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BALLISTIC EFFECTIVENESS OF Zr-CONTAINING COMPOSITE SOLID PROPELLANTS AS A FUNCTION OF BINDER NATURE AND MASS FRACTION

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This paper considers the effects of binder mass fraction on the properties of energetic formulations based on zirconium and zirconium hydride. These ingredients, replacing aluminum in solid rocket motors with low vehicle performance coefficient, may increase the propellant ballistic effectiveness, thanks to the resulting higher density and notwithstanding their lower specific impulse. The propellant ballistic effectiveness is estimated via the vehicle velocity achieved using the propellant under analysis in a real vehicle. For each specific mission, the binder content can be varied to provide the optimal relationship between energetic and physical-mechanical properties, that is, one may sacrifice energy in favor of rheological and physicomechanical properties (increasing binder mass fraction), or *vice versa*.

NOMENCLATURE

Symbols

F $V/M_{\rm fin}$, vehicle performance coefficient
g_0 Reference gravity acceleration
$I_{\rm ef}$ Effective specific impulse (see Eq. (1))
$I_{\rm sp}$ Specific impulse

M	Mass
T	Temperature
V	Volume
α	Oxygen excess coefficient
ΔH_f°	Enthalpy of formation
Δv	Velocity increment
ρ	Density

Abbreviations

AB	Active binder
ADN	Ammonium dinitramide
Al	Aluminum
AP	Ammonium perchlorate
HCB	Hydrocarbon binder
HMX	Cyclotetramethylene-tetranitramine
Zr	Zirconium
ZrH_2	Zirconium hydride
2P	Two-phase flow

Subscripts

c	Combustion (temperature)
fin	Final (mass)
ln	Initial launch (mass)
pr	Propellant (mass)
ref	Reference (baseline)

1 INTRODUCTION

Composite solid propellants are used in both space and defense applications. The simplest formulation consists of an inorganic solid oxidizer entrapped in a polymeric binder that also works as a combustible. To increase solid propellants performance and stability, metal powders (such as Al, B, and Be) are added as high energy density fuel. Among these metals, the most known and used is Aluminum, because it is relatively low-cost, accessible, and widespread. However, metals hardly burn because of difficult ignition, not complete oxidation reaction, and uncertain combustion feed, both in homogeneous and heterogeneous phase [1]. The worst mishaps are connected with the two-phase expansion in supersonic nozzles and gravimetric specific impulse ($I_{\rm sp}$) losses.

Mechanical properties (strain and elasticity) are an essential requirement to certificate a propellant for flight missions. One of the most influential parameters is the volume percentage (with respect to the total compound) of the polymeric binder. If other characteristics are the same, mechanical properties are better, the higher is the binder volume percentage (typically, in the range 16% to 30%). Additionally, it is the binder percentage that especially affects manufacturing: it is very difficult, if not impossible, to make a propellant without enough binder; on the other hand, an excessive binder content depresses specific impulse.

In this paper, the concept of "ballistic effectiveness" is introduced to identify the propellant formulation that allows a missile to reach the highest velocity. So, the higher is the ballistic effectiveness, the higher is the vehicle velocity as shown by Eq. (1) (to be discussed later).

The ballistic effectiveness of composite solid propellants depends on many factors, such as specific impulse ($I_{\rm sp}$), density (ρ), power n in Vieille's combustion law $r_b = a_b p^n$, and combustion temperature (T_c). Especially density and $I_{\rm sp}$ play a considerable role in ballistic effectiveness, although the density value does not enter directly in the rocket velocity increment expression [2]. The effect of the burning rate exponent n is not direct: due to poor stability of the combustor/nozzle coupling, high values of the exponent n imply large pressure fluctuations. If the structure has to support higher pressure, it has to be more massive and so the ratio $M_{\rm ln}/M_{\rm fin}$ decreases and the rocket velocity increment decreases too. For this reason, the exponent n of the burning rate also affects ballistic effectiveness.

Nowadays, the most successful propellants are based on aluminum, binder, and oxidizer. But in rocket motors with comparatively low performance coefficient, namely, if $F = V/M_{\rm fin} < 1.5$ l/kg (V = propellant volume, $M_{\rm fin}$ = final vehicle mass with no propellant), using zirconium (Zr) or zirconium hydride (ZrH_2) instead of aluminum may increase the ballistic effectiveness because of the higher propellant density in spite of its lower specific impulse [3].

Usually, the binder percentage is fixed at 20 %(vol.) and the maximal ballistic effectiveness of formulations with zirconium or its hydride is achieved at Zr content 35%–45% that is considerably higher than the optimal content of Al (20%–22%) in Al-containing formulations. Using Zr or ZrH_2 ensures best ballistic parameters if an active binder is used. Notice that formulations with ZrH_2 are practically equivalent to formulations with Zr, even if the hydride works better in formulations with oxygen-rich oxidizers and active binders (AB).

This paper considers the effects of binder mass fraction in formulations with Zr and ZrH_2. Different kinds of oxidizers — Ammonium Perchlorate (AP), Ammonium Dinitramide (ADN), and Cyclotetramethylene-tetranitroamine (HMX) — and two kinds of binder, Hydrocarbon Binder (HCB) and AB, have been investigated.

It is shown that the effective impulse, $I_{\rm ef}$, is appreciably less sensitive to binder mass fraction growth if an AB is used, so that one may increase the volume fraction of AB with little loss in $I_{\rm ef}$. On the contrary, compositions with HCB are more affected and so less effective with binder percent higher than 20 %(vol.) that is the minimal value in order to obtain the necessary physical-mechanical properties and rheology.

