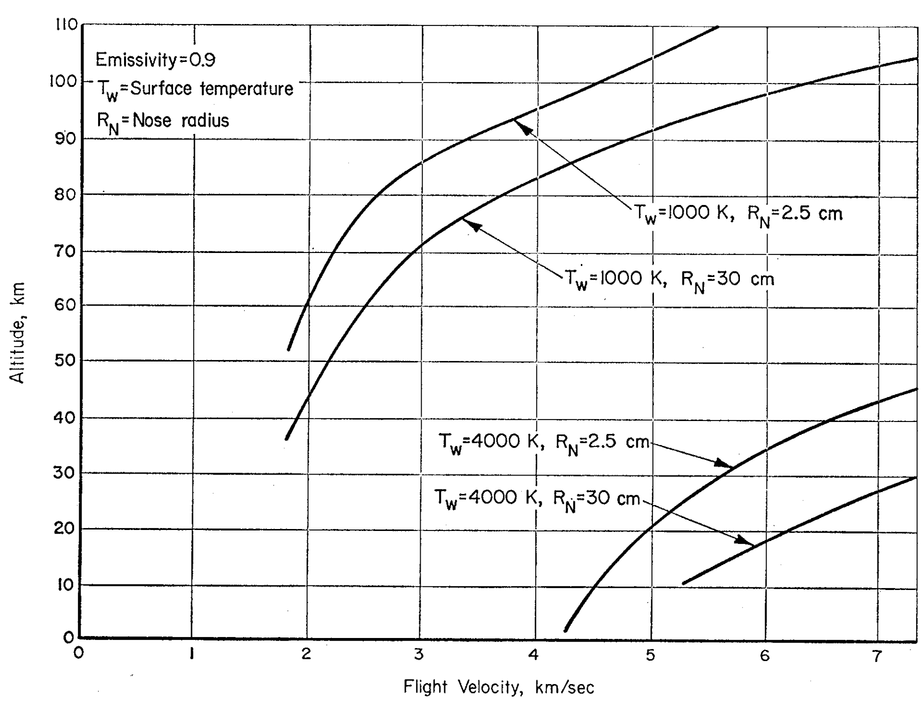


Fig. 2. Map of radiation equilibrium temperatures.

Mechanics of Ablation Processes

The phase changes mentioned above require energy absorption by the coolant. However, further cooling benefits are provided by the presence of liquid films and gas injection. In addition, certain specific material properties are important in the performance of ablation materials. Fig. 4 shows the surface of an ablating material. The illustration is shown for a particularly simple material. Melting is considered to occur at the liquid-solid interface. Boiling occurs at the liquid-gas interface. Specific variations which include gas or liquid production and finite chemical reaction zones below the solid-liquid line are considered later as variations of the simple model. The quantities $\dot{m}_L$ and $\dot{m}_g$ represent the rates of production of liquid and gas, respectively.

A heat balance for steady-state ablation yields the approximate relation

$$\dot{q} = [L_v + c_l\,(T_w - T_s)]\dot{m}_g + \tfrac{2}{3}\,c_l\,(T_w - T_s)\,(\dot{m}_L - \dot{m}_g) + [L_m + c_s\,(T_s - T_o)]\dot{m}_L$$

where $\dot{q}$ is the heat flux at the liquid-gas interface; L_v is the latent heat of vaporization; L_m is the latent heat of melting; c_l is the liquid specific heat; c_s is the solid specific heat; T_0 is the initial body temperature; T_s is the solid-liquid interface temperature; and T_w is the liquid-gas interface temperature. Or, in words, the heat flux at the liquid-gas interface is equal to the energy absorbed in the vaporizing material plus the energy absorbed in the heating material which does not vaporize to the mean melt-layer temperature plus the energy absorbed in melting material. The factor ⅔ on the second term of the heat-balance equation results from taking a mass-weighted average with assumed linear variations in velocity and temperature across the liquid layer. The simple heat balance is still not sufficient to describe the thermal effectiveness of an abla-

