Progress in Propulsion Physics **2** (2011) 67-80

BALLISTIC EFFECTIVENESS OF SUPERDENSE SOLID COMPOSITE PROPELLANTS WITH ZIRCONIUM OR ZIRCONIUM HYDRIDE

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The ballistic effectiveness of propellants depends not only on the value of specific impulse but also on many other performances, primarily on the density. Despite the density itself does not enter the expression of the rocket velocity ($W = I_{\mathrm{sp}} \ln(M_{\mathrm{launch}}/M_{\mathrm{finish}})$ where M_{launch} and M_{finish} are the rocket launch mass and its mass after the propellant is burnt, respectively), it influences the value $M_{\mathrm{launch}}/M_{\mathrm{finish}}$ of the specific rocket. If one charges the construction of fixed volume with a more dense propellant, the ratio $M_{\mathrm{launch}}/M_{\mathrm{finish}}$ increases and, consequently, W increases as well. In this paper, the possibility of creating solid composite propellants (SCP) with zirconium (density 6.49 g/cm^3) and zirconium hydride (density 5.61 g/cm^3) as energetic compounds instead of aluminum is considered. It was found for what kinds of engines these propellants have to be more effective than propellants based on aluminum.

1 INTRODUCTION

When developing new propellants, one has to consider in what kind of engines these propellants could be used. Besides the specific impulse (I_{sp}), the density is one of the most important factors defining ballistic effectiveness. The higher the $M_{\mathrm{launch}}/M_{\mathrm{finish}}$ ratio, the higher the density input.

It is possible to charge the same engine (that is the same propellant volume) with a propellant of lower I_{sp}, but higher density. Therefore, it is possible to achieve the velocity growth for engines with the $M_{\mathrm{finish}}/V_{\mathrm{prop}}$ ratio (V_{prop} is the propellant volume) higher than the predefined value. For example, replacing aluminum by zirconium or its hydride, new propellants can be created with lower I_{sp} (at least, by 20 s) but with a considerably higher density (2.3 g/cm^3 and higher) as compared with the formulations containing aluminum (~ 1.8 g/cm^3).

Article available at http://www.eucass-proceedings.eu or http://dx.doi.org/10.1051/eucass/201102067

2 PROBLEM STATEMENT AND RESULTS

If Al is replaced with Zr or ZrH_2, the I_{sp} value always decreases, but the density grows considerably. The question arises: In what cases the I_{sp} loss can be compensated with the density growth? It is well known that the higher the value of Z ($Z = M_{launch}/M_{finish}$ where M_{finish} is the total mass with no propellant), the higher the contribution of density to the maximum rocket velocity. For multistage space vehicles, the higher the stage, the lower the density contribution.

In this paper, the ballistic effectiveness of the SCP with Zr or ZrH_2 is compared to that of the SCP with Al. Many different oxidizers and two binders have been considered as SCP compounds (Table 1). The I_{sp} values were calculated using the standard ASTRA and TERRA codes [1] at pressures of 40 and 1 atm in the combustion chamber and at the nozzle exit, respectively. For estimating the mutual influence of I_{sp} and density (d) on the ballistic effectiveness, a new variable I_{ef} (effective impulse) was introduced. Consider a reference rocket (index 0) with a definite ratio $F = V_{prop}/M_{finish}$ charged with the propellant possessing $I_{sp0} = 251$ s and $d_0 = 1.85$ g/cm^3 (corresponds to the formulation 20% Al + 9% standard hydrocarbon binder + ammonium perchlorate, $Z_0 = 1 + 1.85F$). This engine would exhibit the value $W_0 = g_0 \cdot 251 \cdot \ln(Z_0)$. When charged with another propellant with I_{sp2} and density d_2, the value of Z for this engine changes

Table 1 Main properties of compounds ($\alpha = \mathrm{O}/[2\mathrm{C} + 0.5(\mathrm{H} - \mathrm{Cl})]$)

Functional purpose	Component	$\Delta^\circ H_f$, kcal/kg	d, g/cm^3	α
Oxidizer	Hydroxylammonium perchlorate (HAP)	−493	2.07	3.33
	Ammonium perchlorate (AP)	−593	1.95	2.7
	Ammonium dinitramine (ADN)	−270	1.82	2.0
	Hyrazinium perchlorate semihydrate (SHHP) $N_2H_5ClO_4 \cdot 1/2H_2O$	−552	1.94	2.0
	Hydrazonium nitroformate (HNF)	−380	1.91	1.33
	HMX	77	1.92	0.67
Binder	Standard Hydrocarbon binder (SHCB) $C_{73.17}H_{120.9}$	−93	0.92	0
	Active binder (AB) 20% polyvyniltetrazol, plasticized with the mixture trinitroglycerole and diazapentane $C_{18.96}H_{34.64}N_{19.16}O_{29.32}$ [2]	−181	1.49	0.53
Energetic compound	Al	0	2.7	0
	Zr	0	6.49	0
	ZrH_2	−455	5.61	0

($Z_2 = 1 + d_2(Z_0 - 1)/1.85$), resulting in $W_2 = g_0 I_{sp2} \ln(Z)$. Then, the task is to calculate what I_{sp} value has to exhibit an SCP formulation with density d_0 for the same engine to reach velocity W_2. This I_{sp} value will be referred to as effective impulse I_{ef}. In Table 2, different Z_0 values are considered together with the corresponding F values: $F = (Z_0 - 1)/1.85$.

