CHAPTER 12

Propellants for Integral Rocket Ramjet Systems

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1. Introduction

Many countries show an increasing interest in better performance for tactical missiles, including range improvements, maneuverability and speed. Solid propellant rocket motor propulsion has proven to be very efficient as long as the range is modest. When using this technology a significant increase in the range and the speed can only be obtained at the cost of a considerable missile weight and volume increase.

In an article published in 1979, R. Marguet, C. Ecary and Ph. Cazin [1] give the example of a 100 km mission at Mach 2 and low altitude with a 200 kg payload. Solid propellant rocket motor propulsion would result in a 9 to 10 m long missile weighing 5000 kg. However, the use of a kerosene ramjet would lead to a missile weighing around 1000 kg and 6 m long.

A ramjet engine (shown in Figure 6 in Chapter 1) consists of several major components. Starting from the front of the missile, they are one or more air inlets followed by the inlet air diffuser, a fuel supply, fuel metering and injection devices, a combustion chamber, and a nozzle. In some configurations the fuel supply is located in the combustor. The air is captured by the air inlet and undergoes compression, resulting in a temperature and pressure increase, and a decrease in speed. The air is heated in the combustion chamber by the burning of a fuel whose introduction also triggers a slight increase in the mass flow rate, of the order of 5–10%. The compressed hot gases are expanded and accelerated in the nozzle.

Although ramjets are capable of functioning at subsonic flight speeds greater than Mach 0.8, albeit with poor performance, they are only advantageous at supersonic speeds ranging between Mach 1.5 and Mach 5, and are in practice used primarily within the Mach 2 to Mach 4 range. Consequently, the operation of a ramjet requires the missile to reach speeds between Mach 1.5 and 2.5 prior to initiation of ramjet engine operation. The initial solution selected involved the addition of separate, detachable boosters; it was followed by the use of a solid propellant grain located in the ramjet combustion chamber. This last configuration, known as the integral rocket ramjet (Fig. 1), has advantages over the separable rocket booster as it results in a much more compact missile, and the problems of jettisoning the boosters after their use are avoided. The chronology of the various stages of operation of a ramjet with an integral booster is as follows: combustion of the rocket booster, lasting usually between 3 and 6 s; transition over a period of less than 1 s during which the booster nozzle and the inlet port covers are ejected, the fuel is injected into the combustion chamber and ignited and, finally, ramjet operation. The booster may be nozzleless, which avoids the problem of jettisoning the rocket nozzle (Fig. 2).

The ramjet concept was invented in 1911 by a French scientist, R. Lorin. The Frenchman R. Leduc applied it to the propulsion of aircraft, and subsonic flight tests were conducted in 1949. Before and during the Second World War the Germans studied the application possibilities of the ramjet concept to missiles and artillery shells. Between the end of the Second World War and the middle of the 1960s, a large number of countries undertook a major research effort, which took the shape (in France) of many flight tests of experimental missiles called CT41, VEGA, R431 and Stataltex; and of operational developments of ground-to-air or surface-to-air missiles such as the BOMARC (1957) and the TALOS (1959) in the United States; the BLOODHOUND (1959) in Great Britain; and the SA4 (1964) in the USSR. After this period, the research and development effort slackened. Activities began again around the 1970s with, in particular, the following: introduction

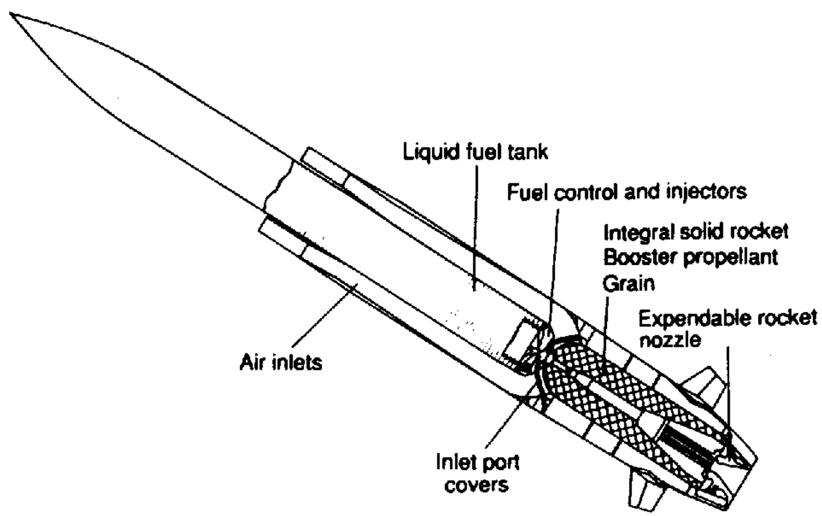

FIG. 12.1. Liquid-fueled integral rocket ramjet.

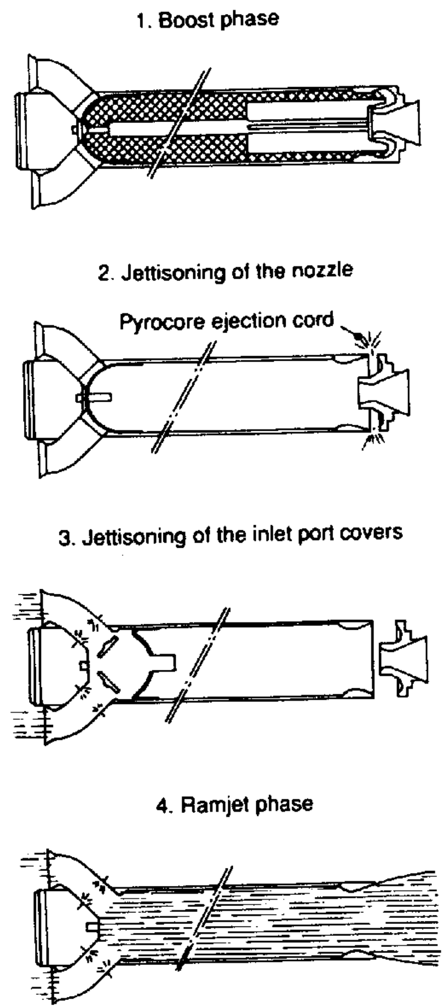

FIG. 12.2. Integral rocket ramjet-operating sequence.

in Great Britain in 1975 of the SEA DART; the in-flight evaluation in the US of the ASALM (advanced strategic air-launched missile) and ALVRJ (advanced low-volume ramjet) experimental missiles; the development of the SLAT (supersonic low-altitude target) [2], which could be operational in 1991 [3]; and in France, the flight test of the ANS missile (supersonic anti-ship) and the operational missile ASMP (medium-range air-to-ground).

The missiles mentioned above are powered with liquid fuel. Another technical solution consists in feeding the combustion chamber with a hot fuel plasma through the decomposition of a fuel-rich solid propellant (the amount

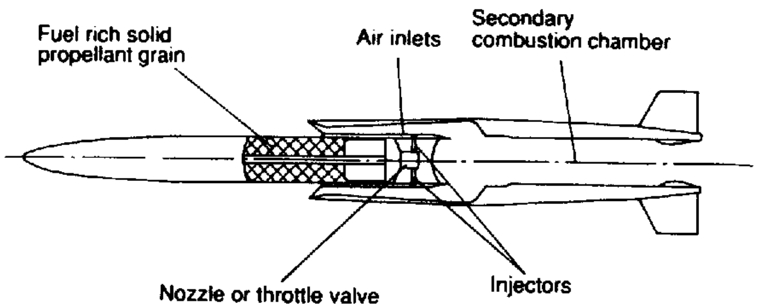

FIG. 12.3. Ducted rocket with choked gas generator.

of oxidizer in the propellant is just sufficient to ensure the required ballistic properties). The fuel-rich grain is placed in a gas generator located upstream from the combustion chamber of the ramjet. Two configurations are used, one with a choked gas generator (Fig. 3) where the combustion pressure of the grain is controlled by one or more nozzles, the other with an unchoked gas generator where the operation of the gas generator is not separated from that of the combustion chamber of the ramjet (Fig. 4). The solid-fueled ramjet engine is referred to as a solid-fueled ducted rocket. In the USSR a ducted rocket-powered antiaircraft missile, the SA-6, became operational in 1967.