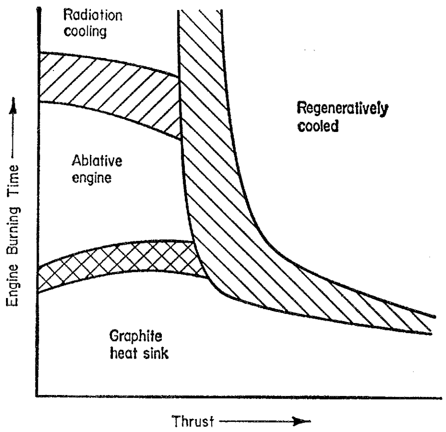


Fig. 3. Regions for application of various heat protection schemes in a rocket motor. [Based on Coulbert (*2*)]

tion material properly. First, the wall temperature and the vaporization rate must be determined from a balance between partial pressure at the liquid-gas interface and diffusion in the gas boundary layer. Second, the heat transfer rate at the liquid-gas interface is substantially reduced from the usual value by the gas injection resulting from vaporization.

Injection of gas into the boundary layer cools the gas adjacent to the surface and thickens the layer, thus reducing heat transfer rates. The effectiveness of the injected gas in reducing heat transfer increases as the molecular weight of the injected gas is decreased. Figure 5 shows the reduction in heat transfer rate, as measured by the Stanton number, as the injection rate, as measured by the blowing parameter, is increased. The Stanton number (*St*) is defined by

$$St \equiv \dot{q}/[\rho_e u_e (\Delta h)]$$

where $\dot{q}$ is the heat flux; ρ_e is the density at the edge of the gas boundary layer; u_e is the velocity at the edge of the gas boundary layer; and Δh is the difference between the gas recovery enthalpy and gas enthalpy at the temperature of the wall. The injection rate as measured by the blowing parameter is the ratio of the mass injection rate to the product of the streamwise mass flux and the Stanton number without gas injection. Curves are shown for the injection of air into air and hydrogen into air for both a laminar stagnation point (*3*) and flat plate without gas-phase reactions (*4*). In addition, an experimental curve is shown for air-air with turbulent flow on a flat plate (*5*). Thus (i) the heat transfer rate reduction is large in all cases, (ii) hydrogen reduces the heat transfer rate more than air, and (iii) turbulent boundary layer flow reduces the effectiveness of gas injection.

The efficiency of an ablation material is frequently measured by the effective heat of ablation defined by

$$H_{eff} \equiv \dot{q}_o/\dot{m}$$

where H_{eff} is the effective heat of ablation, and $\dot{q}_o$ is the heat transfer to a nonablating surface at temperature T_w. The effective heat of ablation includes gas-injection effects. The effective heat of ablation is strongly dependent on the exposure conditions as a result of the factors discussed above. For illustration, Fig. 6 shows the effective heat of ablation of ice as a function of the external temperature. The curves were computed at three pressures by Roberts (*6*) to show the effect of boiling point. The various components of effective heat of ablation are shown on the figure. It is clear that vaporization is the dominant factor and that the effectiveness of ice improves dramatically with increasing external temperature. At the leading edge of the vehicle, the external temperatures shown in Fig. 6 are equivalent to the stagnation temperatures shown in Fig. 1. The increase in effective heat of ablation with severity of environment is a desirable characteristic which is generally common to gas-producing ablators. To carry the illustration further, the previously mentioned flight condition of 6 km/sec at an altitude of 30 km would lead to an effective heat of ablation in excess of 1200 calories per gram if the vehicle utilized ice as a heat shield.

To this point, the discussion has been limited to an ablation system consisting of a single material which melts and boils at specific temperatures. However, certain conclusions can now be drawn regarding material properties that are desirable in an ablation system. The heat-balance relation shows the desirability of high specific heats, melting temperature, and latent heats. High wall temperature also decreases the potential for heat transfer and enhances subsequent radiation from the heated surface to space (if the heated surface is external to the vehicle). As indicated by the heat balance, it is desirable to maximize the mass evaporated relative to the total mass ablation. The additional, important benefit of gas production results from the aerodynamic effects discussed. Enhancement of this heat-blocking effect is achieved if the gases produced are of low molecular

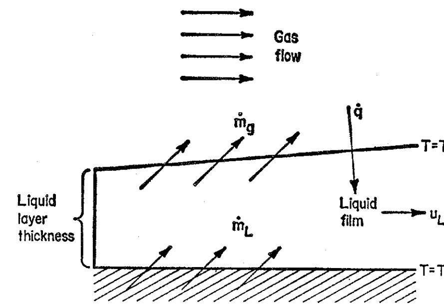


Fig. 4. Simple ablation by melting and vaporization.

weight. In most applications, it is necessary that the interior temperature be kept below some maximum and that the heat shields be of a minimum thickness or weight. Thus, low thermal conductivity of the solid material is generally a desirable property.