Table 2 The calculated F values for the considered Z_0 values

Z_0	F, 1/kg
1.5	0.27
2	0.54
2.5	0.81
3	1.08
3.5	1.35
4	1.62
5	2.16
6	2.70
8	3.78
10	4.86

Each formulation was assumed to contain 20 %(vol.) binder (either SHCB or AB), because if the binder content is less, it is hard to form a propellant with acceptable rheological and physicomechanical properties. Aluminum content was varied from 16 up to 28 %(mass.) whereas Zr and ZrH_2 from 28 to 55 %(mass.).

Figures 1 to 5 represent the calculated data for all formulations containing various combinations of oxidizers and binders with Z_0 values ranging from 1.5 to 3.5 (corresponding to different-purpose realistic rocket engines). In these figures, plotted along Y-axes is the increment of I_{ef}, ΔI_{ef}, with respect to the basic formulation (20% Al+ 20 %(vol.) SHCB + AP, $I_{sp} = 250.9$ s; $d = 1.85$ g/cm^3) while plotted along X-axes is the content of metal or hydride in the SCP formulation.

It is evident from Figs. 1 to 5 that the most of formulations with Zr or ZrH_2 are more effective than the similar formulation with Al, especially at low Z_0. First, consider how this advantage depends on Z_0 for the same oxidizer.

<u>Formulations with HAP.</u> This oxidizer is the most rich with oxygen ($\alpha = 3.33$). If $Z_0 = 1.5$, there is no considerable difference in using either SHCB or AB for both Zr and ZrH_2. ΔI_{ef} achieves 30–35 s only due to replacing Al with Zr or ZrH_2. If $Z_0 = 2.0$, ΔI_{ef} drops to 20–25 s. If Z_0 further increases, the advantage of ZrH_2 in comparison with Zr increases (I_{sp} becomes more important than density). ΔI_{ef} achieves 10–12 s at $Z_0 = 2.5$ and 5–8 s at $Z_0 = 3.0$. At $Z_0 = 3.0$, ΔI_{ef} is already a few seconds only. In Zr + SHCB + HAP formulations, ΔI_{ef} rises to higher levels when Zr or ZrH_2 content is about 50 %(mass.) Zr (that is, about 67% of condensed phase in combustion products).

<u>Formulations with AP</u> have a bit lower ΔI_{ef} values (in comparison with formulations based on HAP) if they contain Zr or ZrH_2 instead of Al. The reason is oxygen deficit in AP in comparison with HAP. Anyway, ΔI_{ef} values are rather high (25–30, 20, 13–15, 10, and 4–5 s at $Z_0 = 1.5$, 2, 2.5, 3, and 3.5, respectively. In the Zr + SHCB + AP system, the maximum I_{ef} values are achieved at Zr or ZrH_2 content $\sim$ 44%–45% Zr (that is, $\sim$ 60% of condensed phase in combustion products).

<u>Formulations with ADN.</u> The advantage of AB over SHCB becomes more distinct. On the one hand, if AB is used, there is no difference between the ΔI_{ef} values for formulations with Zr and ZrH_2 while in the formulations based

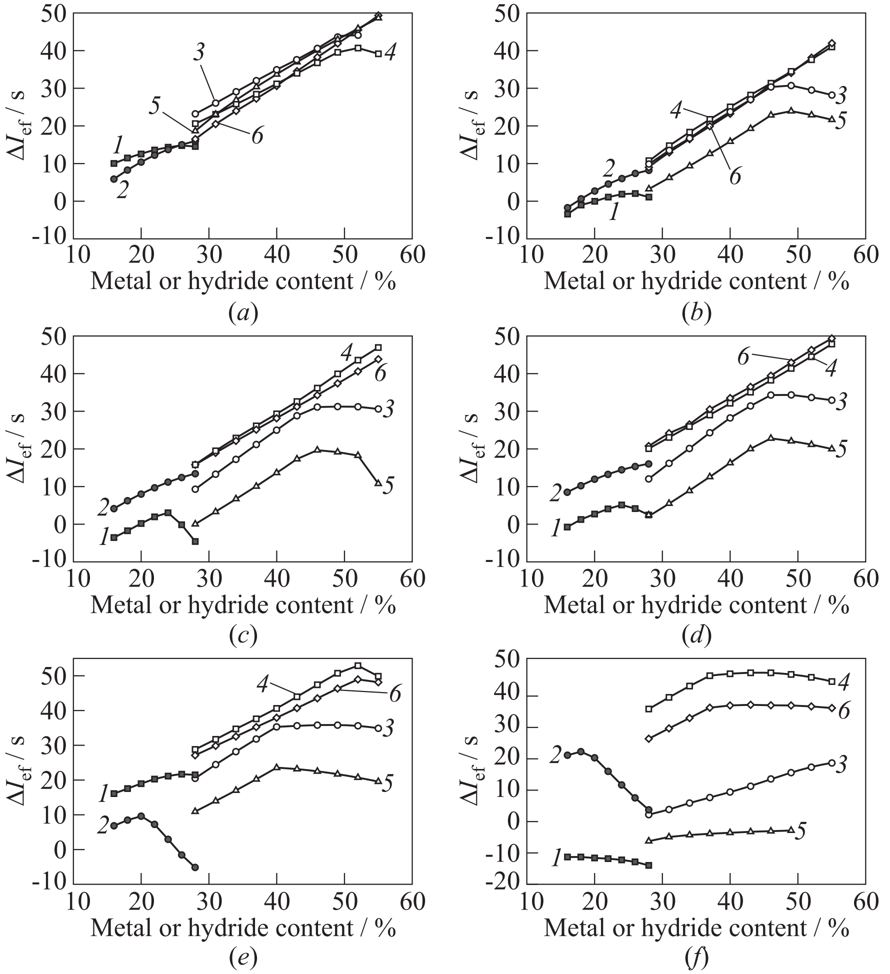

Figure 1 Values of $\Delta I_{\rm ef}$ for $Z_0 = 1.5$ ($F = 0.27$): *1* — Al + SHCB + oxidizer; *2* — Al + AB + oxidizer; *3* — Zr + SHCB + oxidizer; *4* — Zr + AB + oxidizer; *5* — ZrH_2 + SHCB + oxidizer; and *6* — ZrH_2 + AB + oxidizer for different oxidizers: (*a*) HAP; (*b*) AP; (*c*) ADN; (*d*) SHHP; (*e*) HNF; and (*f*) HMX

