



Energetic Performances of Solid Composite Propellants

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Abstract: Different kinds of solid composite propellant (SCP) are described. All ways to increase energetic potential of SCP are considered as well as *pro et contra* of each of these ways. Different kinds of oxidizer (perchlorates of ammonium, hydroxylammonium, and hydrazinium; ammonium salt of dinitramine; other saltlike and molecular oxidizers) are under consideration. The main principles creation of SCP formulation with optimal characteristics in the context of their concrete purpose are discussed, e.g. for rockets with considerably low ratio propellant volume/empty construction mass (V/M lower than 1 Litr/kg or so) the ballistic effectiveness may be increased with the replacement of aluminum by high-dense zirconium or zirconium hydride. Possibilities for creation of special SCP formulations for application at the far space, e.g. for Mars exploration are discussed as well.

Keywords: solid composite propellant, specific impulse, density, combustion temperature, formation enthalpy

Introduction

Ballistic effectiveness of solid composite propellants (SCP) depends on many factors, first, on the specific impulse (Isp) value, on the density (ρ), and on the power v in the combustion law $U=A \cdot P^v$ and on the combustion temperature (T_c).

During last two or three decades the increase of Isp retards abruptly. On one hand it is because in 60th-70th a great growth of Isp has been achieved due to ammonium dinitramine (AND) invention, and formulations based on unsolvated aluminum hydride. On the other hand it happens often that chemists-synthetics

work without close contact with design engineers – today there are many new energetic compounds that are not considered yet as potential compounds of SCP, but only as explosives. Chemistry of energetic compounds is far of being played out, moreover rockets for different goals require different parameters besides high Isp value. Sure, the cost of components and therefore all propellant cost are very important too because further increase of propellant energy is a too expensive task and all *pro et contra* have to be evaluated.

The time has come when we have to reconsider the main conceptions for further developing of the energy of SCP, taking into account that for each kind of rocket systems the optimal (considering all requirements) formulations may differ appreciably. We may look for new ways to increase ballistic effectiveness of SCP by traditional methods, that is increasing Isp, on the other hand one should look for other ways, even beside of the chemistry. In the paper the main attention is devoted to the analysis how enthalpy of formation, element content, density influence Isp, Tc affect ballistic effectiveness. All values of Isp and Tc presented in this paper are calculated using the standard method [1]. It is wide-known that it is necessary to burn at least a propellant sample of 500 kg for obtain Isp and Tc data close to real values that may be achieved in a real rocket engine. Therefore all investigations of energetic properties of different SCP consider the comparison of calculated Isp values. Besides we have to notice that all data of Isp and Tc presented here are obtained in the Institute of Problems of Chem. Phys. Rus. Ac. Sci. by the authors of this paper.

Ways for specific impulse increasing

The main ways to increase Isp are known since the beginning of the XX century. There are only two ways: first, heat release value increasing, and second, the thermal effectiveness increasing, that is element content improving with the rising of light gases (especially, hydrogen) fraction in combustion products. In this paper we are considering quantitative influence of these parameters on Isp value.

The heat release value may be achieved by two ways

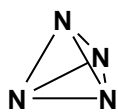
- a) using compounds that release the maximal heat at the interaction – the most universal way of this variant actualization is the use of metals (the most effective are Al and Be) or compounds with active fluorine (with $-\text{NF}_2$ groups).
- b) use of compounds with very high formation enthalpy ($\Delta^\circ H_f$). It means mainly compounds with prestressed functional groups, azides, polynitrogen cycles etc.

The second way – (increase of light gases fraction in the combustion products) may be achieved by different ways, mainly using onium salts of acids – oxidizers, hydrides of light metals (AlH_3 , BeH_2 , boron hydrides).

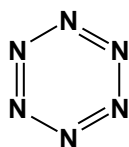
Each of these ways for propellant energy increase has its proper pluses and minuses and, naturally, its proper limitations.

Isp increasing due to the heat release rising

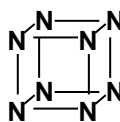
As there are many high-enthalpy organic compounds, mainly, containing N_3 -groups, N-heterocycles with many N-atoms in the cycle, one could hope to obtain very high Isp values, especially, if nitrogen fraction in the compound rises simultaneously together with the fall of the carbon fraction, in this case the formation enthalpy may increase up to 8000-16000 kJ/kg. Actually, it was shown [2], that if compounds with gross formulation N_x (nowadays many teams look for such substances [3]) were obtained it would be possible to obtain Isp (at Pc:Pa = 40:1) up to 400 s if the $\Delta^\circ H_f$ of N_x is $\sim + 15000$ kJ/kg. There are some substances below that are built with only N-atoms, they are not synthesized yet, but their $\Delta^\circ H_f$ values (sure, estimated data) are very high [3])



