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Effect of Fluorinated Graphite on Combustion of Boron and Boron-Based Fuel-Rich Propellants

Tai-Kang Liu*
Chung Shan Institute of Science and Technology, Lungtan, Taiwan 32526, Republic of China
and
Ing-Ming Shyu† and Yen-Sheng Hsia‡
Chung Cheng Institute of Technology, Tashi, Taiwan 33509, Republic of China

The effects of fluorinated graphite (CF_x) with different fluorine contents (x = 0.08, 0.25, and 1.17) on the combustion of boron powder (B) and boron-based fuel-rich propellants were experimentally investigated. The propellants contain ammonium perchlorate (AP) (28%), magnalium alloy (8%), hydroxy-terminated polybutadiene (HTPB) (27%), and boron agglomerates (37%, in 300-, 600-, 850-, and 1180-μm sizes), with immediate contact between CF_x and amorphous boron (1:14 and 1:7 in mass ratio) by means of a small amount of polymethyl methacrylate binder. The reactions between boron and CF_x were investigated by adiabatic calorimetry under oxygen, and thermogravimetry under argon, using different B/CF_x mixtures. The baselines of boron and different CF_x were studied separately. Because of liberation of highly reactive products such as unsaturated fluorocarbon and fluorine from CF_x decomposition, more heat is evolved due to boron reaction compared to the boron baseline without CF_x. Possible exothermic reactions involved in the system containing C, B, O, and F quadruple elements were proposed. Propellants containing CF_x were found to increase the burning rate and/or pressure exponent compared to baseline propellants without CF_x. An interpretation based on the intensive reactions among the decomposition products from CF_x, AP, HTPB, etc., was proposed. Boron agglomerate size can affect the burning rate because of the mixed effects of boron as a heat sink, condensed phase reactions, and flame structures at different pressures.

Nomenclature

CF_x = fluorinated graphite, $0.08 \leq x \leq 1.17$ in mole basis
I_{sp} = specific impulse
y = combustion heat
ε = percentage deviation defined by Eq. (4)
Φ = estimated extent of boron reacted in B/CF_x mixtures

Subscripts
b = boron contribution
c = carbon contribution, see Eq. (5)
t = total carbon and boron fuel contribution
x = mole fraction of fluorine in CF_x molecules

Introduction

IGNITION and combustion of boron and boron-based fuel-rich solid propellants have attracted the attention of numerous investigators over the past two decades. Owing to its high heating value, boron has been used as a primary fuel for ramrocket development programs in many studies. Although the high performance of boron combustion is theoretically attractive based on thermodynamic calculations, practical difficulties in realizing its heating value have been encountered, mainly because of the different kinetic processes such as particle ignition, combustion, agglomeration, and oxide condensation during the course of releasing its combustion energy.[1] Compared with the combustion of aluminum or magnesium, these processes will be detrimental to I_{sp} performance in a practical rocket afterburner, where only limited residence time (2–10 ms) can be provided. Furthermore, boron-based fuel-rich solid propellants exhibit some difficulties compared with regular composite propellants because of a marked reduction in the pressure dependence of the burning rate for this kind of highly metallized propellants that cause thrust modulation problems in ramrocket applications. All of these phenomena suggest the need for more fundamental studies on boron combustion.

Our previous studies[2,3] were concerned with the use of lithium fluoride (LiF), fluorocarbon rubber (Viton), and glycidyl azide polymer (GAP) for coating boron particles and then incorporating the pretreated boron into propellant formulations. Better ejection efficiency, shorter ignition delay time, less degree of slurry viscosity, and higher burning rates were observed. In this investigation, fluorinated graphite (CF_x) with different fluorine contents was mixed with amorphous boron to produce beads of different sizes, which were then incorporated into the fuel-rich solid propellant formulation. It was reported[4] that CF_x can liberate active fluorocarbon and fluorine-bearing species during thermal decomposition. This study examines the effect of this kind of chemical on boron combustion characteristics because of the reported beneficial effect of fluorocarbons for ramjet fuels.[5] Also, the halogen, such as fluorine from CF_x decomposition, was reported[6] capable of promoting the boron ignition reaction. Before investigating the combustion characteristics of the solid propellants, the reactivity between boron and fluorinated graphite was studied by thermal analyses and calorimetry techniques so that the interactions between these two kinds of reactants could be explored. Possible mechanisms governing CF_x/B mixture thermal decomposition characteristics and propellant burning rate behaviors are proposed in this article.

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*Senior Scientist, Chemical System Research Division. Member AIAA.

†Graduate Student, Applied Chemistry Department.

‡Associate Professor, Applied Chemistry Department.

Table 1 Specification of CF_x compounds by Allied Signal Co.

		Physical and chemical properties			
Grade	Raw material	Fluorine weight percentage, %	Decomposition temperature, °C	Median particle size, μm	Color
1000	Coke	62	630	8	Gray
1030	Coke	63	630	8	White
2010	Carbon black	11	380	<1	Black
2028	Carbon black	28	450	<1	Black
2065	Carbon black	65	500	<1	White

Table 2 Propellant ingredient variations

		Agglomerate			
Type	Propellant designation	Size, μm	CF_x, type	CF_x:B	AP size,[a] μm
A	a	300	2065	1:14	225 and 20
	b	300	——	0	225 and 20
B	a	1180	2065	1:7	225 and 2
	b	1180	——	0	225 and 2
C	a	1180	2065	1:14	225 and 10
	b	850	2065	1:14	225 and 10
	c	600	2065	1:14	225 and 10
	d	300	2065	1:14	225 and 10

[a] The fraction of different size is fixed for the same type of propellant.

