Heterogeneous Combustion of Highly Aluminized Hybrid Fuels

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Theme

THE combustion efficiency of highly metallized hybrid propellant compositions is seriously reduced by: a) the microheterogeneous combustion character, which is typical for metal particle combustion; and b) the macroheterogeneous combustion character, which is typical for hybrid propellant combustion. In order to analyze the principal problems of these combustion phenomena, experimental investigations were performed in a transparent slab-burner. High-speed photographs, regression-rate measurements and exhaust product analyses were used to identify the role of the propellant formulation on the combustion behavior, including the effects of: a) oxidizer-composition, b) polymerbinder-type, c) metal-type, and d) metal-loading.

The primary test objectives hereby were to qualitatively determine the causes for inefficient metal combustion and to provide information for the selection of an optimal propellant formulation for future motor firings.

Effect of Oxidizer Composition

To ascertain the role of the oxidizer composition on the combustion behavior of highly aluminized grains, tests with a) pure oxygen, b) pure fluorine, and c) various FLOX mixtures were made in a water cooled transparent slab-burner.

The test results given in Table 1 show that the regression rate $\dot{r}$ is increasing with increasing fluorine content due to lower ignition temperature, growing reactivity, and higher combustion temperature.

High-speed photographs and chemical analysis of exhaust product samples of the aluminized fuel grains burned with pure oxygen indicated that the aluminum particles were only partially combusted, whereas combustion with pure fluorine yielded a smokeless transparent jet, and no exhaust particles could be collected.

The heterogeneous combustion process of the aluminum particles in an oxygen-rich atmosphere is strongly inhibited by the high melting point Al_2O_3-layer, which acts as an effective barrier to mass diffusion and energy transfer to the burning particle. Compared to the vapor phase reaction time, the residence time in this burner is small.

Thermodynamic calculations indicate that aluminum combusted with fluorine-based oxidizers delivers gaseous combustion products. The relatively volatile AlF_3 has already been sublimated at a temperature of 1550 K. Thus, there should be no problem with retardation of the reaction by accumulation of condensed reaction products on the particle surface, as is the case in oxygen based oxidizers. Furthermore, all aluminum-subfluorides, such as AlF and AlF_2, are gases at combustion chamber conditions. This behavior, combined with the fact that aluminum has a higher heat of combustion with fluorine than with oxygen, produces a much more vigorous and complete reaction of the aluminum particles.

It is therefore attractive to select a propellant formulation composed of a highly fluorinated oxidizer, producing AlF_3 as the main combustion product, in order to determine the increase of combustion-efficiency compared to oxygen based propellant formulations.

In spite of lower available combustion energy, it is also attractive to select a stoichiometric propellant combination which contains an equal number of oxygen and fluorine atoms to produce AlOF (aluminum-ocyfluoride) as the primary combustion product. AlOF is a gas, so that a rapid gasphase-reaction on the aluminum particle surface can give more efficient combustion.

Table 1 Effect of oxidizer composition on regression rate[a]

Propellant Composition		$(\dot{G}_{ox})_o$	$\dot{r}$ [b]	Primary	
Fuel	Oxidizer	[g/cm²·s]	[cm/s]	Product	(state)
60 Al/40 PU	O_2	6.51	0.030[c]	Al_2O_3	(l)
60 Al/40 PU	FLOX-40	6.51	0.064	AlOF	(g)
60 Al/40 PU	FLOX-90	6.51	0.086	AlF_3	(g)
60 Al/40 PU	F_2	6.51	0.090	AlF_3	(g)

[a] In all tests $P_c = 10$ bar. [b] $= \dot{r}$ calculated by the average distance burned over the aft 1/3 of the grain length. [c] = reproducibility of regression rate over 22 tests was ±4.5% + $(G_{ox})_o$ = initial oxidizer mass flux.