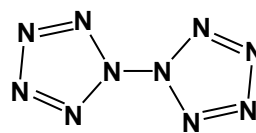
$$\Delta^\circ H_f = 20000 \text{ kJ/kg}$$



$$\Delta^\circ H_f = 17100 \text{ kJ/kg}$$



$$\Delta^\circ H_f = 15300 \text{ kJ/kg}$$



$$\Delta^\circ H_f = 14200 \text{ kJ/kg}$$

But so high Isp values would be accompanied with too high Tc values, entirely unacceptable above 6000 K [2]. The introducing of binder in accustomed amount decreases drastically Isp, up to 320-340 s (though Isp remains still very high in comparison with other SCP formulations), but Tc stays too high. For Tc decreasing up to acceptable values (3800-4000 K) one should either introduce binder in amount considerably higher that it is necessary for physico-mechanic properties support, or after the necessary portion of the binder is introduced one introduces compounds rich of hydrogen at minimum of carbon (e.g. hydrazonium azide) till Tc falls up to the appropriate value. In combination with different binders and compounds N_x it is possible to achieve Isp 290; 310 and 320 s at the condition $T_c \leq 4000$ K if $\Delta_f H^\circ$ of the substance N_x is about 8700; 12500 and 16800 kJ/kg correspondingly. In reality we do not believe that some day someone could create condensed compounds basing on N-atoms only with enough thermal stability level. Anyway compounds with high nitrogen content exist (the chain with nine N-atoms is already known), so maybe (even sure)

compounds containing higher nitrogen content will be obtained. We showed that if there is an organic oxidizer $R-R_1$ (e.g. bisnitrofuoroxane) and it is possible to introduce in the molecule more nitrogen without changing ratio C/O or H/O, e.g. to make $R-N=N-R_1$, one would get winning in propellant energy if additive formation enthalpy of the additional nitrogen is higher than 2000 kJ/kg, (for example if this N-containing group is $-N=N-$).

Heat release increase due to metal (Be, Al) introduction has been used during more than 50 years, this way has been quite answerable to the hopes in compositions basing on such oxidizers as ammonium nitrate (AN), ammonium perchlorate (AP), ammonium dinitramine (ADN), namely oxidizers with negative formation enthalpy values. However as soon as $\Delta^\circ H_f$ increases the effectiveness of the metal introduction falls gradually with the rate depending on the metal nature (it falls in the range Be- Al – Mg, that is when $\Delta^\circ H_f$ of the oxidizer achieves a determinate value Mg is not effective any more while Al and Be are still effective) [4, 5].

40-50 years ago investigations of SCP with compounds (oxidizers and plasticizers), containing NF_2 -groups, began. Advantage of NF_2 -groups over NO_2 -groups based on higher heat release at hydrogen oxidation into HF, than into water, and because active fluorine requires less hydrogen amount for the same heat release, so it is possible to increase the hydrogen portion in combustion products and consequently to decrease average molecular gas mass of combustion products. Effectiveness of the replacement of NO_2 -groups for NF_2 -groups may be demonstrated: if in a formulation with 5% of compound, containing 50 mass % of NO_2 -groups, one replaces this compound for its analogue with groups NF_2 the winning in Isp is about 1.2 s.

Specific impulse increase due to element content improving

Evaluations comparing two ways ($\Delta^\circ H_f$ growth and hydrogen fraction growth) for Isp increasing have been carried out [6]. It was shown that if we increase the $\Delta^\circ H_f$ value (from -1000 up to $+1000$ kJ/kg) of any formulation with no metal, we get the Isp growth ~ 1.8 s per each 100 kJ/kg; for formulations containing 20% Al this winning is only ~ 1.2 s per each 100 kJ/kg. On the other hand hydrogen fraction growth in 1 abs.% in formulation with no metal wins ~ 2 s in Isp value while the winning for formulation with 20% Al is ~ 6.5 s at the same hydrogen fraction growth (Figure 1). It means that the increase of hydrogen fraction in 3-4 abs.% (that is very complicated to accomplish) in formulation with no metal achieves the same growth of Isp as the $\Delta^\circ H_f$ value increase in 500 kJ/kg does. In formulation with 20% Al the same hydrogen content increase is already equal to $\Delta^\circ H_f$ rising in ~ 2000 kJ/kg. Thus the price of hydrogen increases

drastically (and the price of $\Delta^\circ H_f$ falls simultaneously) if there is an active metal in the formulation because in presence of metal the main part of heat release is the consequence of the metal oxidation.