Experimental

Materials

CF_x, used in lithium batteries and high-temperature solid lubricants, can be produced by reacting carbon black or coke with elemental fluorine gas. Five types of CF_x with different fluorine contents obtained from Allied Signal Co. were used in this study (Table 1). Amorphous boron powder (from Hermann Starck Co.) with a purity of about 95% and a median particle diameter of approximately 0.9 μm was used. Polymethyl methacrylate (PMMA), commercially available as Acryrex CM211, was employed as a bonding material between the boron powder and CF_x. In addition to these raw materials, commercially available hydroxy-terminated-polybutadiene (HTPB), magnalium alloy, ammonium perchlorate (AP), plasticizer, and curatives were used as ingredients in preparing the fuel-rich solid propellants.

Agglomeration Process and Solid Propellants

PMMA resins were dissolved in CH_2Cl_2 solvent with adequate agitation. Separately weighed, dried boron powder and CF_x were premixed and added to the previous solution, which was then thoroughly stirred at room temperature. The slurry was passed through several sieves mounted vertically on a vibrating sifter to produce the designated size of agglomerates passing through the uppermost sieve. The small particles in the lower sieve were recycled in CH_2Cl_2 in order to obtain a maximum yield of the designated agglomerate. These wet particles were dried at 80°C for two days, producing agglomerate grains with specific and uniform diameters (300, 600, 850, and 1180 μm). Boron-based fuel-rich propellants that contain AP (28%), HTPB (27%), magnalium (8%), and boron/CF_x agglomerates (37%) were prepared in a Baker Perkins laboratory blender. Propellants with the same composition as those described previously, but without any CF_x in the agglomerates, were also prepared as baselines for the purpose of comparison. The three types of propellant obtained (Table 2) differ in the presence or absence of CF_x for type A and type B propellants, and in boron agglomerate size for type C propellants.

Facilities

The thermal decomposition of CF_x and its mixture with boron were studied by using a DuPont 951 thermogravimetry and a 1090 B thermal analyzer at a 10°C/min heating rate under argon (Ar) atmosphere. A Parr 1241 adiabatic oxygen bomb calorimeter was used to measure the combustion heat of CF_x and its mixture with boron under 25-atm oxygen pressure. An 0.5-g of sample was used in each run. Repeat runs were conducted in order to ensure reproducible measurements. The combustion characteristics of the fuel-rich solid propellants were studied experimentally by means of a windowed strand burner under N_2 atmosphere. The burning rate was measured by a fuse-wire method in a Crawford bomb pressurized with N_2. The DuPont differential scanning calorimeter was employed to study the decomposition of selected propellants at 10°C/min heating rate under Ar atmosphere.

Results and Discussion

Effect of Fluorinated Graphite on Boron Powder Combustion

Thermogravimetric analysis results for the three types of CF_x are illustrated in Fig. 1. As the fluorine mass content in CF_x increases (11, 28, and 65%), the decomposition onset temperature increases (435, 438, and 542°C, respectively); the residue remains at 950°C as the percentage of the original weight decreases (77, 54, and 16%, respectively). The onset temperature is automatically determined from the intersection of the maximum slope line and the baseline by computer analysis of the thermogram data.

CF_x is a nonstoichiometric solid fluorocarbon in which the F/C ratio depends strongly on the fluorination temperature and structural properties of the pristine carbon material. Two kinds of CF_x have been discovered[4]: poly(carbon monofluoride) $(CF)_n$; and poly(dicarbon monofluoride), $(C_2F)_n$. These are considered graphite intercalation compounds because of their layered structures derived from graphite by insertion of covalent–bond–fluorine atoms. CF_x, produced by reaction between coke or carbon black and elemental fluorine at temperatures below 600°C, are mixtures of $(CF)_n$ and $(C_2F)_n$ with the following decomposition reactions[4]:

$$2(CF)_n \rightarrow nC^* + xCF_2 + yC_2F_4, \qquad x + 2y = n \qquad (1)$$

$$(C_2F)_n \rightarrow 2nC^* + n\ (\text{F-bearing species like } \dot{F} \text{ or } F_2) \qquad (2)$$

These equations indicate the initial thermal decomposition products that can further proceed to some secondary reactions

Table 3 Measurements of combustion heat for different types of CF_x and the comparison with theoretical prediction

CF_x compounds	F, wt%	C, wt%	Combustion heat, cal/g	ε, %
1000	62	38	2832.3 ± 14.7	4.8
1030	63	37	2699.3 ± 8.4	6.8
2010	11	89	6855.4 ± 42.0	1.6
2028	28	72	5580.1 ± 30.5	1.0
2065	65	35	2536.7 ± 6.6	7.4