Table 2 Effect of polymer-binder type on regression rate[a]

Propellant Composition		$(\dot{G}_{ox})_o$	$\dot{r}$ [b]	$\frac{\dot{r}_{Binder}-\dot{r}_{PU}}{\dot{r}_{PU}}$ x 100, %
Fuel	Oxidizer	[g/cm²·s]	[cm/s]	
60 Al/40 PU	FLOX-40	6.51	0.064[c]	0
60 Al/40 CTBN	FLOX-40	6.51	0.085	+ 32.8 %
60 Al/40 PBAA	FLOX-40	6.51	0.076	+ 18.8 %
60 Al/40 PIB	FLOX-40	6.51	0.039	- 39.1 %
60 Al/40 PI	FLOX-40	6.51	0.031	- 51.5 %

[a] In all tests $P_c = 10$ bar. [b] $= \dot{r}$ calculated by the average distance burned over the aft 1/3 of the grain length. [c] = reproducibility of regression rate over 22 tests was ±4.5% + $(G_{0x})_o$ = initial oxidizer mass flux.

Effect of Polymerbinder Type

To characterize the role of the polymerbinder, slab-burner tests using PU, CTBN, PBAA, PIB, and PI grains containing 60% aluminum were performed. Typical results are given in Table 2. It is observed that:

1) Aluminized polyisobuthylene (PIB) and polyethylene (PE) propellants melt faster than they burn. During combustion a melted layer forms a protective film which shields the metal particles from the combustion heat. This melted layer is stripped away by the shear forces of the gas stream and flows down to the reaction chamber, where ignition and combustion of the metal particles is severely inhibited by encapsulation in the melted binder. These saturated aliphatic hydrocarbons exhibit a high degree of thermal stability and melt at temperatures significantly lower than those for which boiling or depolymerization becomes predominant.

2) The burning surface of the aluminized PBAA, PBAN, CTBN, and CTPB propellants was dull black after the firings, caused by a char layer. These unsaturated polybutadienes gasify at relatively low temperatures due to the exothermic $-C=C-$ and $-C=N-$ double bonds in the binder structure. The decomposition obviously takes place on these groups involving breakage of the polymer chain into gaseous and solid carbonaceous fragments.

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3) The aluminized polyurethanes (PU) give different results depending on the type studied. The aluminized HTPB polyurethane behave like unsaturated polybutadienes. The burning surface has a glistering black appearance, in contrast to the cleanly burned surface of the aluminized HTPA- and HTPE-polyurethanes. The HTPA (hydroxy-terminated polyether), a saturated polyurethane, was found to melt faster than it vaporized. The HTPE (hydroxy-terminated polyester), an unsaturated polyurethane, was found to gasify more than it melted.

4) Aluminized polyimid (PI) propellants behave in a completely different manner. The regression rate is half of that of HTPE, and there is a strong tendency to leave porous slag deposits on the burning surface, which include large amounts of unburned agglomerated metal particles. (Polymer thermal decomposition- and weightloss- measurements are described in the full length manuscript).

5) The polymer degradation mechanism is initiated by breaking the polymer chain at the weakest chemical bonds and differs with the polymer type. Polymers which are difficult to pyrolyze and are thermally stable, severely inhibit the aluminum combustion. Since the polymer binder should gasify rapidly rather than melt and produce an encapsulating melt layer, and should eject and carry the metal particles from the regressing fuel surface into the combustion zone, polymers with high blowing rates are favorable.

It can be concluded that polymerbinder decomposition in highly aluminized hybrid grains plays a more important role than in composite solid propellants where the NH_4ClO_4, whose decomposition is highly exothermic, behaves as a solid monopropellant and is the burning-rate determining factor.[1]

In the case of highly lithium-loaded hybrid propellant systems, the highly reactive, low melting point lithium is the burning-rate controlling factor.[2] In contrast to this, for the highly aluminized hybrid fuel grains, the aluminum essentially behaves as an inert heat sink, and the polymer decomposition process controls the regression rate.

Effect of Metal Type

Slab-burner tests indicated that the metal type (aluminum, silicon, or boron as fuel additive) had no particular effect on the regression rate. Typical results are presented in Table 3. Magnesium-aluminum (50/50) alloys and pure magnesium did produce a slightly higher regression rate, obviously due to the rapid vapor-phase combustion of the magnesium. The aluminum particle size, which was varied from 0-32 μm to 200-250 μm, did not seem to affect the regression rate.