In compositions with Zr or ZrH_2, the maximal $I_{\rm ef}$ values are achieved at rather high Zr content (37%–46%). In case of AB, the binder mass fraction can be increased up to 30%, especially if the oxidizer has a small oxygen excess coefficient, α, (e. g., HMX). If the $V/M_{\rm fin}$ value increases, the effectiveness of this replacement falls, and in this case, the role of oxidizer α becomes more important — the higher it is, the less, consequently, the replacement is and effectiveness falls.

When creating new composite solid propellants based on Zr or ZrH_2, one can choose between compositions characterized by maximum effective impulse, $I_{\rm ef}$ (with minimum binder content that is about 20 %(vol.) and, consequently, worse properties), or maximum physicomechanical properties but not so high effectiveness.

In companion experimental activities [4], solid propellant formulations containing up to 40% Zr were found to burn stable over a range of pressure from 20 to 80 atm. Using Zr, it was possible to obtain burning rates and burning rate exponents close to the values typical of compositions based on Al. But a strong dependence of the burning rate on the size of metal particles was observed for Zr formulations. This allows obtaining burning rates considerably higher than for similar Al-based compositions, without using ultradispersed metal.

For Zr-based compositions, burning rate and combustion laws can easily be modified by varying the component dispersion, the ratio of Al to Zr content, and by resorting to catalysts.

The cost of components and, consequently, of the whole propellant is very important and all *pro et cons* have to be estimated. It is remarked that the high zirconium price is known (about 50 times more expensive than Al) but it is all the same investigated because there are tasks that have to be reached whatever the price is.

Moreover, it is also impossible to estimate the whole mission cost precisely, because there are not enough data yet and also, the topic of this paper is scientific and not economical. It is necessary to seek for applications in which the benefits of the material would outweigh the associated costs. Surely, for each kind of rocket systems, the optimum formulation may be different.

All thermochemical calculations were carried out using the software package Terra [5] and considering an adiabatic isentropic process with $P_c : P_a = 40 : 1$ (according to the Russian standard). Pressure oscillations and other nonthermochemical issues are out of the scope of this paper.

2 METHOD OF INVESTIGATION

In assessing ballistic effectiveness, the main role is played by specific impulse and density, even if density does not appear directly in the Tsiolkovsky's expression of the rocket velocity increment:

$$\Delta v = g_0 I_{\mathrm{sp}} \ln\left(\frac{M_{\mathrm{ln}}}{M_{\mathrm{fin}}}\right)$$

where M_{ln} is the initial launch mass; $M_{\mathrm{fin}} = M_{\mathrm{ln}} - M_{\mathrm{pr}}$ is the final rocket mass = initial launch mass − propellant mass; $M_{\mathrm{pr}} = \rho V$ is the (propellant density)×(propellant volume); and g_0 is the reference gravity acceleration. Therefore,

$$\Delta v = g_0 I_{\mathrm{sp}} \ln\left(1 + \frac{\rho V}{M_{\mathrm{fin}}}\right) .$$

For a given rocket performance parameter (i. e., for a given $F = V/M_{\mathrm{fin}}$), if the propellant density steps up, M_{ln} value increases too and, consequently, at the same I_{sp}, Δv increases. So, if we have two different propellants (the first characterized by I_{sp1} and ρ_1, and the other one by I_{sp2} and ρ_2, both at the same V/M_{fin}) the propellant with higher ρ-value provides higher Δv if $I_{\mathrm{sp1}} = I_{\mathrm{sp2}}$.

The less is the mass fraction taken by the propellant in M_{ln}, the higher is the propellant density input to the resulting Δv value: the role of density increases for rockets with high $F = V/M_{\mathrm{fin}}$ ratio, that is for the lower stages of multiple stages missiles or missiles with relatively high F ratio.

In this paper, it is discussed how the binder mass fraction can change the ballistic effectiveness of Zr-containing formulations. Three oxidizers [6, 7], with different oxygen excess coefficient (α) and formation enthalpy (ΔH_f°), and two binders, HCB and AB, are analyzed. Relevant data are reported in Table 1.

Table 1 Energetic properties of examined ingredients

Purpose	Ingredient	Formula	ΔH_f, kJ/kg	ρ, g/cm^3	α*
Oxidizer	AP	NH_4ClO_4	− 2478	1.95	2.70
	ADN	$NH_4N(NO_2)_2$	− 1129	1.82	2.00
	HMX	$C_4H_8N_4(NO_2)_4$	322	1.92	0.67
Binder	HCB	$C_{73.17}H_{120.9}$	−393	0.92	0
	AB	$C_{18.96}H_{34.64}N_{19.16}O_{29.32}$	− 757	1.49	0.53
Energetic compound	Aluminum	Al	0	2.70	0
	Zirconium	Zr	0	6.49	0
	Zirconium hydride	ZrH_2	− 1902	5.61	0

*$\alpha = \mathrm{O}/[2\mathrm{C} + 0.5(\mathrm{H} - \mathrm{Cl})]$.

The formulation taken as baseline is Al (20 %(mass.)) + HCB (20 %(vol.)) and the rest being AP. This formulation is characterized by $I_{\rm sp} = 251$ s, density $\rho = 1.85$ g/cm^3, and $T_c = 3610$ K. This baseline was chosen because it is one of the most commonly used propellant formulation, well known, accessible, and easy to produce. If the rocket under consideration is loaded with this basic composition and this composition is replaced with another one with specific impulse value $I_{\rm sp2}$ and density ρ_2, it is easy to calculate the so-called effectiveness impulse ($I_{\rm ef}$) of the second composition if used in a rocket vehicle with the same ratio $V/M_{\rm fin}$. It means that the velocity increment Δv of the vehicle with this value of $V/M_{\rm fin}$ would be equal by using either the second composition ($I_{\rm sp2}$ and density ρ_2) or a composition with density $\rho = 1.85$ g/cm^3 and $I_{\rm sp} = I_{\rm ef}$. Thus, if $I_{\rm ef}$ of the second composition is higher than 251 s, the replacement will augment the velocity increment Δv and will be effective. The comparison of different formulations effectiveness for missiles with different volume-mass parameters, has been developed with several $V/M_{\rm fin}$ values (from 0.27 to 4.86 l/kg). That is equal to $M_{\rm ln}/M_{\rm fin} = 1 + 1.85V/M_{\rm fin}$ from 1.5 to 10, if $\rho = 1.85$ g/cm^3. In this paper, only few of them are discussed, from 0.27 to 1.35 l/kg with step $\Delta = 0.27$ l/kg, because after that value, Zr-based formulations effectiveness decreases and *cons* are more than *pros*, so the replacement is not effective.