The fuel supply for a liquid-fueled ramjet or for a solid-fueled ducted rocket is located upstream of the combustion chamber. On the contrary, in the solid-fuel ramjet concept the fuel is entirely contained in the combustor. The heat feedback from the combustion zone of the fuel decomposition products with air determines the fuel grain regression rate. There are two combustor types [4]. In the non-bypass configuration all of the inlet air passes through the solid fuel grain (Fig. 5). The combustion efficiency is promoted by a mixing device located downstream of the fuel grain [4]. In the bypass arrangement a part of the air is injected downstream of the fuel grain where the combustion of the fuel-rich products is completed (Fig. 6). In the two cases, the flame is

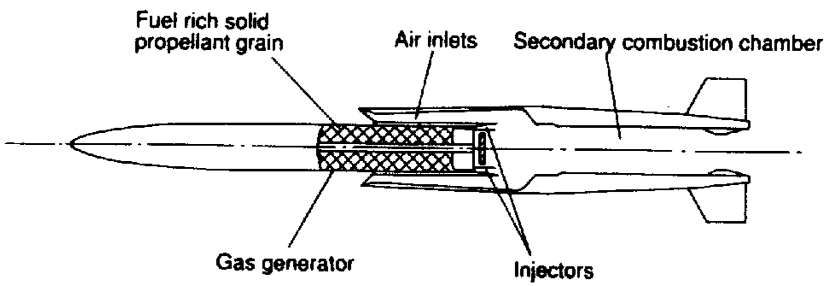

FIG. 12.4. Ducted rocket with unchoked gas generator.

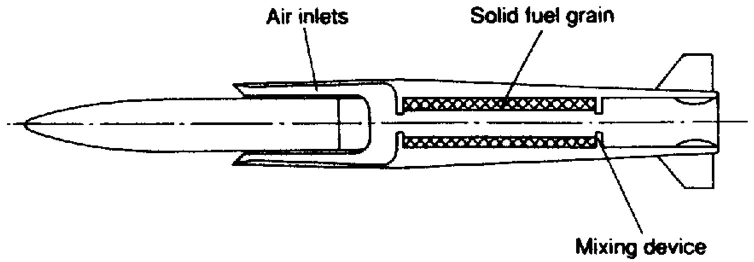

FIG. 12.5. Solid fuel ramjet non-bypass configuration.

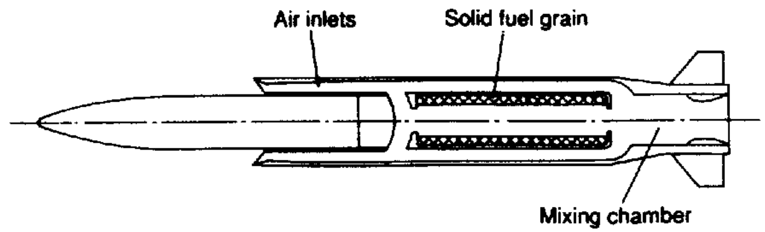

FIG. 12.6. Solid fuel ramjet bypass configuration.

stabilized in the foremost region of the combustion chamber by a recirculation zone created by the inlet step.

Various types of fuel-rich propellant are available. One type is based on pyrolysis of the binder into a fuel-rich plasma. The pyrolysis is caused by the reaction of a small amount of oxidizer with a small portion of the binder. A second type employs a binder and oxidizer in proportions typical of solid rockets, but also contains a large amount of solid-fuel filler. The rocket combustion process generates a hot plasma, containing the solid-fuel filler, and injects it into the secondary combustion chamber where it is mixed with air and recombusted.

This chapter examines the reasons governing the selection of the major fuels likely to be used in the composition of a fuel-rich solid propellant, as well as the main characteristics of typical products belonging to each of the major families, and makes a survey of integral boosters.

2. Fuel-rich Solid Propellants

2.1. SELECTION OF THE MAIN COMBUSTIBLE COMPONENTS

A fuel-rich propellant for ducted rockets consists of:

- A binder, whose function is to ensure the cohesion of the various propellant materials, and to supply combustible fuel fragments through pyrolysis, an oxidizer is employed to react with the binder to produce a plasma which transports the fuel-rich binder fragments to the secondary combustion chamber.

- Combustion catalysts.
- Additives, generally used in all propellants, to improve their aging, processability, including if necessary one or several fuel fillers to increase energy levels.

An initial selection of the propellant components is feasible on the basis of the combustion heat values which, due to the mode of operation of a ramrocket, allow us to assess their energetic quality. The value of components selected in this manner must later be examined in the light of other selection criteria such as cost, processability, usability in gas generator, combustion efficiency in combustor and, if necessary, the signature.

2.1.1. *Selection of a binder*

Some of the first criteria to be considered when selecting a binder for a fuel-rich propellant are: the ease of manufacture, and combustion heat values (Table 1).

Polyesters and polycarbonates contain much more oxygen than polybutadiene. Their gravimetric heats of combustion are therefore much lower than those of the polybutadiene binder, and their much greater density is not sufficient to compensate for the difference. The classification of these binders, in a decreasing order of volumetric heating values is as follows:

CTPB = HTPB > polycarbonate > polyester.

The plasticizers generally used with propellants are highly oxygenized; their incorporation into a polybutadiene binder results in a drop in the combustion heat.

Another parameter which must be taken into consideration is the amount of fuel-rich solids which can be incorporated into the propellant composition. From a physical properties perspective, this analysis can be based on the experience acquired with propellants loaded with ammonium perchlorate and aluminum. The classification of binders, in a decreasing order of maximum accessible total solids based on processability and mechanical properties, is as follows:

plasticized HTPB > HTPB > polyester > polycarbonate.

Polyester and polycarbonate binders, because of their low heating value and their low loading ratio capability, are therefore not very advantageous. The respective importance of each of the criteria discussed above depends on the type of fuel-rich propellant that is considered. In compositions which contain no combustible solid fuel filler the energy level of the material is provided by

TABLE 1 *Properties of binders*

Binder type	Atomic composition % (mass)					Density (g/cm^3)	Heating value		Maximum total solids*
	C	H	O	N	Cl		Gravimetric (kJ/g)	Volumetric (kJ/cm^3)	
CTPB	83.9	10.5	4	0.6	1	0.93	43.2	40.2	86
HTPB	85.4	11.2	2.4	1		0.92	43.4	40	88
Plasticized HTPB	81.6	10.4	7.1	0.9		0.94	40.9	38.3	90-91
Plasticized HTPB and ferrocenic catalyst	80	9.7	5.3	2.6		1.0	39.5	39.5	90 91
Polyester	56.8	8.1	32.7	2.4		1.16	25.2	29.3	86
Polycarbonate	57.5	8.3	29.2	5		1.15	26.2	30.1	85

* Maximum amount of total solids (A.P. and Al) which can be incorporated into a propellant composition (processability and mechanical properties).

the binder. As we will see later, this type of product contains little oxidizer, and its manufacture does not require the use of a low-viscosity binder. Consequently, the choice will often be a non-plasticized polybutadiene binder.