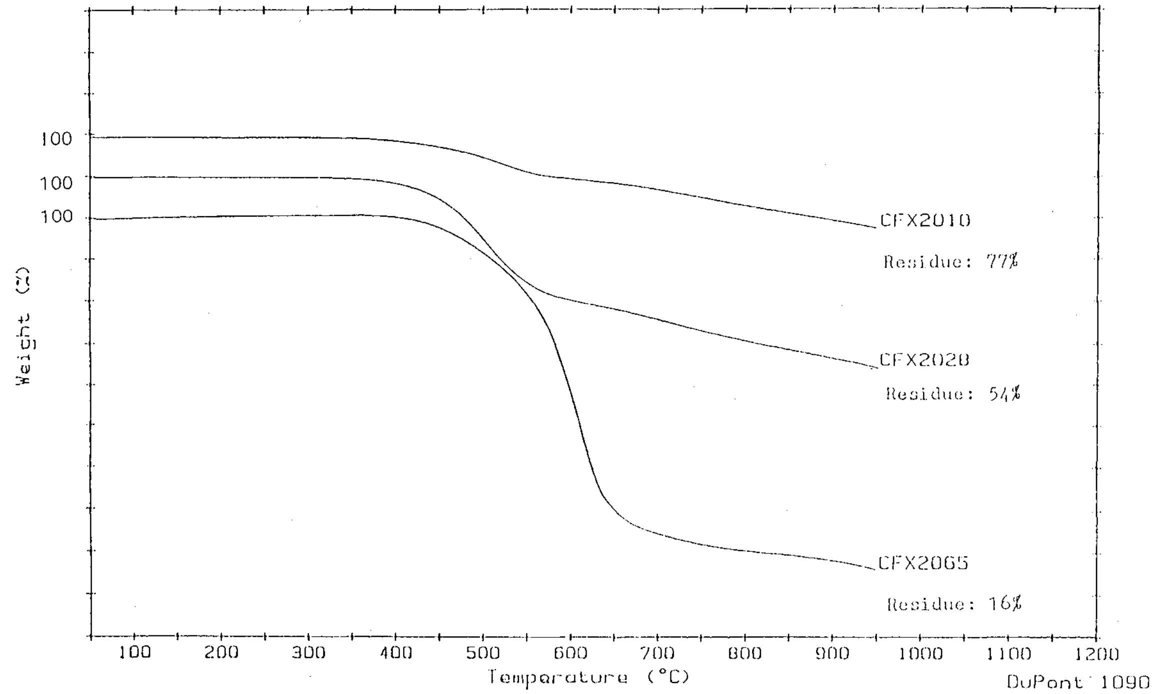

Fig. 1 Thermogravimetric analysis results of three different types of CF_x compounds under Ar atmosphere.

so that the overall thermal decomposition reaction of CF_x can be depicted by[4]

$$
\begin{aligned}
CF_x \xrightarrow{\Delta} & \text{ amorphous carbon} \\
& + \text{saturated fluorocarbon } (CF_4,\ C_2F_6,\ C_3F_8, \text{ etc.}) \\
& + \text{active unsaturated fluorocarbon } (CF_2,\ C_2F_4, \text{ etc.}) \\
& + \dot{F} \text{ or } F_2. \qquad (3)
\end{aligned}
$$

Higher mass loss rate was observed at a higher temperature for CF_x 2065 in Fig. 1, as compared with the other two kinds of CF_x. It is very possible from Eqs. (1–3) that more fluorine-containing active species can be liberated from decomposition of CF_x 2065 due to its high fluorine content. The advantage of high fluorine content in the fluorocarbon binder for larger heat release during metal fluorination was reported.[5] It was anticipated that the strong oxidizing agent (fluorine) would enhance metal burning and increase the combustion efficiency.

Chemical reactions between CF_x and boron powders were studied by thermogravimetry and the adiabatic calorimetry technique. In the calorimetry study the CF_x and boron baseline behaviors were investigated separately to clarify the results from B/CF_x mixtures.

Thermogravimetry results for the 50/50 blend of either 2010-, 2028-, or 2065-type CF_x with boron were found to follow the general trend illustrated in Fig. 1, while the temperature for maximum mass loss rate occurred at 491, 493, and 583°C, respectively. These temperatures are lower than the respective temperatures of 517, 521, and 609°C without boron, but with only CF_x, suggesting the existence of chemical reactions between CF_x and boron. The possible reactions involved will be discussed later in this study.

The measured combustion heat for five different types of CF_x is shown in Table 3. All experiments were conducted under identical conditions. Runs were repeated so that average data and standard deviations are reported. For the system involving C, F, and O ternary elements, the reaction most favored is considered to be the carbon oxidation reaction to CO_2 with a theoretical reaction heat[7] of 7830 cal/gm-fuel. F_2O, with positive heat of formation (5.86 kcal/mole),[8] is unlikely to exist as the stable species under the experimental conditions. The measured data in Table 3 can be compared with the theoretical prediction by assuming that all carbon in CF_x molecules are liberated as amorphous carbon, which is subsequently oxidized to CO_2. The last column in Table 3 shows the comparison results from the equation

$$
\varepsilon = \frac{7830 \text{ cal/g} \times \text{carbon weight fraction in } CF_x \text{ molecule} - \text{measured combustion heat}}{7830 \text{ cal/g} \times \text{carbon weight fraction in } CF_x \text{ molecule}} \times 100\% \qquad (4)
$$

The positive ε values indicate that not all carbon elements in CF_x molecules are oxidized to CO_2; a few retain the saturated or unsaturated fluorocarbon structure. The latter tendency is even more obvious for CF_x with the highest fluorine content.