on HAP, the advantage of ZrH_2 over Zr increases with the Z_0. On the other hand, in the formulations with ADN, the effectiveness of aluminum replacement with Zr or ZrH_2 is almost the same as in the formulations with HAP and AP (30, 20, 12–13, 7–8, and 4–5 s at $Z_0 = 1.5$, 2, 2.5, 3, and 3.5, respectively). In the Zr + SHCB + ADN system, the maximum $I_{\rm ef}$ values are achieved at Zr content 45%–47% (that is, 60%–62% of condensed phase in combustion products).

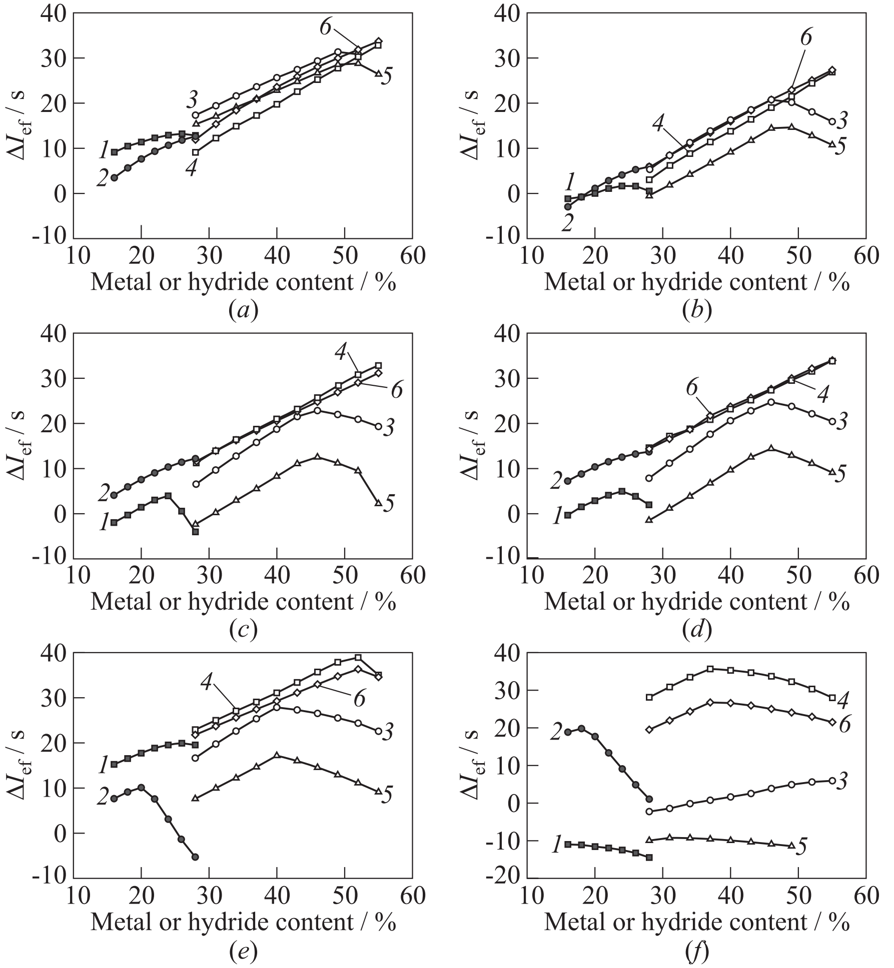

Figure 2 Values of ΔI_{ef} for $Z_0 = 2.0$ ($F = 0.54$). See Fig. 1 for details

Formulations with SHHP. Here, the I_{ef} gain is almost the same as with ADN. Only the formulations with ZrH_2 and with SHCB are not effective enough. If $Z_0 = 1.5$, I_{sp} gain is 30 s (Zr and AB) and 20 s (Zr and SHCB); if $Z_0 = 2$, the gain is $\sim$ 20 s (Zr and AB) and 15 s (Zr and SHCB); if $Z_0 = 2.5$, the gain is $\sim$ 15 s (Zr and AB) and 5 s (Zr and SHCB); if $Z_0 = 3$, the gain is $\sim$ 7–8 s (Zr and AB), if $Z_0 = 3.5$, there is only a small gain for the formulations with Zr and AB. Zr + SHCB + SHHP formulations achieve the maximum I_{ef} values at 45%–47% Zr or ZrH_2 (that is, 60%–62% of condensed phase in combustion products). In the formulations with Zr and AB, I_{ef} continues increasing with