With compositions containing large percentages of fuel-rich solid particles the energy is primarily contributed by those particles. A plasticizer should, therefore, not be automatically excluded if it allows us to significantly increase the solid loading ratio. Polybutadiene, eventually plasticized, is well adapted to this type of use.

2.1.2. Selection of organic energetic additives

Energy can be added to fuel-rich propellants by replacing a portion of the binder with a solid or liquid hydrocarbonated product. Because polybutadiene-type binders contain little oxygen, the increase in gravimetric heating value likely to be obtained from the substitution of a portion of the binder with such a compound is very limited. But a substantial increase of the volumetric heating value can be obtained by using aromatic or aliphatic cyclical products, which are notably more dense than binders. As for solid products, the focus has been mainly on aromatic products with densities appreciably higher than those of the polybutadiene binders [5,6]. The gravimetric heating value of such products is lower than those of binders, but because of their much greater density, their volumetric heating value is much higher (Table 2). The presence of oxygen or nitrogen in the molecule allows us to significantly increase the density of the product, although not sufficiently to compensate for the loss of gravimetric heating value. The gravimetric heating values obtained with liquid products are greater than those of solid compositions, but the densities are usually lower (Table 3). These two types of products can be used simultaneously in a fuel-rich propellant composition.

TABLE 2 *Organic energetic additives (solid products)*

Product	Density (g/cm³)	Formula	m.p. (°C)	b.p. (°C)	Heating value: Gravimetric (kJ/g)	Heating value: Volumetric (kJ/cm³)
Anthracene	1.28	$C_{14}H_{10}$	217	340	39.9	51.1
Fluorene	1.20	$C_{13}H_{10}$	116	294	40.2	48.2
Polystyrene	1.05	$(C_8H_8)_n$	—	—	39.9	41.9
Poly (alphamethyl styrene)	1.07	$(C_9H_{10})_n$	—	—	40.3	43.1
Anthraquinone	1.44	$C_{14}H_8O_2$	286	380	31.4	45.2
Naphthylamine	1.12	$C_{10}H_7NH_2$	50	301	36.9	41.3
Dicyandiamide	1.40	$C_2N_4H_4$	210	d	18.6	26.0

TABLE 3 *Organic energetic additives (liquid products)*

Product	Density (g/cm³)	Atomic composition % (mass): C	H	O	Heating value: Gravimetric (kJ/g)	Heating value: Volumetric (kJ/cm³)
Hydrogenated terphenyl	1.006	90.8	9.2	0	42.6	42.9
Hydrogenated polycyclopentadiene resin	1.053	89.6	10.4	0	44.3	46.6
Poly(styrene-indene)	1.051	91	7.6	1.4	41.0	43.1
Hydrogenated dimer of norbornadiene	1.08	90.2	9.8		43.7	47.2

2.1.3. Selection of inorganic fuel fillers

The interest has generally focused on carbon, zirconium, aluminum, magnesium, and boron [6,7]. Boron carbide and titanium are sometimes also mentioned (Table 4).

Although its combustion heat is high, beryllium is excluded, as for all propellants, because of the toxic properties of its oxide as a combustion product.

The order of classification of these products, as a function of their gravimetric heating value, is:

$$B > B_4C > C > Al > Mg > Ti > Zr$$

In most cases the performance per unit of volume is the important factor which is sought after. Making a distinction between amorphous carbon black and graphite, the classification is as follows:

$$B > B_4C > Ti > Al > Zr > C\,(\text{graphite}) > C\,(\text{carbon black}) > Mg$$

TABLE 4 *Inorganic fuel fillers*

Product	Density (g/cm³)	Heating value: Gravimetric (kJ/g)	Heating value: Volumetric (kJ/cm³)
Beryllium	1.84	66.5	122.5
Aluminum	2.70	31.1	83.9
Boron (amorphous)	2.22	59.3	131.6
Graphite	2.25	32.8	73.8
Carbon black	1.63	32.8	53.3
Magnesium	1.74	24.7	43.0
Zirconium	6.49	12.0	78.2
Titanium	4.5	19.7	88.8
Boron carbide	2.52	51.5	129.8

Due to their high density, titanium and zirconium now attract more interest.

However, we must point out that for an equal volumetric performance it is preferable to have the highest possible gravimetric energy. This is due to the fact that an increase of the density implies a greater weight for the fuel-rich grain, with the detrimental result of a heavier propulsion system, because of the increase in weight of the gas generator and of the booster, which needs to be more powerful.

A preliminary assessment of the increase in performance that might be obtained by switching from a composition without particles to a particle-laden composition can be made by comparing relative heating values. When taking the gravimetric heating value into consideration, only boron and boron carbide have combustion heats greater than that of a polybutadiene-type binder. But because of their greater density, all of these fillers have volumetric heating value that are greater than those of the binder.

2.1.4. *Theoretical energetic performances*

The following thermodynamic calculations for various filled and unfilled compositions are provided to demonstrate their relative energy merits. These examples involve one hydrocarbon-fueled composition and compositions with polybutadiene binder with 25% ammonium perchlorate and 50% of one of the most common energetic fillers quoted in the field, i.e. aluminum, magnesium, carbon, zirconium or boron. These amounts were selected arbitrarily, and do not take into account either the manufacturing problems specific to each of these additives, or the amount of ingredients that must be selected to ensure the functional properties required from the gas-generating grain.

Before an assessment of the theoretical performances of these fuel-rich propellants can take place, we need to establish standard conditions for the operation of the ramjet. For this chapter we have selected a chamber pressure equal to 0.57 MPa, the enthalpy of formation attributed to air corresponding to a flight at Mach 2 and sea level. In addition, the calculations are done on the basis of different proportions of air and fuel. These proportions are expressed in terms of the value of the equivalence ratio, a term that stands for the quotient of the ratio of the mass flow rate of fuel and air versus the same ratio for a stoichiometric mixture (see Chapter 3).

The evolutions of the specific impulse (I_s) and of the volumetric specific impulse ($I_s\rho$) as a function of the equivalence ratio are illustrated in Figs 7 and 8. The specific impulse is the ratio of the thrust to the product of the acceleration due to gravity and the mass flow rate of the fuel-rich propellant.

For a low equivalence ratio the classification of the combustible solids in a decreasing order of specific impulse is as follows:

$$B > C > Al > Mg > Zr$$

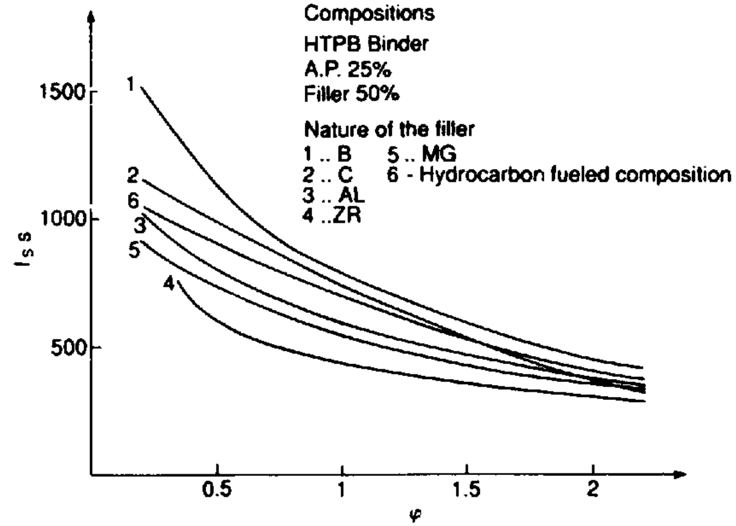

FIG. 12.7. Theoretical performances of fuel-rich propellants (M = 2; Z = 0; P = 0.57 MPa).

