Technical Comments

Comment on "Silicon Carbide in Ablative Chars"

V. R. Gutman*
United Technology Center, Sunnyvale, Calif.

THERE has in recent years been quite some activity, both analytical and experimental, that is concerned with the possibility of solid-solid reactions in the char phase of ablating silica plastics on re-entry shields and in the walls of rocket chambers and nozzles between the reinforcing silica fiber and the surrounding char.[1] It has been pointed out that such reactions are highly endothermic and thereby may account for the "heat of ablation." As a matter of fact, they have about the same endothermicity as the reactions between the char carbon and corrosive gases, mainly carbon dioxide and water, which are generally believed by many in the field to be the principal reaction mechanism in the orderly ablation of the char. As pointed out by Ladacki[1] in his technical note, the inability to find silicon carbide in operational chars has made engineers suspicious of the solid-solid reaction idea. He suggests that the reason the carbide is not found is because the mechanism tends to SiO, which outgasses. But the engineers are also influenced by other evidence, such as: that char ablation rate appears to be controlled by mass transfer of corrosive gas to and into the surface, and that silica chars simply do not ablate in inert gas flows of comparable temperature.[2]

It is all very well to speculate about these reactions and their possible kinetics and to attempt the difficult job of measuring their rates in experiments that are not ruled out by complex realities of the actual ablation process on the shield or in the rocket, as long as one does not lose sight of certain practical matters. One of these matters is that the principal role of the reinforcement is to hold the char to the surface, so that it insulates the uncharred material from the high-mass-velocity, high-temperature, and highly corrosive flow. In the absence of this protection the ablation rate is indeed not only extremely rapid but unstable and uncontrollable; and if the reinforcement fiber is attacked chemically or by melting at below-surface temperatures, the char cannot form at all. In the rocket chamber it is usually adequate to reinforce rubbers with short silica or asbestos fibers, or both, because such fibers will retain the char adequately in the conditions of the local flow, thus making the rubber insulation system possible. This is inadequate in the rocket nozzle, where more highly organized reinforcement systems are required. Chopped fabric serves at lower mass velocities, but in liquid rocket ablative chambers and solid rocket plastic nozzle throats and exits, the ultimate organization of fabric lay-up or wrapped tape in shingle orientation has had to be used.

Then there is the observed limitation of temperature. Silica reinforcement has been the material of choice where the char-corroding influence was strong and oxidative by virtue of this influence being rammed air on the re-entry shield or rich in oxidizing gases in the rocket. Fluorinated gases have had a similar effect on the silica. But as the chamber temperature is increased with hotter propellants (or the velocity of re-entry), the point at which silica will begin to be adequate is pushed farther and farther downstream. Upstream of this point carbonaceous reinforcement is required whether the flow is oxidizing or not.

The point is that it is somewhat academic whether this limitation on silica use is due to melting below char surface temperatures or to rapid char-silica reaction, since it is only the mechanism of limitation rather than that of the orderly ablative process. That the reaction between char and reinforcement fibers is limiting rather than rate-controlling is not merely conjecture since we have had an example of a reinforcement material that is made worthless by this very reason. When the high-silica fiber was developed, it was pointed out that zirconia might be even better, because of a much higher melting point. Yet the zirconia-reinforced plastics always ablated catastrophically in rocket gases, and the idea was abandoned. The reason for this has only relatively recently been confirmed in the laboratory, where it was established that the zirconia-carbon reaction was fast at comparatively low temperatures, and the char on laboratory samples readily fell apart.[3]

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* Technical Assistant, Advanced Systems Design. Member AIAA.

References

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[2] Bachelor, J., Simmons, J., and West, W., "Chemical reactions between plastic composite materials and propellant exhaust products," Aeronautical Systems Div. TDR 63-737 (August 1963).
[3] Blaes, H., Hall, J., and Hale, R., "Application of materials to advanced nozzle and hot-gas control systems," Air Force Materials Lab. TR 65-125 (April 1965).

Reply by Author to V. R. Gutman

Michael Ladacki*
Rocketdyne, a Division of North American Aviation Inc., Canoga Park, Calif.

THE absence of expected SiC in operational chars may appear as evidence of the insignificance of the char-reinforcement interactions or the reason to doubt the whole "solid-solid reactions idea." I have attempted in my Technical Note[1] to show that the absence of SiC in chars could be actually ascribed to any one of the following possibilities: 1) the interaction did not take place (too low a temperature or too high a pressure); 2) the carbon-silica reaction had the equimolar character yielding CO and SiO, i.e., did not produce

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* Research Specialist, Physical Chemistry, Research Division. Member AIAA.