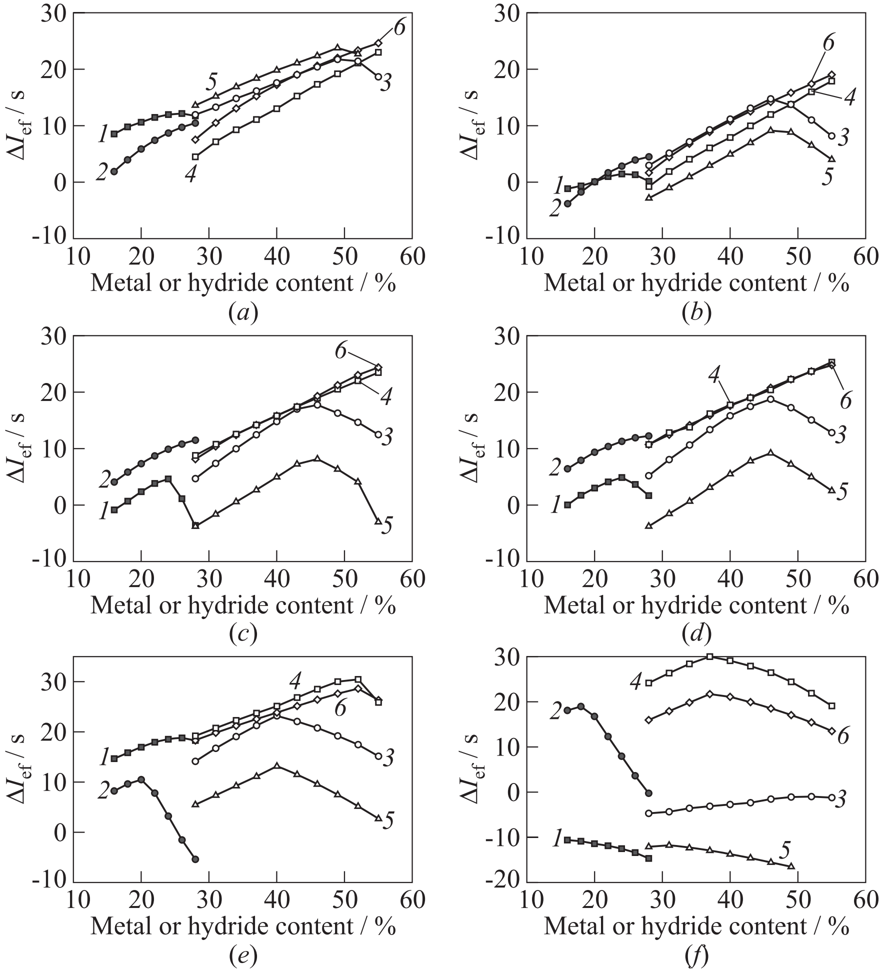

Figure 3 Values of ΔI_{ef} for $Z_0 = 2.5$ ($F = 0.81$). See Fig. 1 for details

the Zr content up to 70% ZrH_2. The same effect relates to similar formulations based on HAP, AP, and ADN oxidizers.

<u>Formulations with HNF.</u> If $Z_0 = 1.5$, the gain is 30 s (Zr and AB); if $Z_0 = 2.0$, it is $\sim$ 20 s; if $Z_0 = 2.5$, it is 10–12 s; and if $Z_0 = 3.0$, it is 5–8 s. All formulations with AB are better than those with SHCB.

<u>Formulations with HMX.</u> This oxidizer differs considerably from all other oxidizers because HMX has the lowest value of α. Therefore, the formulations with SHCB are of no interest at all: they are far worse than the formulations