This ranking order is identical to that established on the basis of the combustion heat.

Based on the volumetric specific impulse, which is the criterion for the selection when the volume available for the gas generator is limited, the classification is as follows:

$$B > C\ (\text{graphite}) > Al > Zr > Mg$$

The relative values of a composition without particles are shown on the same diagram, to serve as a reference.

2.2. SELECTION OF A COMPOSITION TYPE

The criteria for selecting the type of composition must take features of future missions other than theoretical energy into consideration.

The combustion in the chamber of the ramjet of the decomposition products from hydrocarbon-fueled compositions and carbon compositions leads exclusively to the production of gaseous products, provided that high levels of combustion efficiency are obtained. Therefore, these compositions produce low levels of exhaust smoke.

The oxides from aluminum, zirconium, magnesium and boron, on the other hand, are solid at ambient temperature. Therefore, these fuel-rich propellants produce high levels of exhaust smoke.

Based on their energy and exhaust smoke levels, fuel-rich propellants can be classified into three categories: metal-loaded compositions with high phase during which no luminous phenomenon is observed that would

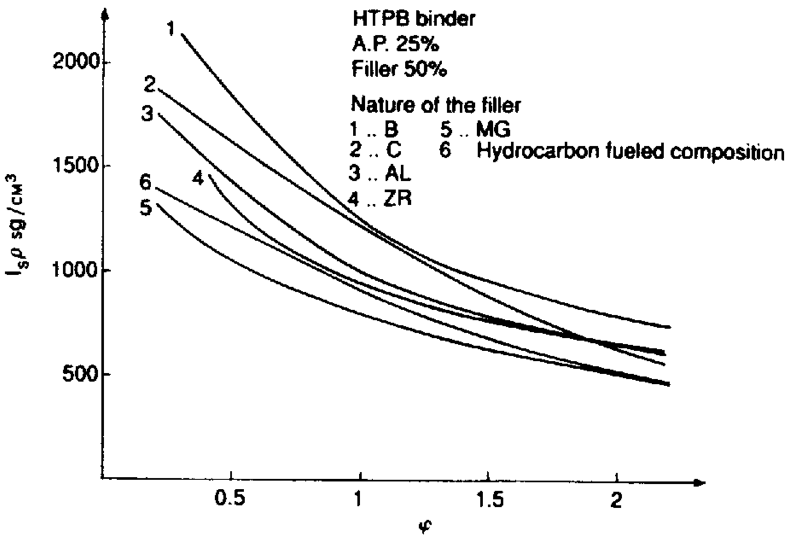

FIG. 12.8. Theoretical performances of fuel-rich propellants (M = 2; Z = 0; P = 0.57 MPa).

smoke levels, carbon compositions and hydrocarbon-fueled compositions with low smoke level.

The hydrocarbon-fueled compositions generate lower molecular weight hydrocarbon fragments which are burnt later in the secondary combustion chamber. Consequently, these compositions exhibit characteristics of combustion similar to gaseous hydrocarbons.

2.2.1. *Compositions with a high content of metal*

Four metals offer the desired properties: boron, aluminum, zirconium and magnesium.

The thermodynamic computations demonstrate that boron fuel-rich propellants are potentially highly energetic. However, the expected energy is only likely to be produced if the boron particles ignite and burn in the air within a very short period of time, compatible with the residence time in the combustion chamber, usually less than 5 ms. It is also difficult to burn at low pressures. For these reasons, boron combustion has been the object of very extensive research [8,9].

Boron particles are naturally coated with a layer of boric oxide, which has a very high boiling temperature (2133 K) that interferes with the combustion.

A. Macek's research [8] revealed that boron particle combustion occurs in two successive phases. First, the particle ignites, followed by an extinction

...e end of the evaporation process of the oxide layer, and then ...mbustion [8,9]. The ignition temperature, defined as the ...ture necessary for combustion, is virtually independent of ...rticle in the case of products with a small particle size. This ...80 K for a particle measuring 1 μm and 1920 to 1930 K for a ... μm under conditions of a dry atmosphere, and under a ...n and an oxygen molar fraction of 0.2 [9]. With large ...n time varies as the square of the diameter, and it is virtually ...the pressure, thereby indicating that kinetic behavior is ...iffusion phenomena. With fine particles the burn time is ...he diameter, and in this case the burning rate is limited by ...etics and depends on the pressure. There are variations in ...meters of a few tens of microns [9].

...in a gaseous mixture with 20% oxygen and 80% nitrogen at ...ximately 0.6 ms for particles measuring 1 μm and 1.5 ms for ...ng 3 μm [9]. Because of the very short residence time in the ...nber, these results show that very fine particles must be used. ...ually selected have particle diameters smaller than 3 μm.

...ons may be considered to promote the combustion of the ... combustion chamber of a ramjet, such as increase of the ...mical modification of the boron, or optimization of the ...he combustion chamber; this last point is discussed in the ...

...tion of a small quantity of metal into the composition may ...bustion efficiency. The additive is supposed to react rapidly ...re the air and the combustible products mix, and cause an ...emperature [9].

...h has demonstrated the advantage of coating the boron ...thium fluoride to facilitate their ignition. The mechanism ... on the formation of a compound with a boiling temperature ...n that of the boron oxide [9].

...pellants with a high content of aluminum cannot be used ... significant tendency to obstruct the nozzles or the dia-... gas generators.

...mic computations show that, for an identical solid loading ...n compositions have a specific impulse greater than those of ...positions. Due to the fact that zirconium is much more dense ..., this result is inverted when the volumetric specific impulse ...Consequently, a comparison between these two types of ...only feasible after a final assessment of their applications has ...general, magnesium compositions have proven to be more ...han zirconium compositions.

...esium is introduced in a gaseous state into the combustion ...e of the very high flame temperature of magnesium compositions, ranging from 1950 to 2400 K, compared to the boiling temperature of magnesium, 1380 K. The combustion of the magnesium in the combustion chamber is therefore very rapid.

2.2.2. *Carbon compositions*

The burning rate of carbon particles is governed either by the kinetic of the oxygen diffusion, or by the speed of the superficial reaction if one of these two processes is much more rapid than the other; otherwise it is governed by both. The nature of the phenomenon that limits the burning rate depends on the temperature and the particle size.

Major studies reported in the literature demonstrate that it is necessary to use very fine particles, for which the burning rate is probably controlled by the chemical kinetic, and consequently that the nature of the carbon used is a very important parameter in obtaining satisfactory combustion efficiency [11-13].