At each $V/M_{\rm fin}$, the vehicle velocity increment Δv is calculated as

$$\Delta v_{\rm ref} = g_0 I_{\rm sp\,ref} \ln\left(1 + \frac{\rho_{\rm ref} V}{M_{\rm fin}}\right) = g_0 \cdot 251 \ln\left(1 + \frac{1.85V}{M_{\rm fin}}\right) \quad \text{baseline;}$$

$$\Delta v_i = g_0 I_{\rm sp} \ln\left(1 + \frac{\rho_i V}{M_{\rm fin}}\right) \quad \text{other cases.}$$

A new parameter, the effective specific impulse $I_{\rm ef}$, can be calculated as follows:

$$\Delta v_{\rm ref} = \Delta v_i \ \text{ implying } \ g_0 \cdot 251 \ln\left(1 + \frac{1.85V}{M_{\rm fin}}\right) = g_0 I_{\rm ef} \ln\left(1 + \frac{\rho_i V}{M_{\rm fin}}\right)\ ;$$

$$I_{\rm ef} = \frac{251 \ln(1 + 1.85V/M_{\rm fin})}{\ln(1 + \rho_i V/M_{\rm fin})}\,. \tag{1}$$

The physical meaning of $I_{\rm ef}$ is the following: the ith composition, characterized by $I_{{\rm ef}\,i}$ and ρ_i, used in a vehicle with a given $V/M_{\rm fin}$ ratio achieves the same Δv value as any composition with $\rho = 1.85$ g/cm^3 and $I_{\rm sp} = I_{{\rm ef}\,i}$.

If $I_{{\rm ef}\,i} > I_{\rm sp\,ref}$ (that is, $\Delta I_{{\rm ef}\,i} = I_{{\rm ef}\,i} - I_{\rm sp\,ref} = I_{{\rm ef}\,i} - 251 > 0$), the investigated formulation is more effective than the basic one. Otherwise, if $I_{\rm ef} < I_{\rm sp\,ref}$, the formulation under investigation is less effective than the basic composition.

The three oxidizers were chosen because they are produced in industry, are less hygroscopic than others, have rather high thermal stability and satisfactory impact sensitivity. Moreover, they have different values of density, enthalpy of formation, and α and, so, in this way, it is possible to summarize many oxidizers.

2.1 Two-Phase Flow Losses

When a condensed phase appears among the combustion products, some heat is carried away from the nozzle with these liquid/solid particles; and they are superheated in comparison with gas phase, because thermal equilibrium between gas and solid phase cannot be established during the short time taken by combustion products to expand through the nozzle. The thermodynamic code "Terra," as well as similar 1-phase programs, assumes that the temperature of the gaseous phase is equal to the temperature of the solid phase (sure, at the same cross section); therefore, the actual value of I_{sp} is a bit lower than the calculated one. This phenomenon is very difficult to be completely accounted for, since the value of I_{sp} losses depends on many factors (propellant mass, kind and size of motor, percent of condensed products in the combustion products, average size and size distribution of particles of condensed phase in combustion products, etc.).

In this paper, two-phase flow (2P) losses are not calculated but only the first estimation is given, to have an idea about their influence on the ballistic effectiveness.

From experimental data, it is known that increasing Al by 1%, I_{sp} decreases by about 0.22% [8]. If condensed phase sizes and all other parameters of the motor are assumed to be the same (only thermal capacity and condensed phase percent are changed by replacing Al for Zr or ZrH_2), one may estimate that 2P losses in compositions with Zr or ZrH_2 would be lower than in compositions with Al. Relevant data and estimates are summarized in Table 2.

The two-phase effect in compositions with Zr or ZrH_2 (for each 1% of the fuel) is about 2.7 times lower because of its smaller specific heat and less amount of condensed products. As the actual compositions with Zr or ZrH_2 contain a higher percent of condensed oxide in combustion products than compositions with Al, the ratio of the corresponding 2P losses $(\text{2P loss})_{\text{Al}}/(\text{2P loss})_{\text{Zr}}$ will be a bit lower than 2.7.

Ballistic effectiveness changes considerably only in formulations with Al: considering 2P losses, formulations with medium metal content are more effective than highly metallized formulations. In Zr-containing formulations, I_{ef} decreases, but compositions with good effectiveness are the same as the ones without considering losses.

Table 2 Two-phase flow losses

	Condensed phase	c^*	ΔI_{sp}
1% Al	1.88% Al_2O_3	162.9 J/(mol·K)	−0.22%
1% Zr	1.35% ZrO_2	78.1 J/(mol·K)	−0.078%
1% ZrH_2	1.32% ZrO_2	78.1 J/(mol·K)	−0.08%

*Molar specific heat values c are taken from Terra, at $T = 2500$ K.

2.2 Temperature

Formulations containing aluminum have lower combustion temperature than formulation filled by zirconium, even though the heat of formation of 1 g of Al_2O_3 is about two times higher than the heat of formation of 1 g of ZrO_2.