Both Fig. 1 and Table 3 reveal the different thermal decomposition behaviors of CF_x with the highest fluorine content. This may be explained by the heat of formation as follows. Since covalent bonds exist between carbon and fluorine atoms in CF_x molecules,[4] the partial bond contribution to heat of formation for the C—F bond was found to be −52.5 kcal/mole.[9] The contribution to heat of formation for the C—C bond in a graphite molecule was taken from the group value as 1.5 kcal/mole.[9] The mass percentage of fluorine of different CF_x compounds in Table 1 can be converted to the mole basis so that the x values of CF_x 2010, 2028, and 2065 are 0.08, 0.25, and 1.17, respectively. With this information and the assumption that the 17% extra fluorine in CF_x 2065 will only exist as F_2 in the graphite structure, and thus, have zero heat of formation, it is possible to estimate the heat of formation of different types of CF_x. The calculated results for CF_x 2010, 2028, and 2065 are −2.82, −12.0, and −52.5 kcal/mole, respectively. Considering that a substance with a larger positive standard heat of formation tends to be a more chemically active species, it is understandable that CF_x 2065 will be more stable than the other two types of CF_x. This can explain the higher decomposition temperature of CF_x 2065 seen in Fig. 1 as well as the lesser amount of amorphous carbon liberated in the calorimetry experiments (last column of Table 3) due to the formation of fluorocarbons.

Measurement of boron combustion heat by calorimetry gives 4041 ± 32 cal/g, which is conceivably lower than the theoretical boron combustion heat[7] of 14,180 cal/g due to limitations of the calorimetry technique in providing proper boron ignition and sustainable combustion conditions. However, since all experiments for either CF_x, boron, or CF_x/boron mixtures are conducted under the same conditions, this result is most useful in assessing the contribution of combustion heat from boron or carbon. Blending 20% of LiF, a compound that is recognized as beneficial to boron ignition,[2,6] to 80% of boron gives a combustion heat of 4301 ± 20 cal/g mixture. Thus, 33% of extra heat per gram of boron was liberated due to LiF, illustrating the adequacy of the calorimeter technique for assessing the merit of the boron ignition/combustion promoter.

Measurements of the combustion heat of the CF_x/B mixtures were conducted so that both the effect of the fluorine mass content in CF_x (11 vs 65%) and the effect of the amount of CF_x in CF_x/B mixtures (20 vs 50%) could be reflected. The average data are shown in Table 4 as y_t, with standard deviations from repeat experiments. The first two digits after CF_xB designation in column 1 denote the weight percentage of fluorine in CF_x; the last two digits denote the weight percentage of CF_x in binary CF_x/B mixtures. Based on results shown in Table 3 and the preceding paragraph, the contribution of CF_x to the extent of boron reaction in CF_x/B mixtures can be estimated as follows:

Assuming that the carbon atoms in CF_x molecules liberated as amorphous carbon were fully oxidized to CO_2, the heat liberated per gram of the CF_x/B mixture due to carbon oxidation is

$$\begin{aligned} y_c = {} & 7830 \text{ cal/g} \times (\text{CF}_x \text{ weight fraction in CF}_x\text{/B mixture}) \\ & \times (\text{carbon weight fraction in CF}_x \text{ molecule}) \\ & \times (1 - \varepsilon \text{ of corresponding type of CF}_x \text{ in Table 3/100}) \end{aligned} \tag{5}$$

Subtracting these data from the measured total heat of combustion y_t in Table 4, the heat contribution due to boron reaction can be obtained as y_b. y_b divided by the weight fraction of boron in the CF_x/B mixtures gives the heat evolved due to the boron reaction per gram of boron. This, further divided by the theoretical boron oxidation heat, 14,180 cal/g,[7] provides the estimated extent of boron reacted in the B/CF_x mixture in a calorimeter, shown in the last column of Table 4 as Φ. It is obvious from the Φ values in Table 4 that, under the same experimental conditions, the introduction of CF_x will enhance the extent of boron reaction since all Φ values in Table 4 are larger than 28.5% (4041/14,180) of pure boron combustion in a calorimeter.

Combustion of CF_x/B mixtures in a calorimeter involves four kinds of elements, namely, C, B, O, and F. It is possible that in addition to the carbon oxidation reaction

$$C + O_2 \rightarrow CO_2 \qquad \Delta H = -7.83 \text{ kcal/g-fuel (Ref. 7)} \tag{6}$$

the following boron-related exothermic reactions could occur

$$4B + 3O_2 \rightarrow 2B_2O_3 \qquad \Delta H = -14.06 \text{ kcal/g-fuel (Ref. 10)} \tag{7}$$

$$4B + C \rightarrow B_4C \quad \Delta H = -1.67 \text{ kcal/g-fuel (Ref. 10)} \tag{8}$$

$$2B + 3F_2 \rightarrow 2BF_3 \quad \Delta H = -25.1 \text{ kcal/g-fuel (Ref. 5)} \tag{9}$$

$$\begin{aligned} & mB + (CF_2)_n \rightarrow 2n/3BF_3 + (m - 2n/3)B + nC \\ & \qquad \Delta H = -76n \text{ kcal/mole (Ref. 5)} \end{aligned} \tag{10}$$

Furthermore, B_2O_3 and B_4C, respectively, from Eqs. (7) and (8), can generate the reaction heat by

$$2B_2O_3 + 6F_2 \rightarrow 4BF_3 + 3O_2 \quad \Delta H = -3.46 \text{ kcal/g-fuel} \tag{11}$$

$$B_4C + 4O_2 \rightarrow 2B_2O_3 + CO_2 \quad \Delta H = -12.46 \text{ kcal/g-fuel (Ref. 10)} \tag{12}$$

The reaction heat of Eq. (10) was calculated from the heat of formation, which is −271.42 kcal/mole for $BF_{3(g)}$.[8] The heat of formation of CF_2 was estimated from the partial contribution of the C—F bond given as −52.5 kcal/mole.[9] The reaction heat of Eq. (11) was calculated from the heat of formation of $BF_{3(g)}$ and $B_2O_{3(s)}$, respectively, given as −271.42 and −302 kcal/mole.[8] It is noted that Eqs. (8–12) are exothermic reactions due to the presence of CF_x. The Φ values in Table 4 reveal that, depending on the relative amount of CF_x and fluorine content in CF_x, about 1.56 (44.6%/28.5%) to 2.46 (70.1%/28.5%) times of boron is reacted compared with pure boron oxidation in a calorimeter under the same conditions. Thus, although the combustion in a calorimeter is different from that in an actual propellant, the beneficial effect of CF_x in promoting boron exothermic reactions in oxidative environments is obvious.