2.3. THEORETICAL ENERGETIC PERFORMANCES

The performance analyses discussed above were intended to compare the advantage of various fuels, without taking into account any of the other characteristics, in particular the processability characteristics. Figure 9 shows

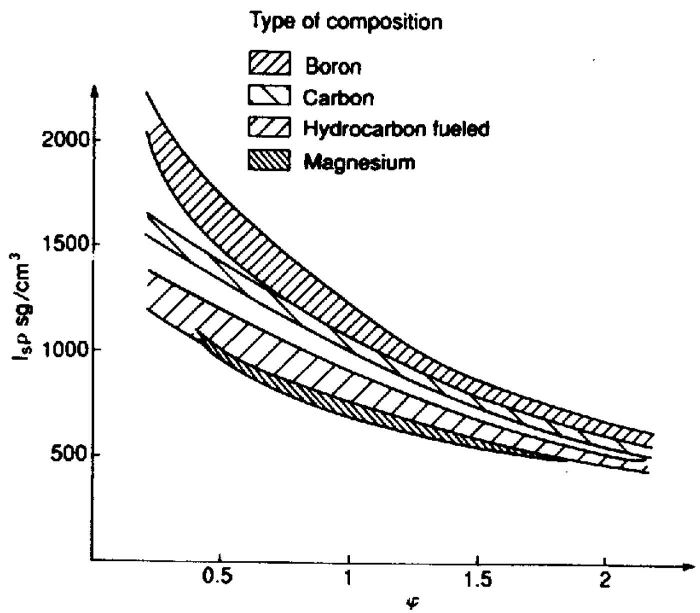

FIG. 12.9. Theoretical performances of fuel-rich propellants (M = 2; Z = 0; P = 0.57 MPa).

the energetic performances of feasible compositions on a graph plotting [volumetric specific impulse] versus [equivalence ratio]. It illustrates the potential advantage of boron compositions which present, for an equivalence ratio of 0.4, a volumetric specific impulse 30-45% greater than the best hydrocarbon-fueled composition included in the figure; and carbon compositions which, together with a low visual signature, have a volumetric specific impulse 12-20% greater than that of the best hydrocarbon-fueled composition. We should add that, within the carbon compositions, we have included carbon black and graphite formulations that are not identical from the point of view of combustion in the chamber of a ramjet. Additionally, hydrocarbon-fueled compositions can be enhanced by the addition of a small amount of metal, carbon or boron.

2.4. MAJOR PROPERTIES OF SEVERAL FUEL-RICH PROPELLANTS

The selection of a fuel-rich propellant is based on various criteria:

- theoretical performances,
- processability,
- mechanical properties,
- safety properties,
- ballistic properties,
- control,
- combustion efficiency,
- signature,
- cost.

Special mention should be made of the capability of modulating the flow rate [14]: it allows us to adjust the combustible flow to the flow of air collected, which varies according to the altitude and the velocity of the missile, in order to remain within a specific range of equivalence ratio. The specification of the ratio of modulation is therefore imposed by the expected flight envelope, speed, and altitude. The more extensive the flight, velocity and altitude envelope, the higher the modulation ratio will have to be. For the trajectory of an air-to-air missile, launched at low altitude, then cruising at high altitude, the range may be increased by over 300% by using a ramrocket with a throttleable gas generator [15].

In the case of the choked gas generator, the modulation of the fuel rate is done by a valve. The modulation ratio can be defined as the ratio of the burning rate at maximum operating pressure for the minimum temperature likely to be encountered by the fuel-rich propellant, versus the burning rate at the minimum operating pressure at the maximum temperature. It is therefore dependent on the pressure exponent (which cannot exceed the value of 0.75 by much for reasons of stability), on the temperature sensitivity coefficient, and on the operating pressure range, whose highest value is limited by the mechanical strength of the case, and whose lowest value is limited by the stable operation pressure limit of the gas generator, and by the pressure existing in the combustor. The architecture of the valve and the materials it is made of, must be tailored to the particular fuel-rich propellant used, to ensure the valve's resistance to the temperature of the effluents and to prevent obstructions caused by deposits or particles.

The pressure inside an unchoked gas generator is not disassociated from the pressure of the combustor. This means that the grain burns at a pressure directly related to the flight conditions. It is therefore "sufficient" when the fuel-rich propellant has the required ballistic properties to have the fuel flow rate self-adjust to that of the air.

For purposes of illustration, the following sections describe the main properties of a smokeless hydrocarbon-fueled composition, and a boron composition tailored to the operation of a choked gas generator.

2.4.1. *Hydrocarbon-fueled composition for a choked gas generator*

The major components of hydrocarbon-fueled compositions are a binder, an oxidizer, and sometimes a hydrocarbon filler.

With a given binder, the theoretical performances depend mostly on the nature and the amount of oxidizer. Figure 10 illustrates, in a polybutadiene binder composition, the evolution of the specific impulse and of the volumetric specific impulse versus the amount of ammonium perchlorate. The energetic performances decrease as a function of the oxidizer content; the maximum values correspond to the pure binder.

The combustion of compositions with very low oxidizer content is characterized by the presence after firing of a compact combustion residue in the gas generator. For compositions with an ammonium perchlorate content ratio ranging from 25 to 30%, the amount of residue in relation to the initial total weight of the grain is usually between 5 and 15%, depending on the formulation of the fuel-rich propellant. The presence of this residue causes first, a drop in the volumetric specific impulse, mostly due to the decrease of the effective weight of fuel loaded on the gas generator for a given volume. More importantly, the presence of the residue runs the risk of affecting the operational reliability of the gas generator, by obstructing the ejection orifices with fragments breaking away from the main body of the residue.

For these reasons the compositions usually selected today contain an oxidizer amount sufficient to prevent the formation of abundant residue.

The formulation of a hydrocarbon-fueled composition follows various specifications concerning energy level and modulation capabilities. According to the type of mission involved and the resulting specifications, the focus is placed on this or that characteristic.

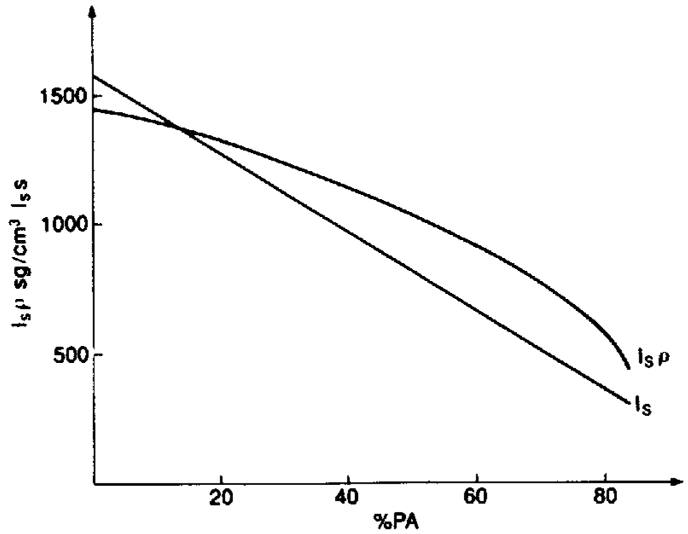

FIG. 12.10. Hydrocarbon fueled compositions influence of the amount of ammonium perchlorate on the theoretical performance (M = 2; Z = 0; P = 0.57 MPa; ϕ = 0.4).

T. D. Myers gives the example of a fuel-rich propellant with extensive modulation capabilities exhibiting a mass flow rate ratio of 1 to 18, for a pressure exponent of 0.55 and a minimum operating pressure of 0.14 MPa [15].

The characteristics described below are those of a hydrocarbon-fueled composition. This composition, which does not contain metal and ammonium perchlorate, is smokeless, but has a low modulation capability. Its basic formula is (1000 g base):

$$C_{47.31}\quad H_{50.19}\quad N_{8.27}\quad O_{16.58}$$

It consists mainly of a polybutadiene binder and an organic oxidizer. Its measured combustion heat is 33 KJ/cm^3.

2.4.1.1. *Theoretical performance*

The temperature inside the gas generator is 1350 K.