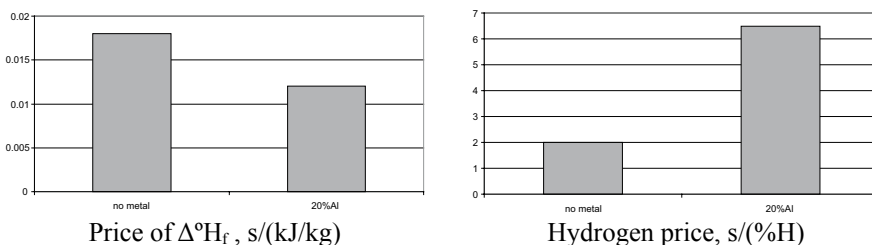


Figure 1. Relative price of formation enthalpy and hydrogen portion in SCP formulations.

The both ways for Isp rising (hydrogen fraction and $\Delta^\circ H_f$ increase) have their own limits and may make other properties worse. For example, abrupt $\Delta^\circ H_f$ increase may rise sensitivity, degrade thermal stability, make the combustion law worse, and increase the Tc value up to impermissible values. So, the opinion that the growth of $\Delta^\circ H_f$ is the best way to Isp increasing is not so reliable (though at first blush it seems namely thus). The way to increase Isp with metal introducing together with hydrogen fraction rising seems sometimes better, the best way is the use of AlH_3 and BeH_2 .

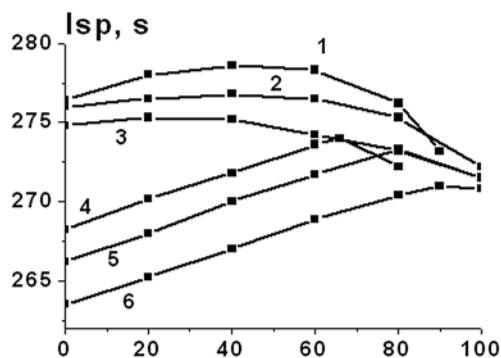
Almost all known oxidizers become closer in energetic properties in the presence of AlH_3 or BeH_2 . Thus, for example, if ammonium nitrate (AN) in formulation with no metal loses 30-40 s to ammonium perchlorate (AP), in formulations with Al this lost is about 10 s only, and in formulations with AlH_3 the lost is a few s only. We should notice that the development of compositions with hydrides showed that the best binders for these formulations were active ones, that contain active oxygen in the forms NO_2 , ONO_2 , NNO_2 and other alike groups because the introduction of additional hydrogen (from hydride) into the formulation decreases drastically the oxygen excess value ($\alpha = \{O / (2C + 0.5(H - Cl))\}$) in comparison with the same formulation where there was the metal instead of the hydride and therefore formulation basing on hydride requires much more oxygen. By this manner such a binder (one calls this type of binder “active binder”) plays partially the role of oxidizer.

In Table 1 a part of calculated data concerning formulations with the active binder, basing polyvyniltetrazol, plasticized with the mixture trinitroglycerole and diazapentane (gross-formula $\text{C}_{18,96}\text{H}_{34,64}\text{N}_{19,16}\text{O}_{29,32}$, $\Delta^\circ H_f = -189$ kcal/kg, $\rho = 1.49$ g/cm³, in this paper this composition of active binder is quoted AB).

Table 1. Energetic opportunities of formulations basing on AlH_3 , AB and oxidizer

Formulation	binder, mass. %	binder, vol. %	Isp	ρ	Tc, K	Ta, K
AlH_3 25%+ AB + ammonium nitrate (AN)	25	26.8	267.4	1.596	3208	2125
	27	28.8	267.6	1.591	3206	2117
	29	30.9	267.9	1.587	3204	2109
AlH_3 25%+ AB + ADN	25	27.4	277.6	1.636	3564	2345
	27	29.5	277.4	1.629	3548	2327
	28	30.6	277.4	1.626	3540	2327
AlH_3 25%+ AB + ammonium perchlorate (AP)	25	28.3	270.3	1.686	3589	2466
	27	30.4	270.5	1.677	3573	2438
	29	32.5	270.8	1.668	3557	2410

Besides, by creating formulations with hydrides it is very important to find the formulation with the optimized element content, e.g. in the system AlH_3 + AB + ADN the introduction of rather low effective oxidizer, dihydrazonium salt of methylenedinitramine (DHMDNA, $\text{N}_2\text{H}_5)_2[\text{CH}_2\text{N}(\text{NO}_2)]$) with relatively high hydrogen portion (8% against 3% in ADN) gives a positive effect (Figure 2).

