

Technical Comments

Comment on "Silicon Carbide in Ablative Chars"

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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 Ladacki¹ 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

References

- ¹ Ladacki, M., "Silicon carbide in ablative chars," AIAA J. 4, 1445-1447 (1966).
- 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

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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 Note¹ 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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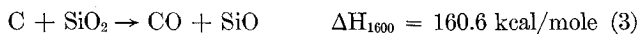
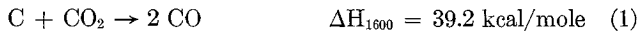
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SiC; 3) the carbide was formed but was subsequently consumed by secondary reactions yielding gaseous products; and, last but not least, 4) the SiC escaped detection because of analytical difficulties. The Note discussed the chemically interesting cases 1 and 2, and provided experimental evidence favoring case 3. The main purpose of the Note was to demonstrate that the mere absence of SiC in chars cannot be taken as a proof of the nonparticipation of the char-reinforcement reactions.

That the solid-solid reactions do occur in ablators is illustrated by the case of zirconia quoted in the Comment, the fact that carborundum is obtained from carbon and sand at comparable temperatures, and the fact that SiC does appear in some chars. The significance of the C-SiO₂ reactions may range from nil to high, depending on temperature and pressure; at relatively moderate conditions ("orderly" ablation) it will certainly be lower than that of the more facile reactions of carbon with volatiles (H₂O, CO₂).

Both the carbon-silica and the carbon-volatiles reactions consume carbon and deplete the protective char layer, hence are detrimental; they bring, however, some thermal compensation. The loss of a carbon atom from char via the interaction with silica is better compensated than the loss incurred by reactions with volatiles (and, of course, by shear forces and spallation):



Reaction (3) consumes also the silica, resulting in problems discussed in the Comment. In the case of the re-entry heat shields, where some material loss can be tolerated, the high endothermicity of the C-SiO₂ reactions (along with that of the dissociative vaporization of silica) is welcome; it does not "account for the heat of ablation," but it may contribute to it significantly. But in cases where dimensional stability is critical, such as rocket nozzles, no heat effect gained can adequately compensate for the damage done. All material-consuming processes are undesirable. Nevertheless, the surface or near-surface potential interactions have to be studied, if only to avoid them by judicious choice of an "ablativ" material.

The Note dealt specifically with the chemistry of the carbon-silica system. Such aspects as structural integrity of ablators, effect of shear forces, effect of external gases, etc., were outside the scope of the Note. The Comment draws attention to these important aspects and to their practical implications. Such practical matters as the form of reinforcement, i.e., whether a chopped fabric or a shingle-oriented wrapped tape is used, may spell a large difference in actual performance. But it is not merely academic to know the reasons for the limitations of materials, if their methodical improvement is contemplated.

Chemical reactions in ablation are often regarded as a source of trouble. Indeed, they consume material, are sometimes exothermic, and altogether bring excessive variability to the orderly system. An engineer's dream is to have a super-material that would serve the purpose and remain itself unchanged. Ablation is then a poor substitute, but the only effective substitute available, at least for re-entry. This attitude was discussed by Gruntfest and Shenker.² Until this super-material is found, chemical reactions with all their benefits and disadvantages will have to be contended with.

References

- ¹ Ladacki, M., "Silicon carbide in ablative chars," AIAA J. 4, 1445-1447 (1966).
- ² Gruntfest, I. J. and Shenker, L. H., "Ablation," *Modern Science and Technology*, edited by R. Colborn (D. Van Nostrand Company Inc., Princeton, N. J., 1965), p. 535.

Comment on "Duct-Flow of Conducting Fluids under Arbitrarily Oriented Applied Magnetic Fields"

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IN Ref. 1, the author considers a generalized transformation to uncouple the system of magnetic and fluid velocity variables. By this transformation he uncouples the system, introducing two variables f and g in place of the magnetic and fluid velocity components h and v in the flow direction, defined in Eqs. (23) of Ref. 1, and arrives at Eqs. (24) for f, g , which satisfy identical equations. Transforming the boundary conditions as well, he finally arrives at the governing equations for f, g together with boundary conditions on f, g , given in Eqs. (27).

The object of this note is to give a slightly different transformation, which uncouples the system; simplifies the boundary conditions on f, g ; and finally, contributes to the simplicity of the solutions. Formulas (30) and (31)¹ can now be replaced by simpler ones from which the solution in the nonmagnetic case is obtained directly by simple considerations. The same transformation applied to the single-series solution gives a much simpler result and from this, the case of Shercliff² can be obtained directly. The case of fully developed flow in the nonmagnetic case cannot be derived from either the double-series or single-series solutions of Eraslan, the difficulty arising from the type of generalized transformation used in Eqs. (23). Further, the single-series solutions of h and v given in Eqs. (37) and (38) do not converge because of the presence of a term

$$[\gamma_2 C_4 / (\omega^2 - \alpha^2)] y e^{-\alpha y}$$

in the expansion of $g(m, y)$ as in (35). C_4 should read

$$\frac{m\pi}{M(\gamma_1^2 + \gamma_2^2)} [1 + (-1)^{m+1} e^{-(M/2)\gamma_1}]$$

The new transformation given in this note overcomes the difficulty of convergence of the single series for h and v and also gives Shercliff's result² as a particular case.

Transformation for Uncoupling the System

Consider the generalized transformations

$$h(x, y) = \frac{1}{2} [e^{-(M/2)(\gamma_1 x + \gamma_2 y)} f(x, y) + e^{(M/2)(\gamma_1 x + \gamma_2 y)} g(x, y)] \quad (1)$$

$$v(x, y) = \frac{1}{2} [e^{-(M/2)(\gamma_1 x + \gamma_2 y)} f(x, y) - e^{(M/2)(\gamma_1 x + \gamma_2 y)} g(x, y)]$$

with the same boundary conditions as given in Eqs. (26) of Ref. 1. They are

$$\begin{aligned} h(0, y) &= 0 & v(0, y) &= 0 \\ h(\mu, y) &= 0 & v(\mu, y) &= 0 \\ h(x, 0) &= 0 & v(x, 0) &= 0 \\ h(x, \lambda) &= 0 & v(x, \lambda) &= 0 \end{aligned} \quad (2)$$

The governing equations for f and g are:

$$\nabla^2 f - \frac{M^2}{4} (\gamma_1^2 + \gamma_2^2) f = -e^{(M/2)(\gamma_1 x + \gamma_2 y)} \quad (3)$$

$$\nabla^2 g - \frac{M^2}{4} (\gamma_1^2 + \gamma_2^2) g = e^{-(M/2)(\gamma_1 x + \gamma_2 y)} \quad (4)$$

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