The thermodynamic computations for the chamber of the ramjet were made by considering an operational pressure of 0.57 MPa and simulating flight conditions of sea level and Mach number 2.

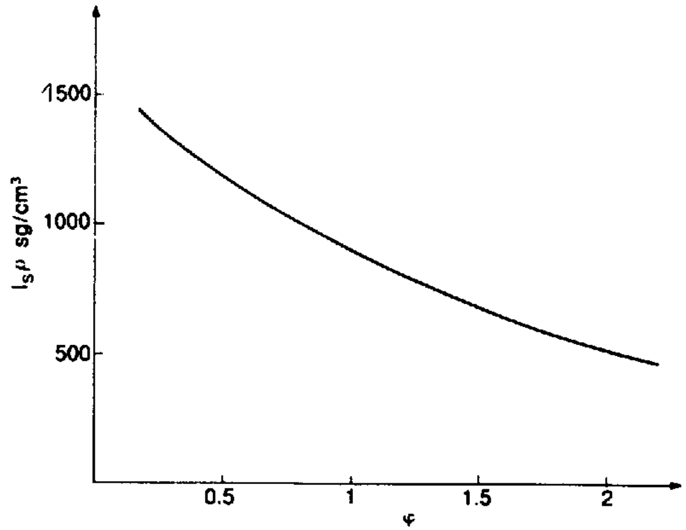

FIG. 12.11. Hydrocarbon fueled composition theoretical performances (M = 2; Z = 0; P = 0.57 MPa).

Figure 11 shows the evolution of the density-specific impulse ($I_s\rho$) versus the equivalence ratio (ϕ).

Figure 12 illustrates the evolution of the temperature as a function of the equivalence ratio. Its maximum value is of the order of 2590 K in an equivalence ratio ranging from 1.1 to 1.35. The stoichiometric fuel-air ratio is 0.143.

2.4.1.2. *Processability*

Because of its low total solids this composition is very easy to manufacture. The viscosity of the slurry at casting is 2300 poises. Pot-life is excellent: the viscosity is 4400 poises for 12 h after casting.

Consequently, the casting of fuel-rich propellant is very easy, even in the case of grains with very complex shapes. Gravity alone is sufficient to fill the molds, without having recourse to any devices.

2.4.1.3. *Mechanical properties*

This composition has excellent mechanical properties, also due to its low filler loading ratio. At 20°C, and with a cross head rate of 50 mm/min, maximum stress is 0.8 MPa, the elastic strain 52%, and the strain at maximum stress 120%.

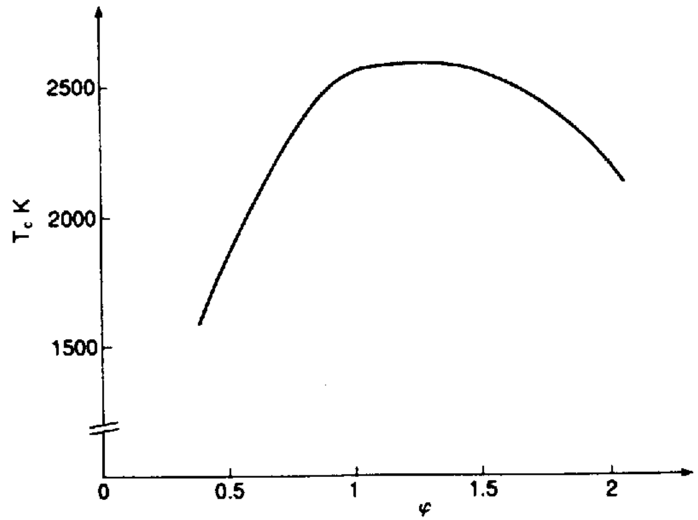

FIG. 12.12. Hydrocarbon fueled composition theoretical combustion temperature in air.

2.4.1.4. *Safety properties*

Table 5 lists the sensitivity characteristics in accordance with the operational modes described in Chapter 7.

2.4.1.5. *Ballistic properties*

The burning rate at 5 MPa is 3.8 mm/s. The pressure exponent is 0.45, providing a mass flow rate ratio of 3.8 at 20°C between 0.7 and 15 MPa. The evolution of the pressure curve versus time indicates low-amplitude pressure fluctuations at low pressure.

The modulation ratio between − 40°C and 60°C is 3 (Fig. 13).

TABLE 5 *Hydrocarbon fueled composition: safety properties*

Tests	Results	
Impact sensitivity (30 kg fall-hammer)	Height of non-propagation of violent reaction	≥ 4 m
	Height of non-reaction to impact	2 m
Sensitivity to friction (Julius Peters)	Coefficient of sensitivity to friction	0% at 353 N
Cook-off	Critical temperature	220°C
Card gap test	Number of cards	110

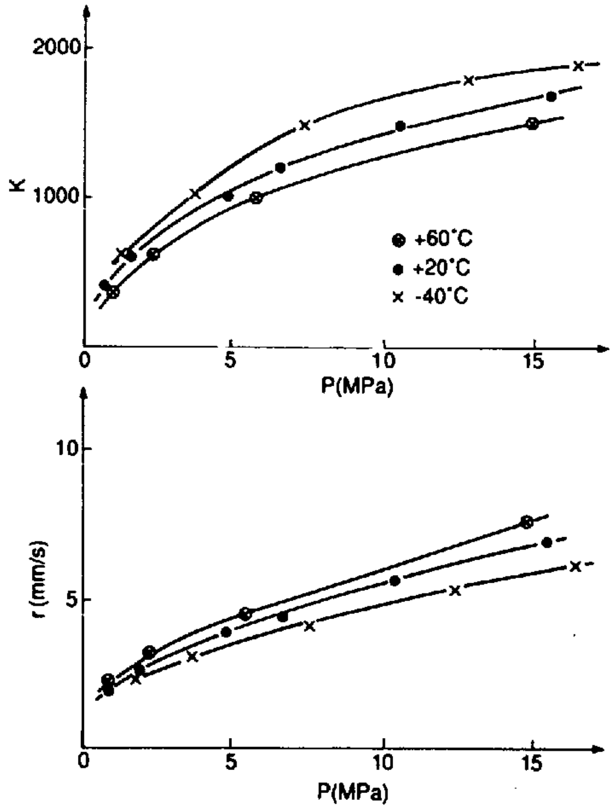

FIG. 12.13. Hydrocarbon fueled composition ballistic properties.

2.4.1.6. *Combustion efficiency*

The composition has been evaluated in a combustor with 200 mm diameter and four lateral air intakes, simulating a flight speed of Mach 2 and an altitude of 1.5 km.

The gas-generating grain operates at an average pressure of 3.2 MPa and releases 0.250 kg/s for 47 s. The equivalence ratio is 0.38. The combustion efficiency, which is defined as the ratio between the burned gas mass flow rate and the injected gas mass flow rate, is 0.91.

2.4.1.7. *Signature*

This composition, which does not contain metal and ammonium perchlorate, is smokeless.

2.4.2. *Boron composition*

Boron composition consists mostly of a binder, ammonium perchlorate, fine boron and sometimes one of several additives designed to facilitate the combustion of the boron.

The boron composition, described here, was selected on the basis of its processability, its mechanical properties, and its operational characteristics in a gas generator. It does not correspond to the higher energetic performances that may be obtained with this type of formulation. It is designed to operate in a choked gas generator.