Table 4 Measurements of combustion heat for various CF_x/B binary mixtures

	CF_x						
CF_x/B mixtures designation	Grade	Fluorine weight percentage in CF_x, %	Weight percentage, %	y_t, cal/g-mixture	y_c,[a] cal/g-mixture	y_b,[b] cal/g-mixture	Φ,[c] %
1150	2010	11	50	8401 ± 45.5	3429	4972	70.1
1120	2010	11	20	6952 ± 29.6	1371	5581	49.2
6550	2065	65	50	5375 ± 27.8	1269	4106	57.9
6520	2065	65	20	5571 ± 50.5	508	5063	44.6

[a] y_c = 7830 cal/g × (CF_x weight fraction in CF_x/B mixture) × (carbon weight fraction in CF_x molecule) × (1 − ε of corresponding type of CF_x in Table 3/100).

[b] $y_b = y_t - y_c$.

[c] $\Phi = y_b$/(boron weight fraction in CF_x/B mixture)/(14,180 cal/g of boron).

Further analysis of the Φ values in Table 4 reveals that Φ increases as the amount of CF_x increases under the same level of fluorine content in CF_x (CF_xB 1150 vs 1120, CF_xB 6550 vs 6520). However, Φ decreases as the amount of fluorine in CF_x increases under the same level of CF_x content (CF_xB 1150 vs 6550, CF_xB 1120 vs 6520). The latter result is attributed to the smaller amount of carbon liberated for higher-fluorine-content CF_x so that heat liberation due to carbon oxidation becomes smaller (see Table 3 and the y_c column of Table 4). Because this may lead to a lower temperature in the calorimeter and an incomplete decomposition endothermic reaction of CF_x 2065, Eqs. (9–11) may occur only to a rather limited extent. An earlier result from Fig. 1 indicates that CF_x 2065 decomposes at a much higher onset temperature (542°C) compared with CF_x 2010 and 2028 (435 and 438°C, respectively), which is in agreement with the hypothesis presented previously.

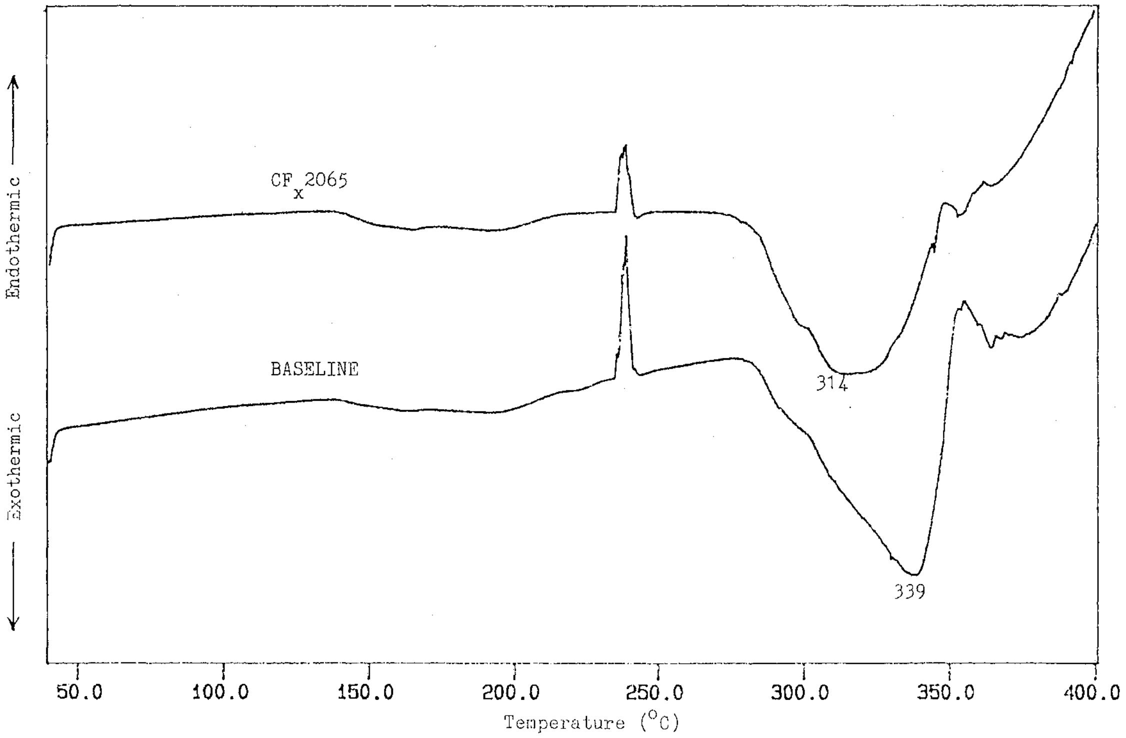

Fig. 2 Differential scanning calorimetric analysis results of type A propellants under Ar atmosphere.