That is because the Zr-based formulations form two times more condensed metal oxide (ZrO_2) in combustion products than Al-based ones do in forming condensed Al_2O_3, and the specific heat capacity of condensed products is substantially lower than heat capacity of gases. Moreover, ZrO_2 dissociates in less amount than Al_2O_3 and the dissociation absorbs a lot of heat (the energy needed to heat 1 g of Al_2O_3 from 3600 to 4000 K is three times higher than the energy required to heat 1 g of ZrO_2 from 3600 to 4000 K).

When the combustion temperature is higher than 3700–3800 K, the nozzle section needs an additional thermal protection, and, consequently, the overall rocket mass increases. The more the combustion temperature is above 3700 K, the more thermal protection is needed and this extramass causes the fall of ballistic effectiveness. This implies that if one has two propellants with the same effectiveness but the second composition features T_c of 100 K lower than the first one, it is like one has two propellants with the same temperature but the second composition offers an effectiveness 1 s higher than the first one. Quantitatively, if a propellant has $I_{\mathrm{sp}} = I_{\mathrm{sp1}}$ and $T_c > 3700$ K, it would be equal to the second propellant with the same density and characterized by $T_c = 3700$ K but with $I_{\mathrm{sp}} = I_{\mathrm{sp1}} - 0.01(T_c - 3700)$.

3 DISCUSSION OF RESULTS

In this first part, general observations about compositions are made. Even if calculations were conducted for a large number of $F = V/M_{\mathrm{fin}}$ values, only the most interesting ones are reported. From the figures and table below, it is clear that I_{ef} depends on oxidizer, binder, and metal nature as well as their amount.

If the V/M_{fin} value is from 0.27 up to about 0.8 l/kg (that is, $M_{\mathrm{ln}}/M_{\mathrm{fin}}$ between 1.5 and about 2.5 if density value ρ is 1.85 g/cm^3), the formulations filled with Zr or its hydride are more effective than Al-based formulations. The lower is the V/M_{fin} value, the higher is the gap. When V/M_{fin} is between 0.8 and 1.3 l/kg, the formulations containing aluminum are equal to formulations with Zr while for V/M_{fin} higher than 1.35 l/kg, Al-based formulations outgo the Zr-based ones.

If V/M_{fin} is low and the composition is filled by Zr or ZrH_2, the binder content can be increased up to 30% (and even 34%) allowing mechanical properties to be improved. At high V/M_{fin} value, it is the binder nature and, especially, the binder oxygen excess that affect the ballistic effectiveness.

3.1 Influence of Oxidizer on Effectiveness

How does the oxidizer nature influence the ballistic effectiveness?

Formulations with AP. If $V/M_{\rm fin}$ is low (under 0.8 l/kg), Zr and ZrH_2 are more effective than Al, especially for AB. In compositions with AB, the maximum effectiveness is achieved at high Zr content (the advantage is bigger when Zr or ZrH_2 content is higher) and in this case, the binder can be increased up to 30 %(vol.) and more, both for Zr and its hydride, without losing $I_{\rm ef}$.

If binder is HCB, the maximum effectiveness is achieved at medium Zr content (43%–46%), $I_{\rm ef}$ is considerably lower and by increasing binder, the effectiveness quickly falls.

If other parameters are the same, Zr achieves the same effectiveness than its hydride in compositions with AB ($I_{\rm ef}$ is always higher than 240 s and binder can be increased as needed; $I_{\rm ef}$ is even always higher than 250 s if $F = 0.25$ l/kg) but it is better if binder is HCB and it is better if the binder content is higher.

If $V/M_{\rm fin}$ is higher than 1 l/kg, the gain decreases, especially if binder is HCB, and binder cannot be increased without losing ballistic effectiveness.

Formulations with ADN. The advantage of AB is more considerable than for systems based on AP: (AB + ADN)-based systems are always better than the corresponding compositions containing AP, while compositions containing HCB and ADN are worse than the AP-based ones at low F-values.

If the binder is HCB, by increasing binder content, $I_{\rm ef}$ soon falls, especially with ZrH_2; the slopes of $I_{\rm ef}$ plotted at growing binder volume percentages are higher in case of Zr, and especially ZrH_2, than in case of aluminum and the gain is so little that the replacement is considered not interesting. The best results are achieved at medium Zr or ZrH_2 content (about 37%–43%). If binder is AB, it can be increased up to 30% and more and if $V/M_{\rm fin}$ is fixed, $I_{\rm ef}$ does not change (e. g., if Zr = 40 %(vol.) and AB = 30 %(vol.), the gain is about 20–25 s at $F = 0.27$ l/kg. By increasing F, the gain falls and at $F = 1.35$ l/kg, it is only 5 s). Best results are achieved at high Zr or ZrH_2 content. Zirconium is better than ZrH_2 if binder is HCB; they are pretty equal in compositions containing AB.

Formulations with HMX. Hydrocarbon binder looses more than AB; formulations containing HCB and ZrH_2 are even much worse than the baseline: if binder content is more than 20%, $I_{\rm ef}$ is always lower than 240 s and, by increasing binder, $I_{\rm ef}$ falls, especially at high F value; in this case, the replacement is a failure. The formulations containing HCB (especially the ones filled with ZrH_2) achieve bad results: $I_{\rm ef}$ is low and, by increasing binder, effectiveness quickly falls, because all of the components have low α value that means they contain much more hydrogen than oxygen and maximum energetic potential it is no longer assured. It is necessary to use more active binders, such as AB with higher oxygen content. The AB-based systems have effectiveness higher than systems containing Al (always, if F is low) both with Zr and ZrH_2 and the best results are achieved at medium Zr or Zr hydride contents (between 37% and 43%). The composition 37%Zr + AB + HMX is the best, being its effectiveness always bigger than all the others (e. g., with AB = 30 %(vol.), I_{ef} is, respectively, at $F = 0.27$, 0.54, 0.81, 1.08, and 1.35 l/kg, about 281, 273, 268, 265, and 261 s) but if $F > 3$ l/kg, Al wins by about 3 s.