The relative desirability of the above properties depends on the interaction of the material with its environment. In fact, the optimum balance of properties is strongly dependent on the specific application. This balance of properties is often achieved by the development of new materials and by the combination of materials into composites. The above arguments are equally valid if there is no liquid phase and the material sublimes, or if the phase changes result from chemical reactions. Thus, there is at least a framework to discuss the specific materials. Deviations from the simple melting vaporization model will be discussed as they pertain to specific materials.

Materials Considerations

Materials selections and directions for development must depend on specific applications. Rather than attempt to catalog applications and materials, the characteristics of several example ablation materials are discussed below.

Glasses. During the ablation of a glass, advantages are derived from both melting and vaporization. The degree of vaporization that occurs depends on the severity of the environment. The high molecular weight in comparison to hydrogen of the vaporized species limits the effectiveness of glasses as ablators. The melting process for glasses involves a gradual softening with increasing temperature, rather than a sharp phase change as shown in Fig. 4. In some cases, additional gaseous products are produced by separation of volatile constituents of the glass. Because of favorable mechanical properties, glasses are often used as a component in a composite material.

Graphite. In most applications, graphite ablates by two processes—sublimation and chemical reaction. The chemical reaction region can be further subdivided. In one region, the mass removal rate is controlled by the rate at which gaseous reactants can diffuse to the solid surface. In the second region, excess reactants are available, and the removal rate depends directly on the rate of chemical reaction. The occurrence of one or another of the mechanisms for removal of material depends on the surface temperature and gas pressure. Surface temperatures up to the sublimation temperature depend on the heat conduction in the solid structure. The net heat input to the solid depends on convection heat transfer with mass injection, chemical reaction energies, and radiation at the gas-solid interface.

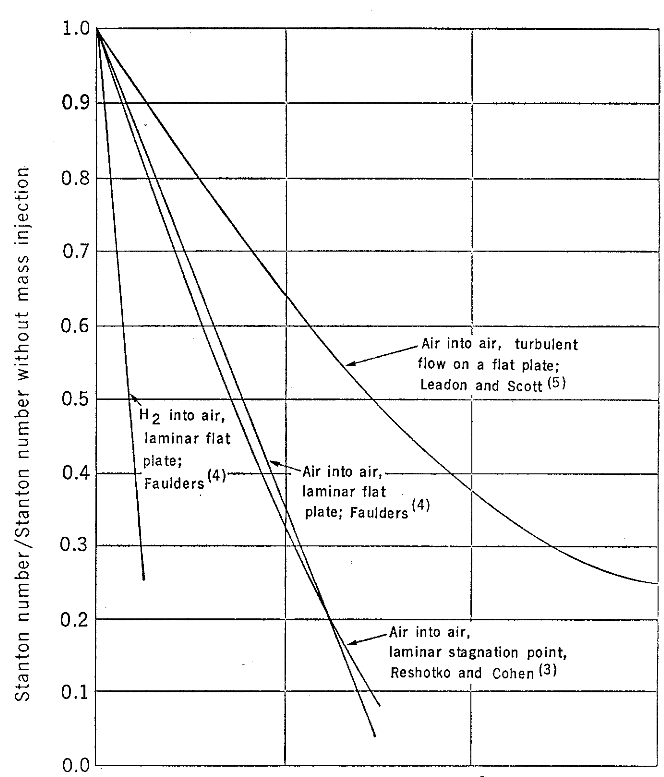
The sublimation process in ablating graphite is itself complex in that a large number of carbon species are produced. The sublimation process is endothermic and, therefore, its rate is limited by the heat transfer.

In the reaction-controlled ablation region, the rate of removal of the graphite material is not limited by the applied heat flux. The oxidation reaction in air is, in fact, quite exothermic. However, in view of the relation between mass and heat transfer for specified aerodynamic conditions, it is still possible to define an effective heat of ablation in the region of the diffusion-controlled reaction. Effective heats of ablation of the order of 25,000 to 30,000 calories per gram are obtained in the region where the oxidation reaction rate is controlled by diffusion through the laminar boundary layer for the stagnation point of a hypersonic vehicle (see, for example, *7*). At very high pressures and where the heat flux is sufficient to maintain high surface temperatures, melting of graphite could occur and produce a change in the ablation mechanism.