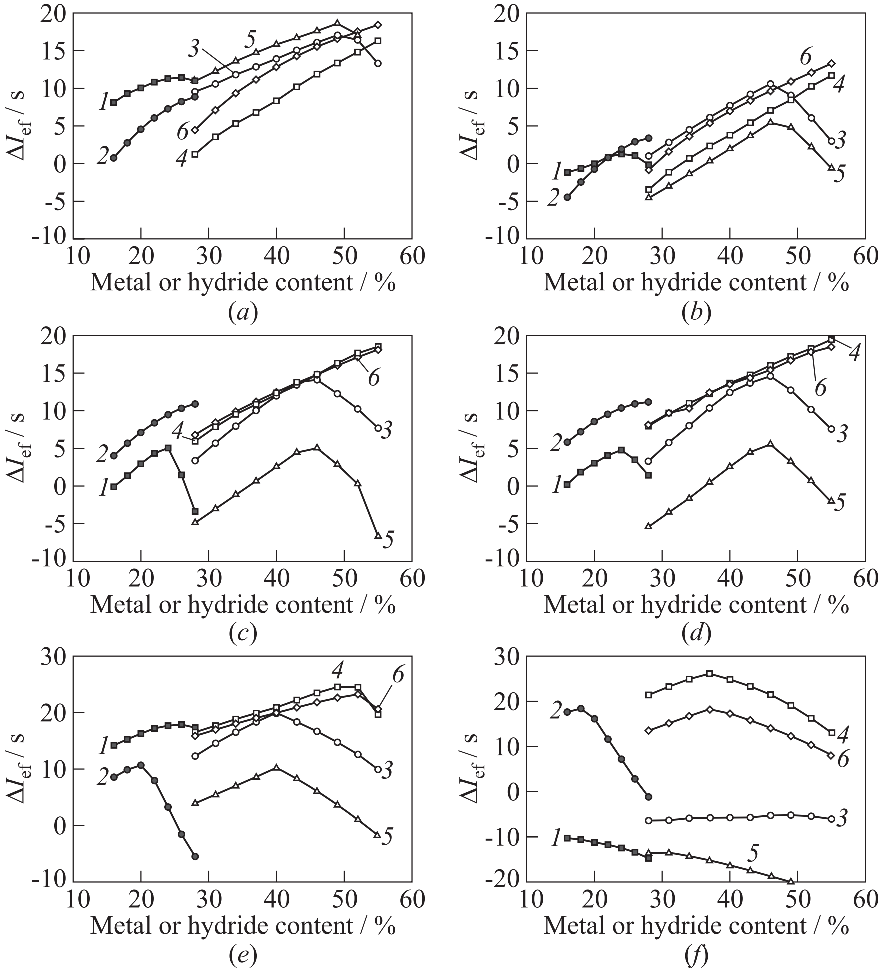

Figure 4 Values of ΔI_{ef} for $Z_0 = 3.0$ ($F = 1.08$). See Fig. 1 for details

with AB. The formulations with AB and Zr are considerably better than the formulations with AB and ZrH_2 for all values of Z_0. If $Z_0 = 1.5$, the I_{ef} gain is 15–20 s (Zr and ZrH_2); if $Z_0 = 2.0$, the formulations with AB and Zr win 15 s while the formulations with AB and ZrH_2 win 7 s. If $Z_0 = 2.5$, the I_{ef} gain is 10 s (Zr) and a few seconds only for ZrH_2. If $Z_0 = 3$, there is a gain of 7 s for the formulations with Zr and AB and no gain for ZrH_2. In the Zr + SHCB + HMX system, the maximum I_{ef} values are achieved at Zr or ZrH_2 content of 38%–41% (that is, 52%–55% ZrO_2 in combustion products).

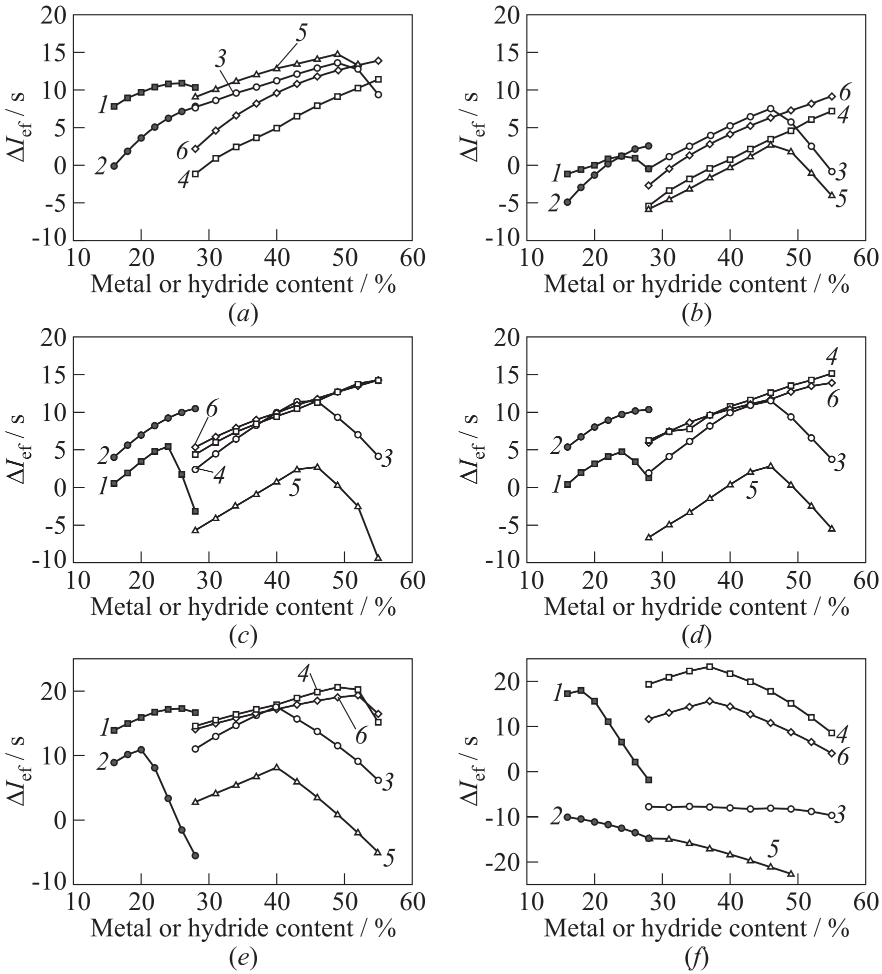

Figure 5 Values of ΔI_{ef} for $Z_0 = 3.5$ ($F = 1.35$). See Fig. 1 for details

When comparing the formulations with different oxidizers, a particular regularity can be noticed for oxidizers with high oxygen content ($\alpha \geq 2.0$: HAP, AP, ADN, and SHHP). As a matter of fact, I_{ef} increases with the Zr or ZrH_2 content in the formulations with AB, while in similar formulations based on the oxidizers with lower α (HNF or HMX), there is a maximum at Zr or ZrH_2 content, corresponding $\sim$ 70% and 50% of ZrO_2 for HNF and HMX, respectively.

Therefore, the oxidizers with lower α values require replacing SHCB with AB and the gain due to using a Zr-containing energetic compound instead of Al is

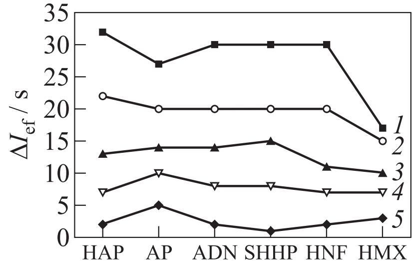

Figure 6 Maximum ΔI_{ef} values due to replacing of Al with Zr or ZrH_2 in the formulations based on different oxidizers for different Z_0: *1* — 1.5; *2* — 2.0; *3* — 2.5; *4* — 3.0; and *5* — 3.5

getting higher if Zr rather than ZrH_2 is used. All said above is illustrated in Fig. 6.