3.2 Influence of *F* Coefficient on Effectiveness

Below, there are some draft resumes concerning the relative effectiveness of formulations with Zr or ZrH_2 compared to baseline at few values $F = V/M_{fin}$ (Fig. 1). The aim is to identify the best formulation at every V/M_{fin}:

(*a*) $\boldsymbol{F}$ **= 0.27 l/kg** (Fig. 1*a*). The highest ballistic effectiveness is achieved in case of Zr + AB + HMX (+27 s when AB = 28 %(vol.) and +23.5 s when AB = 32 %(vol.), if Zr content is 31%). In compositions with Zr, HCB (curves *4* and *6*) is better at low binder percentages, but increasing binder percentages, AB is better because it feels less the effects of the raising binder (curves *5* and *7* are almost horizontal). Zirconium hydride gives the highest I_{ef} (always > 270 s) in composition with AB and binder can be increased up to 28%–30% (in this case, the gain is, at least, 15 s). All oxidizers give about the same results. There are no advantages in using HCB because I_{ef} starts decreasing as soon as binder content begins increasing.

The Al-based formulations (curves *2* and *3*) are worse than others: Al + HCB is definitely affected by binder increasing. That is why, at low F, density plays an important role. Generally, in every case, considering Zr- or ZrH_2-based propellants and AB, binder can be increased up to 30% and I_{ef} is always higher than 251 s;

(*b*) $\boldsymbol{F}$ **= 0.54 l/kg** (Fig. 1*b*). Binder can still be increased up to 30% and I_{ef} is higher than 251 s but ZrH_2 starts loosing I_{ef} — the more, the bigger is α of the oxidizer. I_{ef} of Al + AB + HMX (curve *3*) compositions starts growing;

(*c*) $\boldsymbol{F}$ **= 0.81 l/kg** (Fig. 1*c*). At high binder percentage, all I_{ef}, except for Zr + AB + HMX (curve *8*), are lower than 260 s. Compositions containing HCB (curves *4* and *6*) are not effective. The bigger is the oxidizer α-value, the higher the effectiveness is;

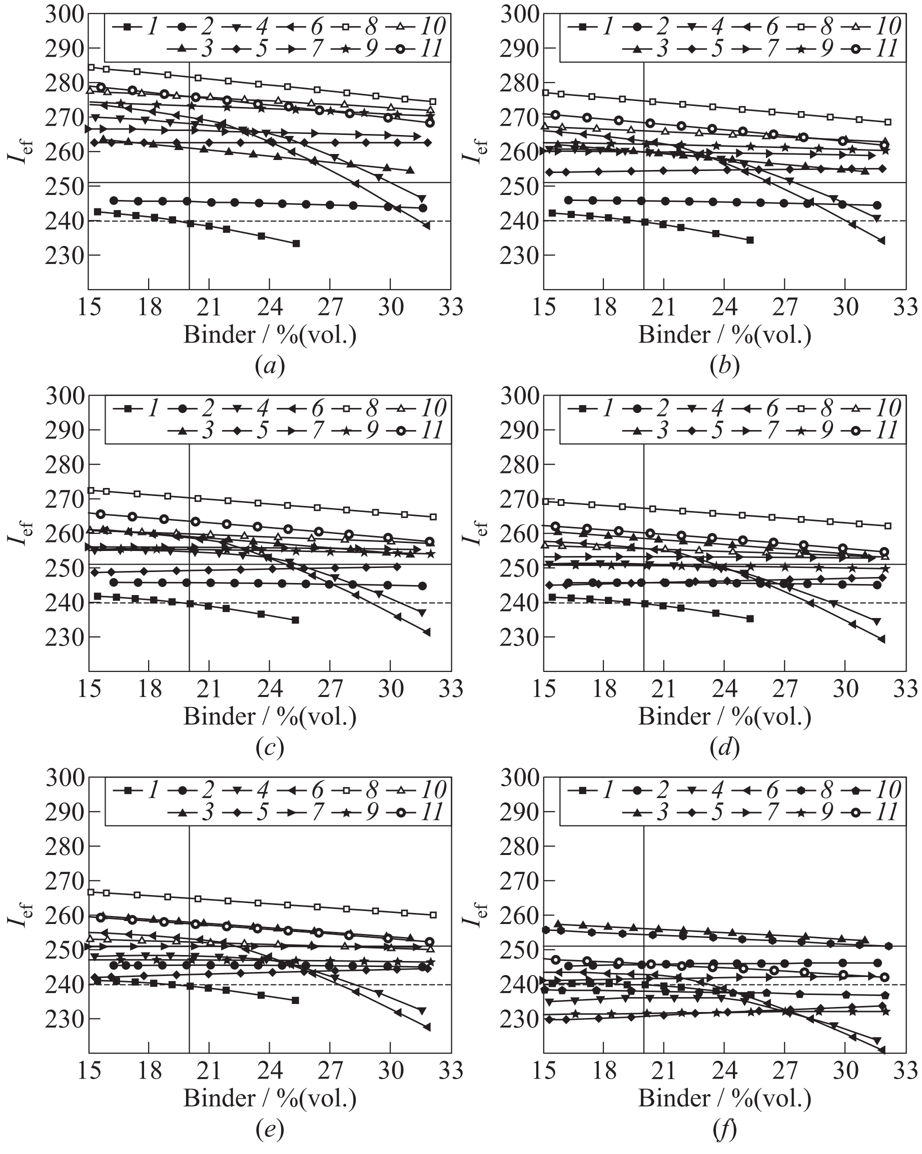

Figure 1 Binder mass fraction influence on I_{ef} (best formulations only): (*a*) $F = 0.27$; (*b*) 0.54; (*c*) 0.81; (*d*) 1.08; (*e*) 1.35; and (*f*) 4.86; *1* — basic; *2* — 16% Al + AB + ADN; *3* — 18% Al + AB + HMX; *4* — 43% Zr + HCB + AP; *5* — 37% Zr + AB + AP; *6* — 43% Zr + HCB + ADN; *7* — 34% Zr + AB + ADN; *8* — 31% Zr + AB + HMX; *9* — 49% ZrH_2 + AB + AP; *10* — 49% ZrH_2 + AB + ADN; and *11* — 37% ZrH_2 + AB + HMX