**Figure 2.** Dependence of Isp of formulations AlH_3 +AB (25%) + mixed oxidizer (ADN + DHMDNA or AN + DHMDNA). X-coordinate – content of DHMDNA in the mixed oxidizer.

- 1) 25% AlH_3 + mixture ADN + DHMDNA.
- 2) 23% AlH_3 + mixture ADN + DHMDNA.
- 3) 21% AlH_3 + mixture ADN + DHMDNA.
- 4) 25% AlH_3 + mixture AN + DHMDNA.
- 5) 23% AlH_3 + mixture AN + DHMDNA.
- 6) 21% AlH_3 + mixture AN + DHMDNA.

Table 2. Energetic parameters of some formulations with 18% BeH₂. Binders: AB, hydrocarbon binder (HCB) C_{73.17}H_{120.9} ($\Delta^{\circ}H_f = -93$ kcal/kg, $\rho=0.92$; and polyvinylmethoxidiazene-N-oxide (PVMDAO), [-CH₂-CH-N(O)=N-CH₃]_n, $\Delta^{\circ}H_f = 0$ kcal/kg, $\rho=1.31$)

Oxidizer	Binder			I _{sp} , s	d, g/cm ³	T _c , K
	type	% mass	% vol.			
AP)	HCB	18.0	25.2	288.4	1.276	2849
	PVMDAO	29	29.5	300.0	1.341	3203
	AB	33	30.3	294.6	1.369	3473
	AB	50	44.3	299.2	1.320	3331
Hydroxylammonium perchlorate (HAP)	HCB	18	25.9	295.0	1.308	2868
	PVMDAO	31	32.0	303.6	1.351	3325
	AB	33	30.9	295.1	1.397	3594
	AB	54	48.0	301.1	1.314	3372
ADN	AB	35	39.6	304.4	1.31	3355
	PVMDAO	25	25	307.1	1.31	3232
	HCB	19	25.7	291.7	1.231	2778
	AB	39	33.8	304.6	1.29	3162
Hydrazonium nitrate	AB	29	29	304.2	1.3	3169
	PVMDAO	26	25.1	304.0	1.267	2860
	AB	29	25.3	304.2	1.30	3170
Hydrazonium nitroformate	PVMDAO	25	25.5	300.1	1.331	3174
DHMDNA	AB	29	25.4	299.3	1.305	2851

Only two metal hydrides (AlH₃ and BeH₂) increase considerably Isp. BeH₂ allows to obtain much higher Isp values, than AlH₃ does, that is if Isp of the formulation 25% AlH₃ + AB + ADN is about 276 s, the use of BeH₂ in analogue formulations increases Isp up to 300 s and even higher. In Table 2 there are some formulations basing on BeH₂ and different oxidizers and binders. Compositions with BeH₂ have rather lower density than compositions with AlH₃ have (1.25-1.35 against 1.60-1.65 g/cm³), but even with so considerable density drop BeH₂ is rather more power energetic compound than AlH₃. The possibility of the using SCP with Be or BeH₂ on the Earth is very problematic because of extremely high toxicity of BeO, however, one may consider the possibility to use such SCP in far space.

The density role in ballistic effectiveness

The density of SPC plays a considerable role in ballistic effectiveness together with specific impulse value although the density value does not enter directly in the expression of the rocket velocity growth $W = g_0 \cdot I_{sp} \cdot \ln(M_{start}/M_{finish})$, where M_{start} – the launching (start) mass, M_{finish} – the final rocket mass ($M_{finish} = M_{start} - M_{pr}$, where M_{pr} is the propellant mass; $M_{pr} = V \cdot \rho$, where V is the the propellant volume, ρ is the propellant density), but at the given volume-mass rocket parameters (at the given value M_{finish}/V) the propellant density rise increases the M_{start} value too, and therefore the W value rises at the same I_{sp} . The less mass fraction occupies the propellant in total launching mass the higher is the propellant density input into the resulting W value. That is why the density role increases for lower stages of multiple-stage missiles and other ones with relatively high ratio $(M_{start} - M_{pr})/M_{pr} = (M_{start} - V \cdot \rho)/(V \cdot \rho)$ or the ratio M_{finish}/V .