Effect of Metal Loading

The effect of metal loading on the regression rate was not intensively investigated because only the highly metallized fuels were of primary interest. However, aluminum loading variations of 40, 60, and 80%, as shown in Table 4, did not affect the regression as significantly as in the case of LiH[3] and Li.[2] This can be explained by the lack of a metallic melt layer, as is observed in highly lithium-loaded fuels, in which the liquid lithium is stripped from the surface by the shear forces of the boundary layer.[4]

The degree of particle agglomeration at the burning surface of the aluminized grains was difficult to identify. However, the burned surfaces of the aluminized HTPE-polyurethane grains were dry and clean after the test firings, and microscopic examination of the surface did not show any aluminum agglomerates.

Table 3 Effect of metal type on regression rate[a]

Propellant Composition		$(\dot{G}_{ox})_o$	$\dot{r}$ [b]	$\frac{(\dot{r}_{Metal}-\dot{r}_{Al})}{\dot{r}_{Al}} \times 100$, %
Fuel	Oxidizer	[g/cm²·s]	[cm/s]	
60 Al/40 PU	FLOX-40	6.51	0.064[c]	0
60 Si/40 PU	FLOX-40	6.51	0.061	− 4.7 %
60 B /40 PU	FLOX-40	6.51	0.058	− 9.4 %
60 AlMg-3/40 PU	FLOX-40	7.36	0.062	− 3.1 %
60 AlMg-50/40 PU	FLOX-40	7.36	0.073	+ 14.0 %
60 Mg/40 PU	FLOX-40	7.36	0.074	+ 15.6 %

[a] In all tests $P_c = 10$ bar. [b] $= \dot{r}$ calculated by the average distance burned over the aft 1/3 of the grain length. [c] = reproducibility of regression rate over 22 tests was ±4.5% + $(G_{0x})_o$ = initial oxidizer mass flux.

Table 4 Effect of metal loading on regression rate[a]

Propellant Composition		$(\dot{G}_{ox})_o$	$\dot{r}$ [b]
Fuel	Oxidizer	[g/cm²·s]	[cm/s]
40 Al/60 PU	FLOX-40	7.36	0.047
60 Al/40 PU	FLOX-40	6.51	0.064
60 Al/10C/30 PU	FLOX-40	6.51	0.070
80 Al/20 PU	FLOX-30	6.51	0.066

[a] In all tests $P_c = 10$ bar. [b] $= \dot{r}$ calculated by the average distance burned over the aft 1/3 of the grain length.

Conclusions

The test results can be summarized as follows: a) increasing the aluminum loading in the solid fuel grain moderately increases the regression rate; b) increasing the fluorine content in the FLOX oxidizer greatly increases the regression rate; c) the type of polymerbinder influences both the combustion behavior and the regression rate of highly aluminized grains; d) the unsaturated HTPE-polyurethanes provide the best pyrolization properties for combustion of highly aluminized hybrid fuels; and e) aluminum-based fuels combusted with fluorinated oxidizers yield a higher combustion efficiency than with oxygen-based oxidizers.

Based upon these results, two specific propellant combinations are selected for further motor firings to better determine quantitatively the relationships between fuel ballistics, combustion efficiency, and motor performance of the hybrid combustor[5]: a) 60 wt% Al/40 wt% PU, as solid fuel with FLOX-40 (40 wt% F_2/60 wt% O_2) as the oxidizer; and b) 80 wt% Al/20 wt% PU, as solid fuel with FLOX-90 (90 wt% F_2/10 wt% O_2) as the oxidizer. These propellant compositions yield gaseous AlOF and AlF_3, respectively.

References

[1] Beckstead, M. W., Derr, R. L., Price, C. F., "The Combustion of Solid Monopropellants and Composite Propellants," *13th Symposium on Combustion*, Pittsburgh, Pa., 1971.

[2] Lips, H. R., "Experimentelle Untersuchungen am Tribriden-System; Li, LiH, PIB/FLOX-90/He," DFVLR-Jahresbericht, Köln, 1974, p. 236.

[3] Smoot, L. D., Price, C. F., "Regression Rates of Metalized Hybrid Fuel Systems," *AIAA Journal*, Vol. 4, May 1966, pp. 910-915.

[4] Drew, W. B., "An Analytical Method for Determining the Melt-Layer Thickness and Regression Rates for a Hybrid Rocket Motor," NASA TN D-5699, May 1970.

[5] Lips, H. R., "Experimental Investigation on Hybrid Rocket Engines Using Highly Aluminized Fuels," *Journal of Spacecraft and Rockets*, to be published.