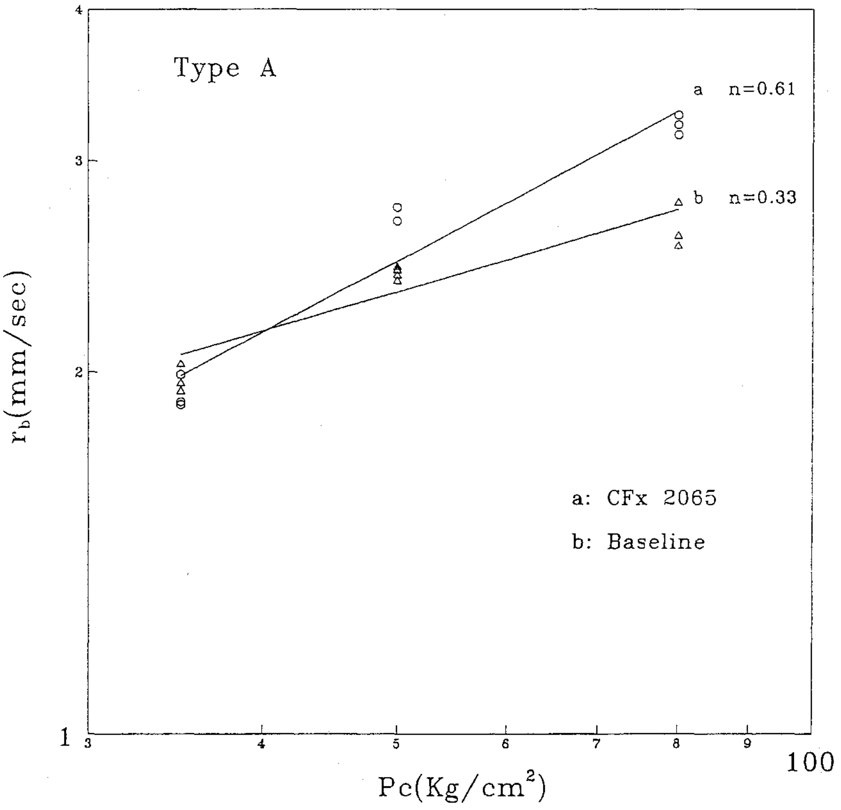

Fig. 3 Burning rates of type A propellants.

Effect of Fluorinated Graphite on Combustion of Boron-Based Propellants

The effects of CF_x on the combustion of propellants shown in the experimental section were investigated. Figure 2 shows the differential scanning calorimetry results for type A propellants. The burning rates of type A propellants are shown in Fig. 3. Because of rather coarse AP and fine boron agglomerate size, the burning rates are low. However, an increase of the burning rate exponent through the addition of CF_x is observed. Figure 2 shows that both propellants exhibit an endothermic peak around 240°C, recognized as the crystal transformation of AP from orthorhombic to cubic structure. The large exothermic peaks between ca. 300 and 350°C account for the decomposition reactions between decomposition products from AP and HTPB. With incorporation of CF_x, the peak temperatures of the exothermic peak of baseline and CF_x 2065 propellants, respectively, occurred at 339 and 314°C. The 25°C advance in the peak temperature illustrates the effect of CF_x on the thermal decomposition behavior of the propellant. Since boron can advance the decomposition temperature of CF_x (as indicated earlier in this article for B/CF_x mixtures), it is possible that AP and other ingredients in the propellant matrix can also advance CF_x decomposition at a lower temperature than CF_x alone. Similar CF_x effects on increasing the pressure exponent as shown in Fig. 3 can be observed in the type B propellants shown in Fig. 4. Compared with Fig. 3, the burning rates are higher due to smaller AP and larger boron agglomerate size; the effect of CF_x on pressure exponent diminishes as the burning rate also increases. Nevertheless, it is an established fact that CF_x can increase the burning rate. Based on the results shown in Figs. 3 and 4, it is evident that with a boron-based propellant, an increase of burning rate or/and pressure exponent can be expected with the addition of CF_x in boron agglomerates.[11] Earlier results presented in this article have shown that because CF_x contains more fluorine, it is able to liberate more active species such as fluorine radicals, fluorine molecules, and unsaturated fluorocarbons during thermal decomposition. It is postulated that these highly active species can react with the decomposition products from AP, HTPB, or PMMA, thus contributing to the higher burning rate and/or higher pressure exponents observed in Figs. 3 and 4.

The effect of the size of boron agglomerates containing CF_x 2065 on burning rate is depicted in Fig. 5 for type C propellants. It must be noted that all propellants in Figs. 3 and 5 have the same chemical composition, differing only in AP size and agglomerate size. Figure 5 indicates that the larger agglomerate size will result in a higher burning rate; however, the effect diminishes as the agglomerate size becomes larger. This can be explained as follows. Because of the fuel richness of the propellant in this study, the boron behaves essentially as an inert heat sink during combustion. Motor C* data for boron-based fuel-rich propellant (40% AP/30% B/30% binder) has demonstrated that less than 10% of boron content is reacted in the gas generator, and that this percentage declines with increased fuel richness.[12] Now, as the combustion wave vertically propagates, the larger agglomerates will absorb a lesser amount of heat before being ejected from the burning surface due to the lesser specific area exposed to the combustion flame. Thus, a larger portion of heat from the gas phase reaction is contributed to the heating of the binder and oxidizer in the condensed phase. The result is that higher regression rates were observed for propellants containing larger agglomerates (Fig. 5).