(*d*) **F = 1.08 l/kg** (Fig. 1*d*). The best results are achieved in case of low α oxidizers. If oxidizer is HMX (curves *3*, *8*, and *11*) and binder is 28 %(vol.), the gain is between 4 and 12 s (the bigger the higher metal density is). Formulations containing high α oxidizer (see, e. g., curves *4* and *5*) start losing $I_{\rm ef}$, because they have lower $I_{\rm sp}$ in spite of higher density but density role starts decreasing;

(*e*) **F = 1.35 l/kg** (Fig. 1*e*). The binder can be increased with a winning ($I_{\rm ef}$ is about 260 s when AB is about 28 %(vol.)) only in case of HMX + AB filled by Al (curve *3*), Zr (curve *8*), or ZrH_2 (curve *11*) and at least AB + ADN filled by Zr (curve *7*) or ZrH_2 (curve *10*); in this case, $I_{\rm ef}$ is only about 251 s but binder can be increased up to 28 %(vol.) and more. At this F value, oxidizer has more influence than metal (or hydride) on ballistic effectiveness; and

(*f*) **F = 4.36 l/kg** (Fig. 1*f*). The Al-based formulations win (best results at high ΔH_f and low α) over Zr and, especially, ZrH_2. If binder is increased up to 28 %(vol.), (Al + AB)-based formulations have $I_{\rm ef}$ about 254 and 247 s, respectively, with HMX (curve *3*) and ADN (curve *2*); Zr + AB + HMX has $I_{\rm ef}$ = 251 s, while in other formulations, $I_{\rm ef}$ is lower than 243 s. The compositions with Zr or its hydride and HCB + any oxidizer (curves *4* and *6*) or AB + AP (curves *5* and *9*) are less effective than the baseline. Independently of metal or hydride content, formulation effectiveness is the worse, the bigger is the oxidizer α-value.

3.3 Best Formulations Analysis

Some formulations are not interesting at any F-value because $I_{\rm ef}$ is too low or T_c is too high (see subsection 2.2): formulations containing Al and HCB have too low $I_{\rm ef}$ and it is the same in case of formulations based on HCB, HMX, and Zr or ZrH_2. In case of ZrH_2 and HCB, there is a gain only if F is low; otherwise, basic formulation overpowers. Some formulations, especially the ones with ZrH_2, have good ballistic effectiveness without any problem related to too high temperatures.

Now, the ballistic effectiveness of the best formulations is reported. The gains of effective impulse are shown in the best cases, at different binder contents, in Table 3.

From Table 3, it can be seen that formulations containing Zr or its hydride and the AB have a great ballistic effectiveness with any oxidizer and, in these cases, binder can be increased up to 32 %(vol.) and more.

If binder percentage is fixed at 32 %(vol.), if F is low (let say, 0.27 l/kg), the gain is high (from 13 to 24 s, depending on the formulation), while if F is

Table 3 Best formulations gain at different F and binder volume percentage

I_{ef} (gain)*									
F, l/kg	0.27			0.81			1.35		
Binder, %(vol.)	22	24	26	22	24	26	22	24	26
20 Al + HCB + AP					−10 (0)				
16 Al + AB + AD	−5,5	−5,7	−6,1	−5,3	−5,4	−5,6	−5,3	−5,3	−5,4
18 Al + AB + HMX	8,7	7,6	6,5	7,0	6,1	5,2	6,1	5,3	4,5
36 Zr + HCB + AP	16,1	14,5	10,5	3,2	2,3	−1,0	−2,8	−3,5	−6,4
37 Zr + AB + AP	11,7	11,7	11,6	−1,5	−1,3	−1,1	−7,6	−7,4	−7,1
43 Zr + HCB + ADN	16,7	12,0	6,8	6,0	1,9	−2,6	0,9	−2,8	−7,1
34 Zr + AB + ADN	14,9	14,6	14,3	4,9	4,8	4,7	0,2	0,1	0,1
31 Zr + AB + HMX	29,5	28,3	27,0	18,5	17,6	16,6	13,3	12,5	11,7
49 ZrH_2 + AB + AP	21,7	21,3	20,8	4,1	4,0	3,8	−3,9	−3,9	−4,1
49 ZrH_2 + AB + ADN	24,3	23,7	23,0	8,4	8,0	7,5	1,0	0,7	0,3
37 ZrH_2 + AB + HMX	23,9	22,7	21,5	11,7	10,7	9,8	5,9	5,1	4,3
Binder, %(vol.)	28	30	32	28	30	32	28	30	32
16 Al + AB + ADN	−6,4	−6,8	−7,1	−5,8	−6	−6,2	−5,5	−5,6	−5,8
18 Al + AB + HMX	5,3	4,1	2,9	4,2	3,2	2,2	3,6	2,7	1,9
36 Zr + HCB + AP	5,8	−3,6	−5,4	−5,0	−13,5	−14,7	−10,1	−18,2	−19,1
37 Zr + AB + AP	14,0	13,9	13,8	0,1	0,2	0,3	−6,4	−6,2	−5,9
43 Zr + HCB + ADN	0,6	−5,9	−12,9	−8,0	−13,8	−20,2	−12,1	−17,7	−23,7
34 Zr + AB + ADN	14,0	13,7	13,3	4,6	4,4	4,2	0,1	0,0	−0,1
31 Zr + AB + HMX	25,9	24,5	23,5	15,7	14,8	13,9	10,9	10,1	9,3
49 ZrH_2 + AB + AP	20,3	19,8	19,3	3,5	3,3	3,0	−4,2	−4,3	−4,5
49 ZrH_2 + AB + ADN	22,4	21,6	20,9	7,1	6,5	6,0	0,0	−0,5	−0,9
37 ZrH_2 + AB + HMX	20,2	19,0	17,7	8,8	7,8	6,8	3,4	2,5	1,6

*Gain = 240 − $I_{ef\,i}$ = (basic I_{ef}) − $I_{ef\,i}$.

high (e. g., 1.35 l/kg), every formulation containing Zr is worse than the baseline, except for the ones with AB and HMX (the gain is 9.3 and 1.6 s with Zr and ZrH_2, respectively).