It should be noticed additionally that the formulations with Zr and AB exhibit very high combustion temperatures (T_c). If ZrO_2 content in combustion products reaches 50%, T_c is already higher than 3700–3800 K; if ZrO_2 content in combustion products reaches 65%–70% (that is, when I_{ef} attains the maximum value), the T_c values become 4000 K and even higher (Fig. 7). The fact that the formulations with Al exhibit lower T_c values than the formulations with Zr (though the heat of formation of 1 g Al_2O_3 is about twice higher than the heat of formation of 1 g ZrO_2) has a simple explanation. First, the compositions with a high content of condensed phase in combustion products (in Zr-containing compositions, this value is about twice higher than in Al-containing compositions) exhibit higher T_c because the specific (per 1 g) heats of condensed products are considerably smaller than the specific heats of gases (particularly, H_2O and H_2). Besides, the specific heat of solid ZrO_2 is almost twice lower than that of solid Al_2O_3. Second, at temperatures exceeding 3600 K, ZrO_2 dissociates to a considerably less extent than Al_2O_3, and for Al_2O_3 dissociation, a rather high amount of heat is consumed. For example, for heating a system with the gross formula ZrO_2 from 3600 up to 4000 K, the needed amount of heat is a factor of 3 less than that needed to heat Al_2O_3, other conditions being equal.

Unlike the compositions with Zr and AB, the formulations with ZrH_2 and AB have rather acceptable T_c values (not higher than 3800 K for all oxidizers except HAP) because these formulations contain more hydrogen and have a bit lower $\Delta^\circ H_f$. The formulations with Zr and SHCB have considerably lower T_c values than those with Zr and AB, and these T_c values are also quite acceptable. The compositions with HMX, ZrH_2, and SHCB show too small T_c values.

Compare now the ballistic properties of compositions with all oxidizers under consideration at different values of Z_0. The task is to find the best formulations for different engines with different Z_0 or F values. As the baseline

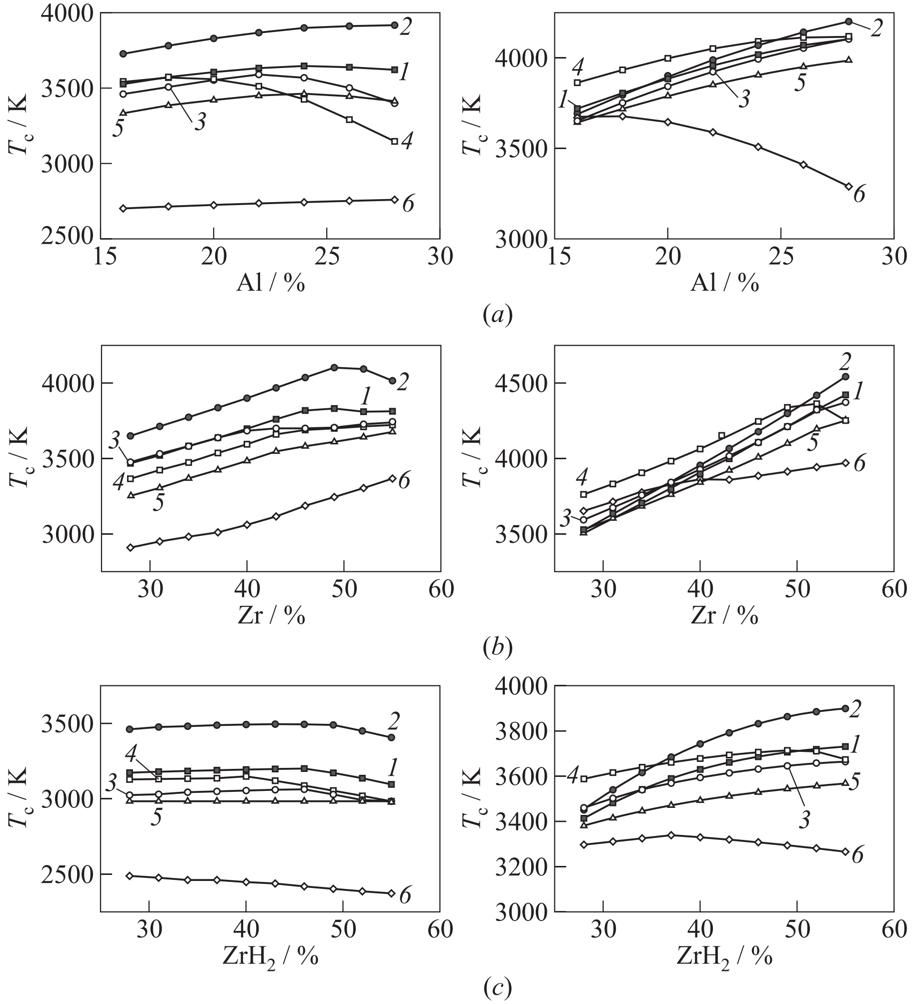

Figure 7 Values of T_c for formulations with different oxidizers (*1* — AP; *2* — HAP; *3* — ADN; *4* — HNF; *5* — SHHP; and *6* — HMX), energetic components ((*a*) Al; (*b*) Zr; and (*c*) ZrH_2), and binder (SHCB — left column or AB — right column, both 20 %(vol.))

formulation, the above-mentioned 20% Al + 20 %(vol.) SHCB + AP system is still considered.

The brief conclusions on the relative effectiveness of the formulations under investigation are:

$Z_0 = 1.5$ ($F = 0.27$). The formulations with HAP show the maximum gain $\Delta I_{\rm ef} = 40$–47 s for Zr and ZrH_2; ZrH_2 is a bit better than Zr. The formulations with AB are a bit better than those with SHCB (if $T_{\rm c}$ values are not considered). The lower the value of α in the oxidizer, the higher the difference between the effectiveness of formulations based on AB and SHCB, that is, the lower the α, the worse are the formulations with SHCB. Then, the lower the α, the higher the gain of Zr over ZrH_2. The formulations with Zr and AB are capable of ahieving $\Delta I_{\rm ef}$ of about 40–45 s as compared with the baseline formulation. Using the formulation with Zr and SHCB, the gain depends much on the oxidizer nature: 40–43 s for HAP, 22–30 s for AP, 25–31 s for ADN, 28 s for SHHP, 30–35 s for HNF, and only for HMX, the gain is at least ~ 15 s.