Larger agglomerates and higher burning rate propellants accompanied by a lower pressure exponent are observed in Fig. 5. Fourest,[13] investigating the combustion mechanism of fuel-rich solid propellant, concluded that the solid phase degradation process becomes important when compared to regular composite propellants. This mechanism contributes to his observed phenomena that the pressure exponent of the fuel-rich propellant is less sensitive to AP particle size than regular composite propellants. Since all propellants in Fig. 5 have the same AP size (they differ only in boron agglomerate size), it is postulated by following Fourest's argument that the

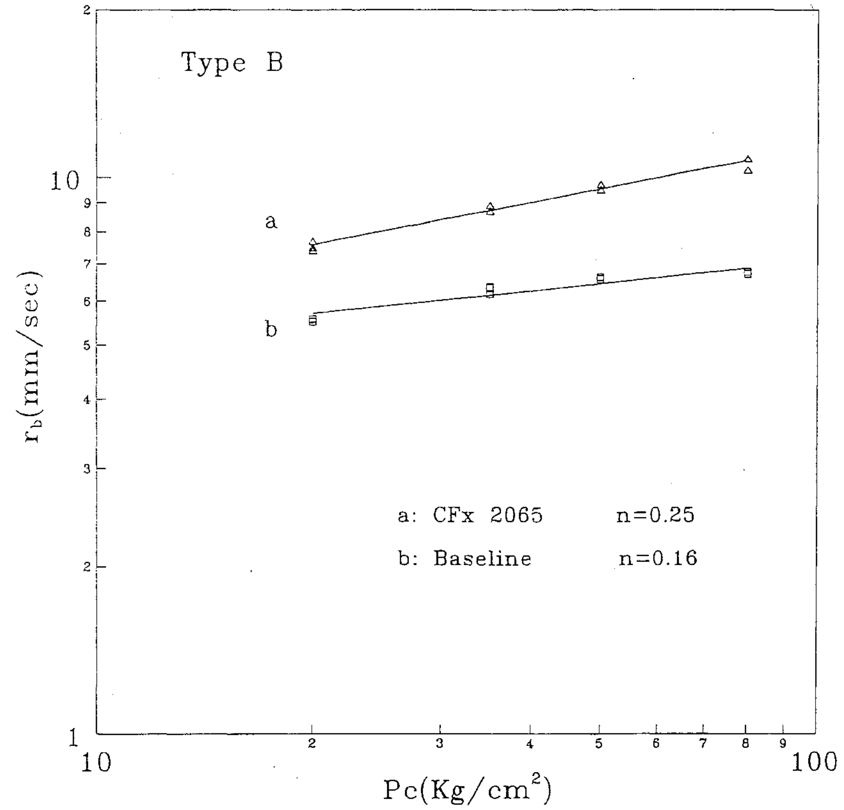

Fig. 4 Burning rates of type B propellants.

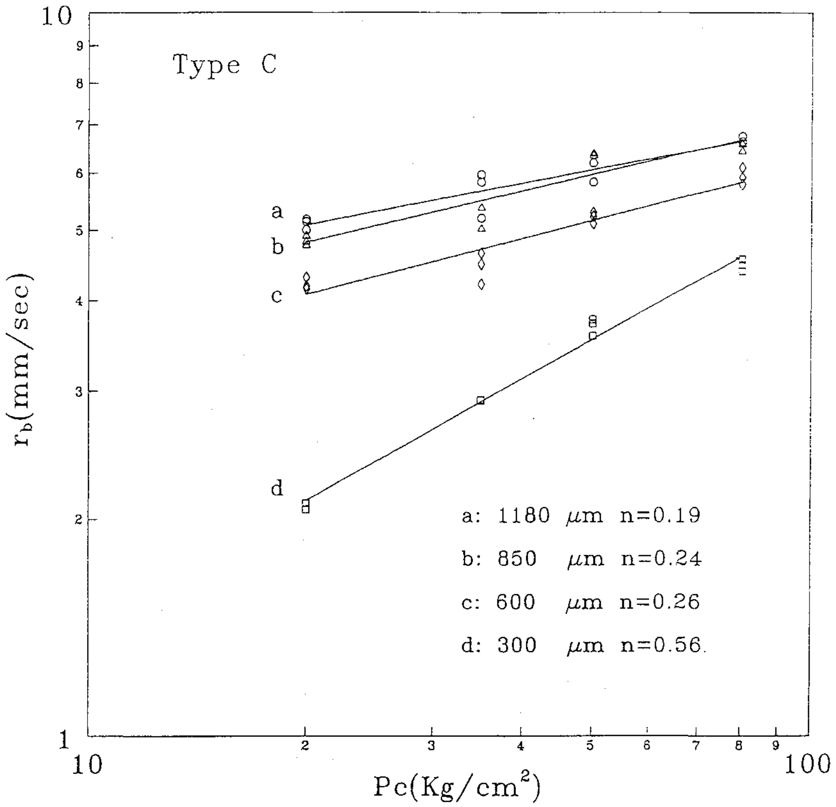

Fig. 5 Burning rates of type C propellants.