2.4.2.1. *Theoretical performances*

The theoretical performance of these compositions depends greatly on the amount of boron. For a 25% content of ammonium perchlorate, the volumetric specific impulse changes, according to our standard calculations ($P = 0.57$ MPa, $M = 2, Z = 0, \phi = 0.4$), from 1778 to 2028 sg/cm^3 (i.e. a 14% increase), when the amount of boron increases from 40 to 50%.

Figures 14 and 15 show respectively the evolution of the volumetric specific impulse and the combustion temperature versus the equivalence ratio for the above composition. The peak temperature is at an equivalence ratio of 1.15.

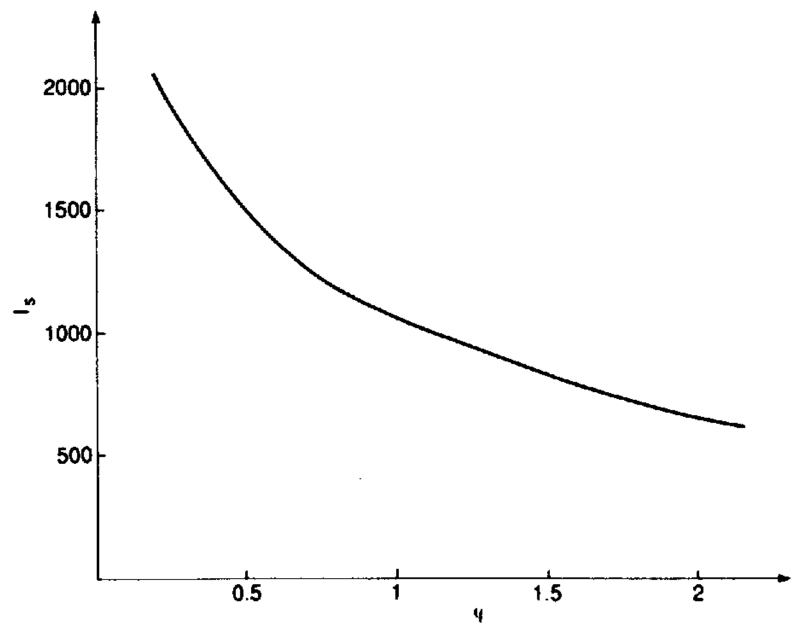

FIG. 12.14. Boron composition theoretical performances ($M = 2$; $Z = 0$; $P = 0.57$ MPa).

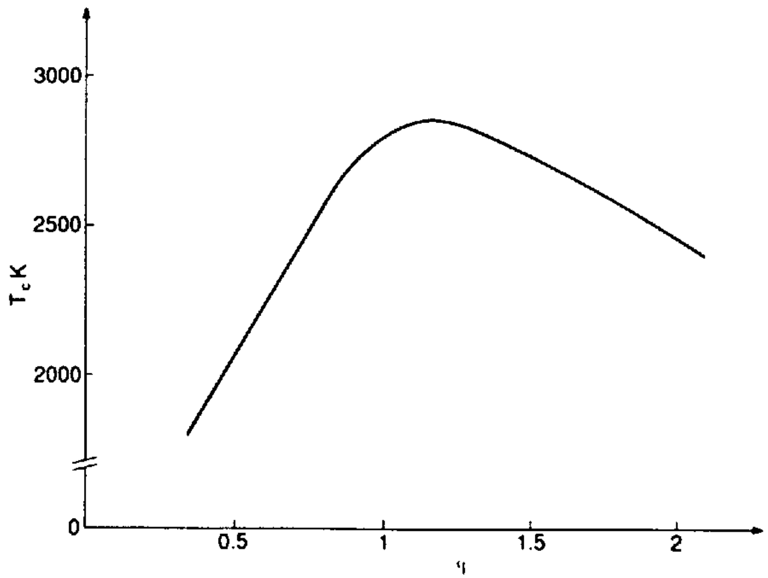

FIG. 12.15. Boron composition theoretical combustion temperature in air.

The temperatures obtained are much higher than with hydrocarbon-fueled compositions.

2.4.2.2. *Processability*

The manufacture of boron compositions with good mechanical properties is made somewhat difficult by the chemical reactions between impurities usually coating boron and the constituents of the binder, requiring a definition of the specification for the raw material, and the creation of a specially designed method for the mixing operation. Once this has been done, the manufacturing qualities and the mechanical properties are highly satisfactory. The viscosity of the slurries at casting is between 10000 and 15000 poises. The manufactured grains are end-burning. They are manufactured using the casting and gravity process.

2.4.2.3. *Mechanical properties*

In terms of the mechanical properties for the binder, the maximum stress is between 1.8 and 2.4 MPa, and the strain at maximum stress is between 37 and 44 %.

2.4.2.4. *Safety properties*

These properties are shown in Table 6.

TABLE 6 *Boron composition: safety properties*

Tests	Results	
Impact sensitivity (30 kg fall-hammer)	Height of non-propagation of violent reaction	≥ 4 m
	Height of non-reaction to impact	2.5 m
Sensitivity to friction (Julius Peters)	Coefficient of sensitivity to friction	0% at 253 N
Cook-off	Critical temperature	187°C
Card gap test	Number of cards	≤ 1

2.4.2.5. *Ballistic properties*

The compositions shown in Fig. 16 burn at a pressure of 5 MPa between 10 and 15 mm/s. They produce no combustion residue, but leave in the gas generator slag with a mass corresponding to less than 1 % of the initial mass of the grain. The compositions discussed here have low-pressure exponents, smaller than 0.1 when the pressure exceeds 3 MPa.

Because the boron compositions are heavily particle-laden they show a high propensity to create obstructions in the nozzle, resulting in pressure evolution curves versus time that are progressive. Two factors have influence

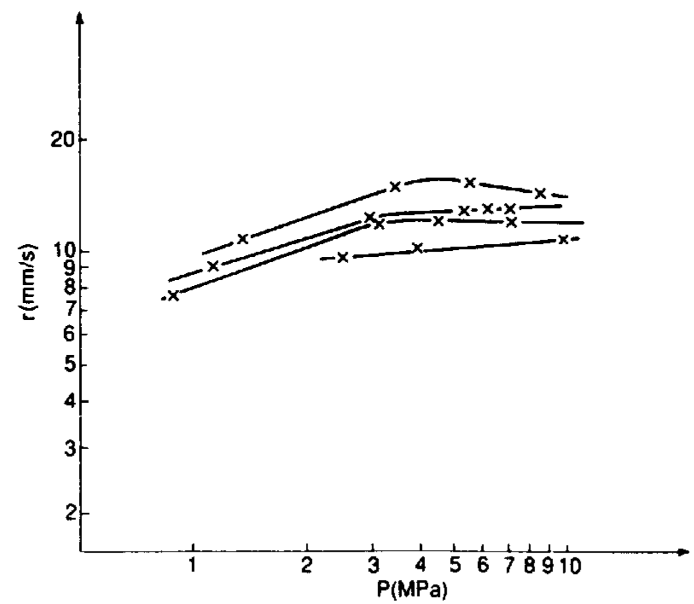

FIG. 12.16. Boron composition ballistic properties (end burning grain—90 or 117 mm diameter).