$Z_0 = 2$ ($F = 0.54$). All oxidizers in the formulations with AB show the $I_{\rm ef}$ gain up to 35 s. The formulations with SHCB continue to loose the effectiveness, particularly, with ZrH_2.

$Z_0 = 2.5$ ($F = 0.81$). The $I_{\rm ef}$ gain is up to 21–23 s with HAP, 15–18 s with AP, 30 s with HNF, 23–24 s with ADN, 24–25 s with SHHP, 30 s (Zr), and 20 s (ZrH_2) with HMX.

$Z_0 = 3$ ($F = 1.08$). In the formulations with AB, the $I_{\rm ef}$ gain is up to 30 s with HNF, 22–23 s with ADN, 15–20 s with HAP, 25 s with SHHP, 22 s with AP, and 30 s (Zr) or 22 s (ZrH_2) with HMX.

$Z_0 = 3.5$ ($F = 1.35$). The $I_{\rm ef}$ gain is up to 17–20 s with ADN, 17–18 s with HAP, 17–19 s with SHHP, 12–13 s with AP, 23–25 s with HNF, 25 s (AB + Zr), and 17 s (AB + ZrH_2) with HMX.

Thus, the replacement of Al with Zr or ZrH_2 only (if the best formulation in each kind of composition is considered) with the best binder (for Al-containing as well as for Zr-containing formulations) allows obtaining the $I_{\rm ef}$ gain of 30 s at $Z_0 = 1.5$; ~ 20 s at $Z_0 = 2$; 13–14 s at $Z_0 = 2.5$; 8 s at $Z_0 = 3$, and ~ 5 s at $Z_0 = 3.5$.

However, for further development of the compositions containing Zr and ZrH_2, one should not seek only $I_{\rm ef}$ growth. The problem is not to increase the combustion temperature $T_{\rm c}$ very much, because if $T_{\rm c}$ is too high (≥ 3800 K), one should weight considerably the nozzle section with a heat shield. Tables 3 to 5 represent a part of data obtained with the most acceptable formulations for further investigations. In these tables, only formulations based on AP, ADN, and HMX oxidizers are included, because these oxidizers are rather developed while the others are not widely used in practice yet. All formulations in Tables 3 to 5 contain 20 %(vol.) of binder.

Analysis of the results shows that there is a considerable reserve to increase the ballistic effectiveness for engines with $Z_0 = 1.5$–2.0 (there are many missiles with such Z_0 values) only by replacing of Al with Zr or ZrH_2.

All said above relates to a comparative analysis of the formulations based, on the one hand, on Al and, on the other hand, on Zr or ZrH_2 with respect to their values of I_{ef} and T_c. However, the replacement of Al with Zr or ZrH_2 can have other consequences, both positive and negative. Among possible negative consequences of such a replacement is the fact that Zr powder is rather pyrophoric, which may complicate propellant production and use. ZrH_2 is less pyrophoric than Zr and, therefore, ZrH_2 can be a good alternative to Zr. Moreover, it was shown above that in many formulations, ZrH_2 can create compositions with higher ballistic effectiveness than Zr. A considerably higher cost of Zr in comparison with Al is one of the serious barriers in using Zr in propellants, especially, in engines with large propellant volume.

Consider now the problem of the I_{sp} loss due to the presence of condensed phase in combustion products (that is, two-phase loss). Usually, the compositions with 20% Al lose about 0.22% I_{sp} per each Al percent. Surely, this value depends on the particle size (the smaller the solid particles, the less the loss level), specific heat (the higher the specific heat, the higher the I_{sp} loss), mass percentage of solid particles in combustion products (the higher the percentage, the higher the I_{sp} loss). Tables 3 to 5 show that the formulations with 46%–49% Zr or ZrH_2 (that is, with 60–65 %(mass.) ZrO_2 in combustion prod-

Table 3 The best formulations for engines with Z_0 values of 1.5 and 2.0 ($F = 0.27$ and 0.54)

Formulation	d	T_c	Condensed phase, %		I_{sp}	Z_0			
						1.5		2.0	
			mass	vol		I_{ef}	ΔI_{ef}	I_{ef}	ΔI_{ef}
20% Al + AP + SHCB	1.847	3605	37	17.5	250.9	250.9	**0.0**	—	**0.0**
46% Zr + AP + SHCB	2.571	3820	62.1	27.9	215.9	281.2	**30.4**	271.6	**20.7**
43% Zr + AP + SHCB	2.494	3760	58.1	25.3	218.4	—	—	269.3	**18.4**
46% Zr + ADN + SHCB	2.451	3690	62.1	26.6	224.7	282.0	**31.1**	273.8	**22.9**
37% Zr + AP + AB	2.507	3804	50.0	21.9	212.0	270.8	**19.9**	262.3	**11.4**
34% Zr + ADN + AB	2.322	3760	45.9	18.6	227.6	273.8	**22.9**	267.6	**16.7**
37% Zr + ADN + AB	2.390	3844	50.0	20.9	225.1	277.0	**26.1**	269.6	**18.7**
34% Zr + HMX + AB	2.411	3783	45.9	19.3	236.0	292.4	**41.5**	284.4	**33.5**
37% Zr + HMX + AB	2.480	3830	50.0	21.6	233.3	295.6	**44.7**	286.6	**35.7**
46% ZrH_2 + AP + AB	2.654	3687	60.8	28.2	211.4	282.2	**31.4**	271.6	**20.7**
49% ZrH_2 + AP + AB	2.730	3707	64.8	30.9	209.2	285.4	**34.5**	273.8	**22.9**
46% ZrH_2 + ADN + AB	2.544	3632	60.8	27.0	220.7	285.1	**34.3**	275.7	**24.8**
49% ZrH_2 + ADN + AB	2.621	3646	64.8	29.6	218.0	288.3	**37.4**	277.9	**27.0**
37% ZrH_2 + HMX + AB	2.423	3340	48.9	20.7	229.7	285.7	**34.8**	277.7	**26.8**