There are wide variations in graphite materials. These result from differences in starting materials, processes, and purity. These variations manifest themselves as differences in thermal and mechanical properties and degree of isotropy. These factors can, in some environments, produce failure before completion of the orderly thermochemical ablation process.

The relatively high thermal conductivity of ordinary graphite complicates heat-shield design. To reduce interior wall temperatures, an intermediate high temperature insulator is generally required. This problem can be reduced if a pyrolytic form of graphite is used. The pyrolytic material is formed by vapor deposition and has extremely directional properties. Low thermal conductivities are achieved in the direction normal to the deposition surface. The use of pyrolytic graphite would permit high thermal conductivity along the surface and low thermal conductivity normal to the surface. However, the design and fabrication of structures from pyrolytic graphite remains a difficult art which has limited the application of the material.

Plastics. Plastics have been widely applied in thermal protection systems. Upon heating, the plastics generally decompose. The decomposition reaction generally produces a gaseous product and a residue. In the case of hydrocarbons, the gaseous products are generally hydrocarbons and hydrogen. The residue is a mixture of porous graphite and nonvolatile hydrocarbons. The porous material of the residue is generally referred to as a char. In general, the ablation process is somewhat complex since the decomposition takes place over a wide temperature range. Thus, the graphite and the nonvolatile hydrocarbon content of the residue varies with position in the char. As the surface is approached and the temperature increases, the char composition approaches that of pure graphite. The process is further complicated by the



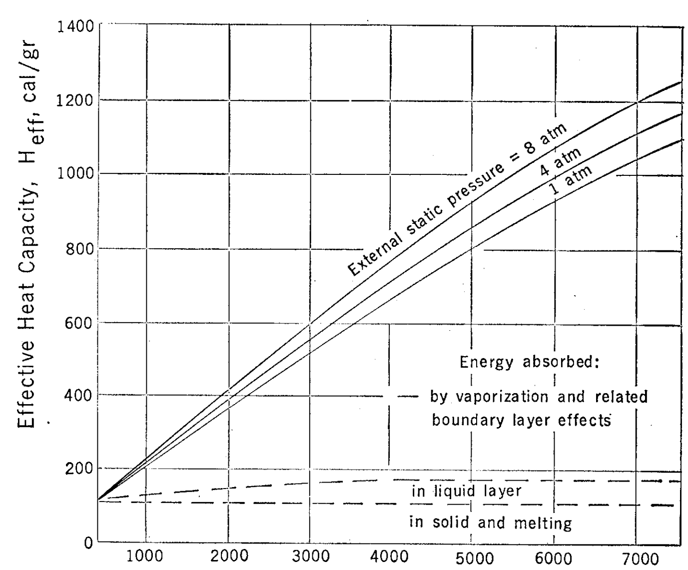


Fig. 5 (left). Heat transfer reduction due to gas injection.

Fig. 6 (above, right). Variation of effective heat capacity H_{eff} of ice with external temperature T_e for axisymmetric flow (*6*).