The formulations containing Zr and HCB (curves *4* and *6* in Fig. 1) show good performance at low F and low binder percentage. For example, at $F = 0.27$ l/kg and binder 22 %(vol.), the gain is about 16 s for both AP and ADN; but at $F = 0.81$ l/kg and binder 26 %(vol.), there is already no gain (AP looses 1 s and ADN 2.6 s).

At high F value, Al-based formulations are better than Zr-based ones. With Al and AB, HMX is better than ADN; for example, in case of 18% Al + AB + HMX (curve *3*), when $F = 0.25$ l/kg, ΔI_{ef} is between 8.7 and 2.9 s, respectively, with binder from 22 to 32 %(vol.) and these gains are lower than Zr-based formulations; when $F = 1.35$ l/kg, the gain is between 6.1 and 1.9 s (they seem low but are higher than Zr-based).

The best formulation (curve *8* in Fig. 1) is always 31% Zr + AB + HMX that, in the worse case (that is, $F = 1.45$ l/kg and a binder content of 32 %(vol.)), achieves a gain of 9.3 s, while at $F = 0.7$ l/kg achieves $\Delta I_{\rm ef}$ of 29.5, 28.3, 27, 25.9, 24.5, and 23.5 s, respectively, with binder from 22 to 32 %(vol.).

So, for every missile with a certain $V/M_{\rm fin}$ value, there is a specific formulation that better fits the mission.

These results are summarized in Fig. 1. The black vertical line indicates the reference binder content (20 %(vol.)). The black horizontal line is the baseline formulation $I_{\rm sp} = 251$ s without considering 2P losses [remember that the basic formulation is Al (20%) + HCB (20 %(vol.)) and the rest AP] and the dashed one is $I_{\rm sp}$ for the same formulation but considering two-phase effects.

3.3.1 Specific impulse and density

How specific impulse and density rely on binder percentage is illustrated in Fig. 2. As said, the importance of density decreases when F increases. The formulations containing Al (curves *1*–*3*) have the higher $I_{\rm sp}$ but the lower density.

On the contrary, compositions containing Zr or ZrH_2 (especially with AP as oxidizer and ZrH_2 + AB + ADN) have the lower $I_{\rm sp}$ but very high density (curves *5*, *4*, *9*, and *6*, respectively). These formulations are better when F is

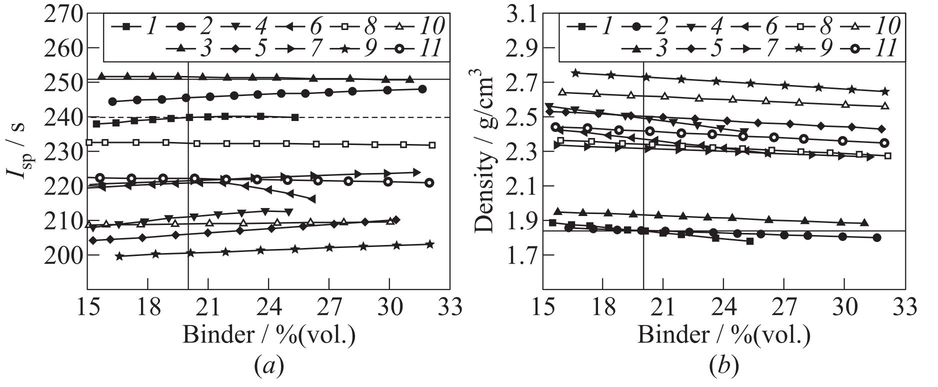

Figure 2 Binder mass fraction influence on specific impulse (*a*) and density (*b*): *1* — basic; *2* — 16% Al + AB + ADN; *3* — 18% Al + AB + HMX; *4* — 43% Zr + HCB + AP; *5* — 37% Zr + AB + AP; *6* — 43% Zr + HCB + ADN; *7* — 34% Zr + AB + ADN; *8* — 31% Zr + AB + HMX; *9* — 49% ZrH_2 + AB + AP; *10* — 49% ZrH_2 + AB + ADN; and *11* — 37% ZrH_2 + AB + HMX

low and density holds the main role. At high F, ballistic effectiveness is higher in case of low density but high I_{sp} (Al-based formulations).

The compositions that show (always) the higher I_{ef} are the ones with average properties: not too low I_{sp} and not too high density. Obviously, because binder density is very low, the resulting composition density is the lower, the bigger is the binder content. The compositions containing HCB are less dense than the same compositions with AB and, moreover, HCB-based propellants density are affected by binder growth more than AB-based compositions. So, the lower is the binder density, the bigger is the lost, when binder increases.

3.3.2 Temperature

The influence of binder mass fraction on flame temperature T_c is illustrated in Fig. 3. Formulations containing Al and AB have too high T_c (about 3800–4000 K) if metal percentage is higher than 20%. Only compositions containing AB + HMX have acceptable T_c (3500–3700 K, decreasing if Al content increases). Al + HCB shows T_c about 3500–3700 K but I_{ef} is too low; if the oxidizer is HMX, T_c (2650–2750 K) is quite too low.