Table 4 The best formulations for engines with Z_0 values of 2.5 and 3.0 ($F = 0.81$ and 1.08)

Formulation	d	T_c	Condensed phase, %		I_{sp}	Z_0			
						2.5		3.0	
			mass	vol		I_{ef}	ΔI_{ef}	I_{ef}	ΔI_{ef}
20% Al + AP + SHCB	1.847	3605	37	—	250.9	250.9	**0.0**	—	**0.0**
46% Zr + AP + SHCB	2.571	3820	62.1	27.9	215.9	265.6	**14.7**	261.5	**10.6**
43% Zr + AP + SHCB	2.375	3662	62.1	25.7	228.4	267.9	**17**	264.7	**13.8**
37% Zr + ADN + AB	2.390	3844	50.0	20.9	225.1	265	**14.1**	261.8	**10.9**
34% Zr + HMX + AB	2.411	3783	45.9	19.3	236.0	279.3	**28.4**	—	—
37%Zr + HMX + AB	2.480	3830	50.0	21.6	233.3	281	**30.1**	276.9	**26.0**
49% ZrH_2 + AP + AB	2.730	3707	64.8	30.9	209.2	265.1	**14.2**	261.9	**11.0**
46% ZrH_2 + ADN + AB	2.544	3632	60.8	27.0	220.7	269.8	**18.9**	265.8	**14.9**
49% ZrH_2 + ADN + AB	2.621	3646	64.8	29.6	218.0	271.4	**20.5**		
37% ZrH_2 + HMX + AB	2.423	3340	48.9	20.7	229.7	272.7	**21.8**	269.2	**18.3**

Table 5 The best formulations for engines with Z_0 values of 3.5 ($F = 1.35$ and 1.08)

Formulation	d	T_c	Condensed phase, %		I_{sp}	$Z_0 = 3.5$	
			mass	vol		I_{ef}	ΔI_{ef}
20% Al + AP + SHCB	1.847	3605	37	**17.5**	250.9	—	**0.0**
43% Zr + ADN + SHCB	2.375	3662	62.1	**25.7**	228.4	262.3	**11.4**
37% Zr + ADN + AB	2.390	3844	50.0	**20.9**	225.1	259.3	**8.4**
37% Zr + HMX + AB	2.480	3830	50.0	**21.6**	233.3	274.1	**23.2**
49% ZrH_2 + AP + AB	2.730	3707	64.8	**30.9**	209.2	261.9	**11.0**
46% ZrH_2 + ADN + AB	2.544	3632	60.8	**27.0**	220.7	262.7	**11.8**
37% ZrH_2 + HMX + AB	2.423	3340	48.9	**20.7**	229.7	266.5	**15.6**

ucts) exhibit the most optimal ballistic properties. Conventional compositions containing 20% Al have 37% condensed Al_2O_3 in combustion products. As the specific heat of ZrO_2 is more than twice lower (0.49 against 1.05 J/(g · K)) than the specific heat of Al_2O_3, it can be estimated to the first approximation that in Zr-containing compositions, the two-phase loss will be a bit less than in Al-containing compositions (other conditions being equal, that is, if the particle size is the same).

There is another problem accompanying the replacement of Al with Zr or ZrH_2. It is the possibility of slag formation during the combustion process. Usually, one does not increase Al percentage higher than 21%–22% in order not to achieve Al_2O_3 percentage of 38%–40% in combustion products; otherwise, some slag forms during the combustion. The compositions with 46%–49% Zr or ZrH_2 have higher mass percentage (a factor of 1.7) of solid metal oxide in combustion products than the compositions with 20% Al. However, because of higher ZrO_2 density, the volume percentage of condensed metal oxides in combustion products is almost the same. As slag formation is the consequence of partial coagulation of metal and its oxide at initial combustion phase in the combustion chamber, the probability of slag formation in Zr-containing compositions can be less than in Al-containing compositions because the melting point of ZrO_2 is by 700–800 K higher than that of Al_2O_3.

A similar study of formulations with titanium and its hydride (instead of aluminum) has been carried out. It was shown that unlike the formulations with Zr and ZrH_2, the formulations with Ti or TiH_2 are not that promising because the densities of Ti (4.5 g/cm^3) and TiH_2 (3.9 g/cm^3) are considerably less than those of Zr and ZrH_2. Therefore, in the formulations with Ti and TiH_2 (instead of Al), the growth of propellant density does not compensate the loss of I_{sp}.

3 CONCLUDING REMARKS

The replacement of aluminum with zirconium and its hydride in almost all solid composite propellants can increase the missile velocity for engines with the propellant volume-to-construction mass ratio less than 1.0–1.4 l/kg.

The optimal ballistic effectiveness of propellants with zirconium or its hydride is attained at 35%–40% Zr or ZrH_2 in the formulation which is considerably higher than the optimal content of aluminum in the Al-containing compositions.

The compositions with ZrH_2 are virtually equivalent to the compositions with individual Zr. However, ZrH_2 is better when used together with oxygen-rich oxidizers, while Zr is better when used with oxidizers containing less oxygen.

For all oxidizers under investigation (except HAP), the most optimal formulations are those with Zr or ZrH_2 with an active binder.

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