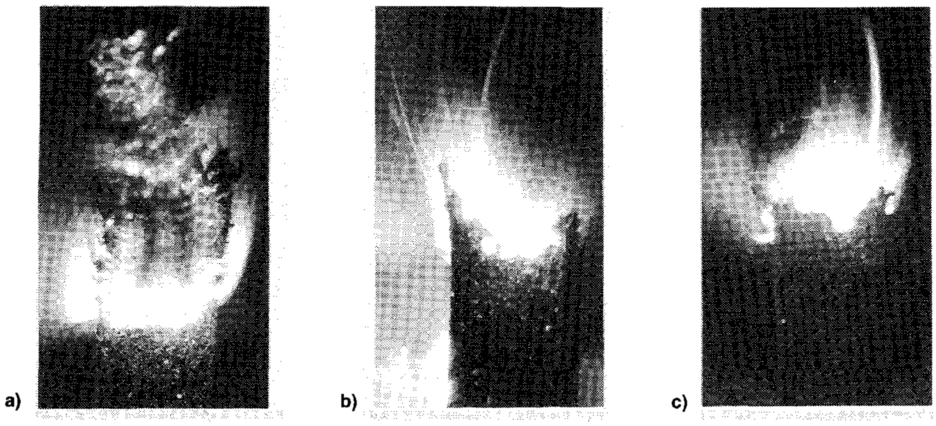

Fig. 6 Effect of different types of CF_x compounds on propellant strand combustion phenomena under 35 kg/cm^2 N_2: a) baseline, b) CF_x 2010, and c) CF_x 2065.

solid phase degradation process during propellant combustion becomes more important when the agglomerate size becomes larger, resulting in the diminishing pressure exponent effect shown in Fig. 5. Alternatively, the flame structure of propellant at different pressures may also affect the pressure exponent variations and large low-pressure burning rate variations shown in Fig. 5. The pressure dependence of composite propellant burning rate results from the kinetics of binder–oxidizer reaction.[12] Generally, the premixed flame between pyrolyzing oxidizer and binder predominates under lower pressure, and diffusion flame between pyrolyzing oxidizer and binder predominates under higher pressure.[14] It is conceivable that smaller boron agglomerates can be more uniformly dispersed at the burning surface than can larger boron agglomerates. Since the 28% of AP in the propellant matrix comprises many 225-μm AP, which is close to the small agglomerate size (37%), these small agglomerates tend to disturb the premixed flame structure at lower pressures, and thus, decrease the burning rate. On the other hand, large agglomerates on the propellant burning surface are locally segregated. The binder and oxidizer are in more immediate contact so that less-disturbed premixed flame can be developed to give a higher burning rate at low pressures. The lesser dependence of burning rate on agglomerate size at high pressures compared to the low pressure in Fig. 5 is attributed to the lesser dependence of diffusion flame structure vs boron agglomerate size at high pressures.

The effect of CF_x on propellant strand combustion behavior under 35 kg/cm^2 N_2 is depicted in Fig. 6. All propellants contain 300-μm B/CF_x agglomerates. Because of to the fuel richness of the propellant, large amounts of combustion residues will be expected when this kind of propellant is burned, thus rendering the combustion wave difficult for quantitative analysis. However, it is noted from Fig. 6 that there is a lesser amount of combustion residues on top of the solid propellant for propellants containing CF_x: this could result in higher ejection efficiency during gas generator motor firing. The reduced tendency for retaining combustion residues atop the propellant surface for CF_x propellants is possibly the result of the exothermic reactions depicted in Eqs. (8–12), due to CF_x, which generates more energy to reject the combustion products. Moreover, brighter flames can be observed for CF_x propellants, again suggesting vigorous gas phase combustion reactions due to CF_x. The incandescent traces from the combustion flame for CF_x propellants may come from the burning of the ejected amorphous carbon particles from CF_x decomposition or from the burning of boron particles. Our earlier study[2] on the same-composition propellant, but without CF_x and boron agglomerates, revealed that the environmental temperatures of boron particles, or nonequilibrium temperature T^*, are between 1373–1983 K (depending on pressure and percentage of inert boron). When producing boron agglomerates, T^* in the inner agglomerates will be probably below these temperatures due to the deficiency of AP inside the agglomerates. However, inner temperatures reach the CF_x decomposition temperature so that the reaction between its decomposition products and boron can be expected because of the immediate contact between CF_x and boron. This could result in attacking the B_2O_3 layer of the boron particles by fluorine to decrease the boron ignition time. For boron particles located on the agglomerate surface, a higher T^* temperature can be expected due to more neighboring AP particles.

Conclusions

1) Fluorinated graphite with different fluorine content exhibits different thermal decomposition behaviors. Higher-fluorine-content CF_x is more stable than lower-fluorine-content CF_x, which is in agreement with the heat of formation predicted from the partial bond contribution method.

2) By subtracting the heat contribution from carbon oxidation for boron/CF_x mixtures in calorimetry experiments, the heat contribution due to boron reaction can be derived. The decomposition products from CF_x can enhance boron reactivity in oxidative environments, leading to more heat evolved per unit weight of boron compared with the pure boron baseline case. Possible exothermic reactions are proposed, with the reaction heat calculated from either available heat of formation data or the partial bond contribution method. Although reaction conditions between boron and CF_x in a calorimeter are definitely different from those in real propellant combustion, the viability of our approach was justified by statistically reproducible data and the observed beneficial boron reaction effect due to LiF, a compound well known for promoting boron ignition reactions.

3) An increase in the pressure exponent and/or burning rate was observed for propellants containing CF_x. This is attributed to the combustion reactions between pyrolyzing products of CF_x and other species in the propellant matrix such as AP, HTPB, etc. The latter reactions may also contribute to the observed strand-burner combustion phenomena due to CF_x. Owing to the immediate contact between boron and CF_x in agglomerates, attacking the B_2O_3 layer by fluorine from CF_x decomposition may be postulated.

4) Agglomerate size can affect propellant burning rates and pressure exponents due to the mixed effects of boron as heat sink, condensed phase reactions, and flame structures. Single boron particle environmental temperatures are anticipated to be different for different boron agglomerate sizes due to different propellant microstructures.

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