As known, Zr-based formulations have higher temperature than the Al-based ones; especially the ones with AB as binder have too high T_c at high Zr percentage (the higher is the oxidizer α value, the higher are I_{ef} and T_c, too); so, AP, ADN,

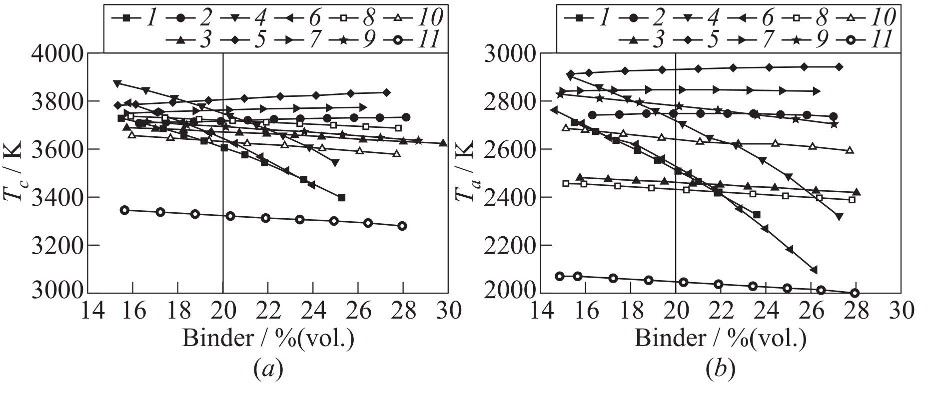

Figure 3 Binder mass fraction influence on temperatures T_c (a) and T_a (b): *1* — basic; *2* — 16% Al + AB + ADN; *3* — 18% Al + AB + HMX; *4* — 43% Zr + HCB + AP; *5* — 37% Zr + AB + AP; *6* — 43% Zr + HCB + ADN; *7* — 34% Zr + AB + ADN; *8* — 31% Zr + AB + HMX; *9* — 49% ZrH_2 + AB + AP; *10* — 49% ZrH_2 + AB + ADN; and *11* — 37% ZrH_2 + AB + HMX

and HMX can be used in formulations with maximum, respectively, 37, 34, and 31 %(vol.) of Zr (curves *5*, *7*, and *8*, respectively). In compositions containing Zr with HCB and HMX, T_c is too low and the results are not good, but, because T_c increases if α becomes bigger, if the oxidizer is ADN or AP, T_c is allowable (3300–3700 K); even if at low binder volume percentages is higher than 3800 K, increasing binder percentage up to 26 %(vol.), T_c decreases in 250–300 K and becomes acceptable.

In compositions with ZrH_2 (curves *6* and *9*), T_c is considerably lower than with Zr, because of lower enthalpy of formation and content of hydrogen. In formulations with HCB and HMX, T_c is too low (2100–2600 K). If AB and HMX are used, T_c is between 3200 and 3700 K. It has to be remarked that in formulations with AB, increasing binder percentage, temperature does not change, and in compositions with HCB as binder, T_c decreases considerably, if binder increases. The temperatures are higher in AB-based formulations because of its enthalpy of formation.

If ZrH_2 is used instead of Zr, T_c decreases, and, increasing metal content, it does not grow up too much (so, metal percentage can be increased more). Moreover, increasing binder, temperature decreases or, at least, it is the same that the one at minimum binder content.

All the chosen formulations have T_c in the range 3500–3800 K, except for Zr + AB + AP (curve *5*), which has a higher T_c (from 3800 up to 3850 K if binder increases up to 28–30 %(vol.)) and ZrH_2 + AB + HMX (curve *11*) that shows the lowest one (from 3350 to 3300 K, if AB increases up to 26 %(vol.)).

When creating new composite solid propellants based on Zr or ZrH_2 instead of Al, a choice is given — to create compositions either with maximum value of I_{ef} (in this case, it is necessary to use binder in minimum acceptable volume percentage that complicates the process of propellant production and degrades the physical-mechanical properties of the propellant) or with a bigger volume percentage of binder. The second way gives compositions with effectiveness not so high as at 20 %(vol.) of binder, but with better physical-mechanical properties.

So, for every propulsive mission, one can choose the binder volume percentage that would be optimum: sometimes, we will sacrifice a bit I_{ef} to account for better physical-mechanical properties, sometimes *vice versa*.

4 CONCLUDING REMARKS

The replacement of aluminum for zirconium or zirconium hydride increases specific impulse and allows binder to grow up to 28–30 %(vol.), if $F = V/M_{\mathrm{fin}}$ (propellant volume / final vehicle mass) is lower than 1 l/kg. Increasing V/M_{fin}, it is the oxidizer nature that influences effectiveness more than metal does and effectiveness decreases more and more with increasing the α value of the oxidizer.

In comparison with HCB-based formulations, the same composition, containing an AB, achieves higher ballistic effectiveness and binder portion can be increased up to 30 %(vol.) (and also, in compositions containing HCB, density decreases quickly if binder percentage is increased and that makes effectiveness falling).

Maximum ballistic effectiveness in compositions containing Zr or ZrH_2 is generally achieved when metal percentage is about 37–46 %(vol.), much higher than optimum Al content (18–22 %(vol.)). High metallic formulations are soon penalized if binder percentage increases and, also, T_c is too high.

Binder fraction can be increased more (up to 30 %(vol.)) and without effectiveness falls in compositions containing Zr or ZrH_2, AB and low α oxidizer. Increasing V/M_{fin}, binder growth is as penalizing as higher is oxidizer α.

For each task, it is possible to choose the binder volume percentage that would be optimal: sometimes I_{ef} can be preferred to physical-mechanical properties, sometimes, *vice versa*, increasing binder content, I_{ef} can be sacrificed in behalf of physical-mechanical properties.

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