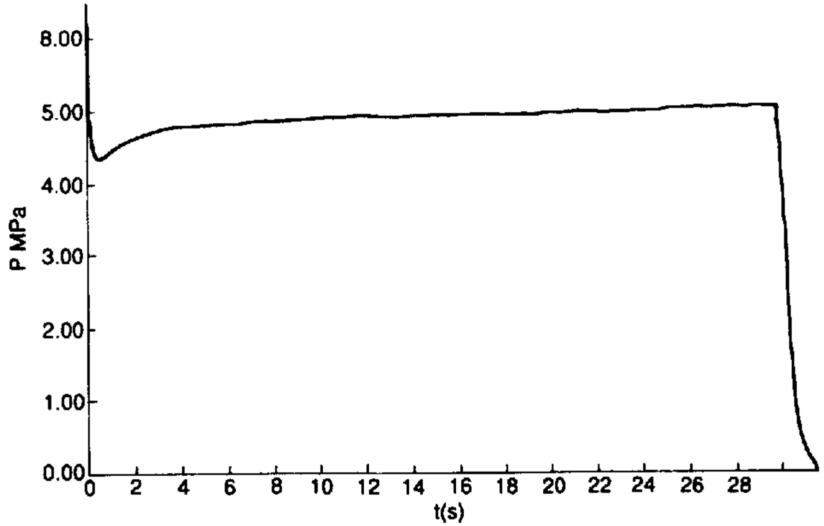

FIG. 12.17. Boron composition static test-end burning grain (177 mm diameter; 300 mm length).

on this phenomenon: one is the internal architecture of the gas generator, and the other is the formulation of the fuel-rich propellant. Figure 17 shows the recording of a firing corresponding to an optimal configuration.

2.4.2.6. *Combustion efficiency*

For reasons briefly discussed in the preceding section, obtaining high combustion efficiency in a combustor is difficult, and requires a careful organization of the flows inside the combustion chamber.

The research done by K. Schadow [16,17] and S. W. Abbott, L. D. Smoot and K. Schadow [18] demonstrated that because the temperature in the gas generator is generally lower than the 1950 K ignition temperature of boron, good combustion efficiency can be attained only when the gas generated by the composition burn with the air at sufficiently high equivalence ratio levels to produce a temperature high enough to guarantee that the heated boron particles will be able to ignite. They have also demonstrated that combustion efficiency drops when the pressure of the combustor decreases.

C. Vigot, L. Bardelle and L. Nadaud [10] have studied the combustion of a fuel-rich propellant with 35% boron. They demonstrated that the combustion efficiency can be improved by injecting the fuel at the forward end with converging jets, and by introducing only a portion of the air close to the forward end. This arrangement creates an area where the temperature

attained is sufficiently high to guarantee the ignition of the boron, since the ratio of the fuel-air mixture is close to the stoichiometry. The remainder of the air is injected downstream. It is important that the distance separating these two injection planes not exceed a certain specific value. This value depends on many factors such as the geometry of the air intake connections in the combustion chamber, and the distribution of the velocity of the air.

2.4.2.7. *Signature*

Because the boron compositions are heavily particle-laden, they are smoky.

3. Boosters for Integral Rocket Ramjets

Ramjets and ducted rockets are accelerated to or above the minimum required takeover speed by a solid propellant booster [19-22]. Three basic configurations are generally described: externally mounted boosters, whether permanent or droppable, tandem rocket ramjet and integral rocket ramjet. The integral rocket ramjet concept permits the overall missile dimensions to be minimized and so has significant drag, weight and volume advantages when compared to the two other configurations. There are also disadvantages to the integral concept. Specifically, the booster and the combustor share a common chamber. This requires that additional design emphasis be placed on the propellant booster grain, the ramburner thermal protection and the bonding of the grain to the thermal insulator.

The booster operating pressure is between 7 and 14 MPa and the ramjet operates under 1 MPa. The case is fabricated to withstand the high booster pressure and the thermal protection must resist the case mechanical deformation induced during the booster phase. The booster requires a smaller nozzle throat area than the ramjet due to the order of magnitude difference between the ramjet and the booster operating pressures. Two configurations can be used: ejectable nozzle system and nozzleless booster.

The booster is sized to accelerate the missile from ground or air launch speed to a velocity at which ramjet thrust exceeds drag by some margin. The Mach number for ramjet takeover is generally between 1.5 and 2.5.

For a given diameter, this requirement dictates a minimum grain length. Generally, this length exceeds the value required to reach the required ramjet combustion efficiency. This is true even for missiles launched from aircraft. One notable exception is the boron propellant ducted rocket. For a given ramjet configuration, greater booster length results in a shorter fuel tank and therefore a shorter range. According to Myers [19], a 1% increase in propellant grain length could result in a 5-10% loss in vehicle range. Thus a high volumetric specific impulse propellant and a high volumetric ratio grain are important requirements.

It is necessary to restrict drag losses during the booster phase. Consequently, the grain operating time is minimized within the limits dictated by the maximum acceleration allowed by the missile. The grain burn time is generally between 3 and 6 s. Therefore, medium-to-high burning rate propellants are required for boosters.

The thermal protection of the case must withstand heat during the booster and the ramjet phases. During the booster phase the combustion gases are reduced and are produced at temperatures up to 3600 K and pressures up to 14 MPa, but gas velocities and operating times are short. In the ramjet the temperature and the pressure are much lower, but the gases are oxidizer-rich and velocities can reach 300 to 340 m/s with operating times between several tens and several hundred seconds. In order to reduce inert weight and volume, thermal protection thickness is limited.

The different thermal protection concepts are discussed in Chapter 13.

During the transition phase the rocket motor transforms itself to a ramjet combustor (Figure 2). The vehicle drag forces are high and the missile quickly slows down. According to Myers [19] typically slowing down is about 0.1 Mach number per second. Therefore, transition must be done swiftly. Energy is released after booster operation by the combustion of propellant grain slivers, part of liner and decomposition products resulting from booster heating. The fuel injection and its ignition must be timed so that the total energy released does not cause excessive combustor pressure increase which would result in inlet unstart. Shortening the transition phase requires that careful attention be focused on residual booster materials and the careful shaping of booster burning profiles at the end of operation. Consequently, the transition phase dictates new requirements for the booster grain:

- Sliverless grain, although grain slivers always exist to some extent, caused primarily by dimensional tolerance variations during manufacture.
- Minimum liner thickness. One technical answer to direct bonding is described in Chapter 13.

The nozzleless booster represents an alternative concept to the ejectable nozzle system [23,24]. The advantages of this design are indicated in Chapter 2. This configuration places additional requirements by comparison with the nozzled motor design:

- the burning rate must be higher,
- the stress capacity at the high operating temperature must be raised to avoid grain damage under the shear loads caused by the pressure difference between the head-end and the aft-end,
- small pressure exponent — lowering the pressure exponent permits a significant performance increase. According to Procinsky and McHale [23], lowering the pressure exponent from 0.48 to 0.28 induces a 3.0% increase in total impulse.

The booster propellants are generally of the high-energy aluminized composite type as low visual signature is not required (Chapter 10). The formulations are optimized to achieve the mechanical properties suitable for a case-bonded grain. They include a liquid or a solid burn rate catalyst to achieve the required burning rate (between 20 and 35 mm/s at 7 MPa). An alternative propellant composition is one which employs zirconium. The interest in zirconium is due to its high density (6.49). Typical compositions include an HTPB binder, ammonium perchlorate and high loading of zirconium (up to 45%). Typical zirconium propellants possess lower specific impulse, higher density and higher volumetric specific impulse than typical aluminized formulations.

Aluminum and zirconium compositions show some ballistic property differences. The specific impulse efficiency losses for zirconium-loaded compositions are more important than those for aluminum compositions. Also zirconium propellants show greater sensitivity to motor scaling effects [25]. Nevertheless, the substitution of an aluminum composition by zirconium formulation in a given configuration grain would induce a shorter but heavier booster [23]. Another disadvantage of zirconium composition is the relatively high cost of zirconium.

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