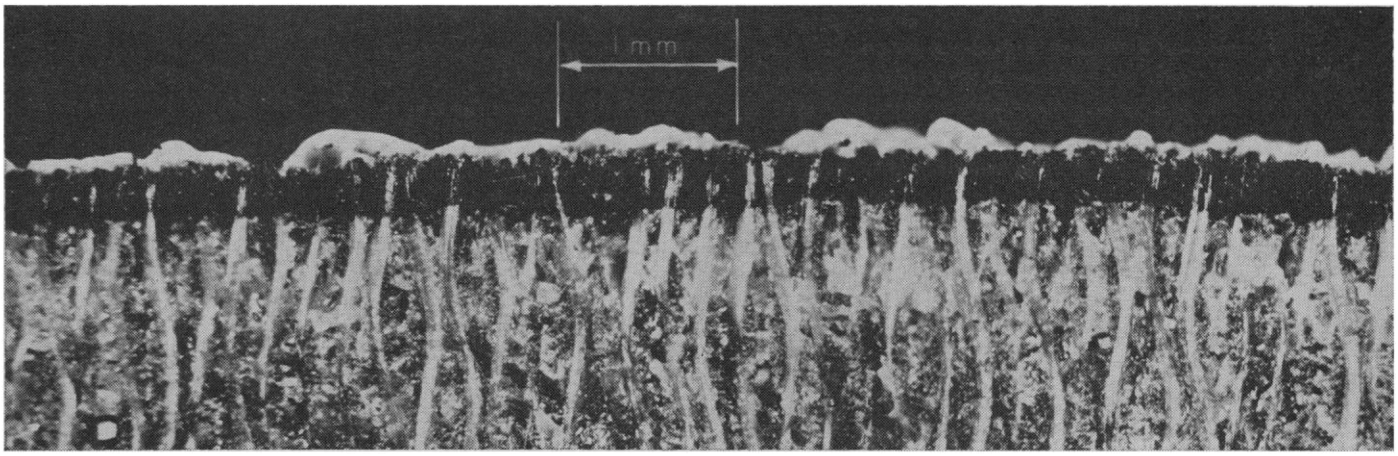


Fig. 7. Magnified cross section of an ablated glass-reinforced plastic material.

fact that the volatile hydrocarbons continue to crack as they flow through the char towards the exposed surface. Additional gaseous products are produced by the sublimation or chemical reaction of the graphite residue with the externally flowing gases.

Principal contributions to the effective heat of ablation are made by (i) the gas injection into the boundary layer—with the Stanton number reductions enhanced by low molecular weight products, (ii) the heat required to produce the decomposition reactions, and (iii) the effects of graphite sublimation or reaction as described in the previous section. The performance is further enhanced by the high wall temperature and by further radiation associated with the char material.

The maintenance of the char layer greatly enhances the performance of these materials. In applications where significant magnitudes of shear stresses at the surface are produced by the gas flow, char material can be mechanically removed. This mechanical removal can degrade the performance of the material (*8*) significantly. Complete description of the performance of charring ablators is currently limited by the inadequacy of available data on properties of the char. Collection of such data is, in turn, limited by the difficulties inherent in producing samples in the same condition as the char produced during ablation.

Noncharring plastics have been applied to thermal protection systems that require a low wall temperature. These materials generally exhibit poorer thermal performance than the charring materials. Teflon is typical of the noncharring materials. It exhibits a relatively low ablation temperature. In addition, the fluorine in the ablation products tends to produce stable molecules in the main gas stream, though molecules with low-ionization potential can be formed by reactions involving traces of metallic impurities. Reduction in the ionization might be useful in reducing the observability of a vehicle during reentry.

Composite materials. Combinations of the properties of the various ablation materials are frequently needed to develop an optimum system. Consequently, composites are frequently used. Figure 7 shows a cross-section of a typical composite material (a hydrocarbon plastic and a glass fiber) after exposure to a hyperthermal environment. Gaseous products and char are produced by the plastic. The glass fibers provide a liquid layer and the required mechanical strength.

There are a number of ways to obtain strength via fibers. The material shown in Fig. 7 actually contains layers of glass cloth bonded together by the plastic. In other materials the glass is chopped into short fibers and dispersed in the plastic.

Many types of glasses are available for use in ablation materials. Other materials are frequently used for the fibers. Graphite cloth is one of the commonly used reinforcing materials. The use of graphite as the fiber material has the advantage of providing the desirable ablation properties of graphite in addition to strength.

Other types of composite materials include combinations of ceramics with refractory metals and refractory metals with lower melting points materials. This last-named group includes tungsten and other refractory metals which are impregnated with materials such as copper, silver, or lead.

Advanced materials. There are many new materials systems which are being investigated for thermal protection. The most interesting of these involve ablation processes with extremely refractory ceramics (*9*) and new forms of graphite. These may lead toward improved performance when integrated into vehicle designs. In addition, there is a renewed interest in the application of transpiration cooling to reentry vehicles. This renewed interest is tied to advances in refractory materials fabrication technology.

Summary

The performance of ablation thermal protection systems is intimately related to the mass transfer, heat transfer, and chemical reactions which occur within the gas boundary layer. Production of a liquid layer and phase change or chemical reaction heat sinks greatly improve materials performance. Materials are available which achieve many goals for thermal protection. However, advanced materials which are now being developed provide hope of further reductions in the weight of heat-shielding structures.

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