One of interesting examples of ballistic effectiveness growth at the replacement of one compound by another one – it is the replacement of AP by hydroxylammonium perchlorate (HAP). For lower stages of three-stage rocket complexes this replacement gives the same winning in ballistic effectiveness due to I_{sp} growth due to density growth. For example, two close formulations “oxidizer + 9% HCB + 25% HMX + 20% Al”, where the oxidizer is either AP or HAP, I_{sp} values are 254 and 258.3 s while ρ are 1.856 and 1.91 correspondingly. Thus, both I_{sp} and ρ increase, the first in 5.3 s while the second – in 0.055 g/cm³. One may estimate (according to standard method [7]) for heavy rocket complexes how the flight range increases due to these two factors – due to the I_{sp} growth the flight range increases in about 300 km, while due to the density growth in 0.055 g/cm³ the flight range increases in the same 300 km, that is in this case a half of the flight range growth is due to the density growth. Unfortunately, it is very hard to use HAP in SCP because of its extreme hygroscopicity (it begins to absorb water already at 7% humidity) and because of its high reactivity and therefore bad compatibility with other compounds.

Superdense compositions with zirconium

In the case described above (HAP against AP) both I_{sp} and ρ increase, and naturally ballistic effectiveness increases too. However we have to compare two formulations where one of them has higher I_{sp} but lower ρ than the second one (for example the replacement of HMX for CL-20 decreases I_{sp} but increases ρ , the replacement of AP for ADN – *vice versa*). That’s why we have to study accurately for which kind of rockets such a replacement may be useful, as it was notices above that the higher is the ratio M_{start}/V than higher is the price

of the density. We are considering a very interesting example – how ballistic effectiveness changes at the replacement of Al ($\rho=2.7$) for Zr ($\rho=6.49$) or ZrH_2 ($\rho=5.61$, $\Delta^\circ H_f=-455\text{kcal/kg}$). So the propellant density decreases much as well as the I_{sp} falls considerably. For which kinds of rockets such a replacement may increase the ballistic effectiveness? We may estimate the flight range growth ΔL with formulas like $\Delta L = (\partial L/\partial I_{sp}) \cdot \Delta I_{sp} + (\partial L/\partial \rho) \cdot \Delta \rho$ [7], but parameters $\partial L/\partial I_{sp}$ and $\partial L/\partial \rho$ depends strongly on the rocket type, on amount of stages etc. We have estimated the effectiveness of the replacement of Al for Zr or ZrH_2 for rockets with different values of the ratio V/M_{finish} . If the rocket under consideration is fulfilled with the composition Al (20%) + hydrocarbon binder (HCB) 10 mass %, that is 20 vol.%) and the rest 70% AP ($I_{sp}=251$, $d=1.85$, we are considering this composition as the basic one), and we replace this composition for another one with specific impulse value $I_{sp}(1)$ and density $\rho(1)$, it is easy to calculate so called effectiveness impulse (I_{ef}) of the second composition for being used in rocket with the same ratio V/M_{finish} . It means that the W growth of the rocket with this value V/M_{finish} would be equal by using either the first composition ($I_{sp} = 251$, $d = 1.85$) or the second ($I_{sp} = I_{ef}$, $\rho = \rho(1)$). Thus if I_{ef} of the second composition is higher than 251 – the replacement increases W and L . I_{sp} values for many formulations basing on either Al or Zr (ZrH_2), different oxidizers and two binders (AB or HCB in amount 20 vol.%), and, that is the most important, for different values of ratio V/M_{finish} (from ~ 0.3 till ~ 6 L/kg) have been calculated. Figure 3 illustrates some results. We should notice that for obtaining higher I_{ef} values one has to introduce Zr or ZrH_2 in rather high amount (up to 40% and sometimes even higher).

Tables 3 and 4 contain calculated data of formulations, that seem the best for further investigation for being used in rockets with the given value V/M_{finish} .

At $V/M_{\text{finish}} > \sim 2-3$ the advantage of Zr-containing formulations already disappears. The most effective is the replacement of Al for Zr or ZrH_2 at $V/M_{\text{finish}} < 1-1.4$. Compositions with ZrH_2 have almost the same I_{ef} values than compositions with Zr, but if there are active binders or/and oxidizers rich in oxygen compositions with ZrH_2 are more effective.

However all hopeful results concerning Zr and ZrH_2 discussed above and presented in Table 3 and 4, do not allow yet to affirm that in summary the replacement of Al by Zr or ZrH_2 would be useful. One should study many service properties, including the production cost. Namely a considerably higher cost may become the main obstacle in the task of Zr-containing propellants creation. We have not estimated yet the ballistic effectiveness of propellants basing on hafnium ($\rho=13.3$), they will have higher density (~ 2.8) than Zr-containing compositions have and lower I_{sp} values (~ 200). Anyway their cost will be too high.

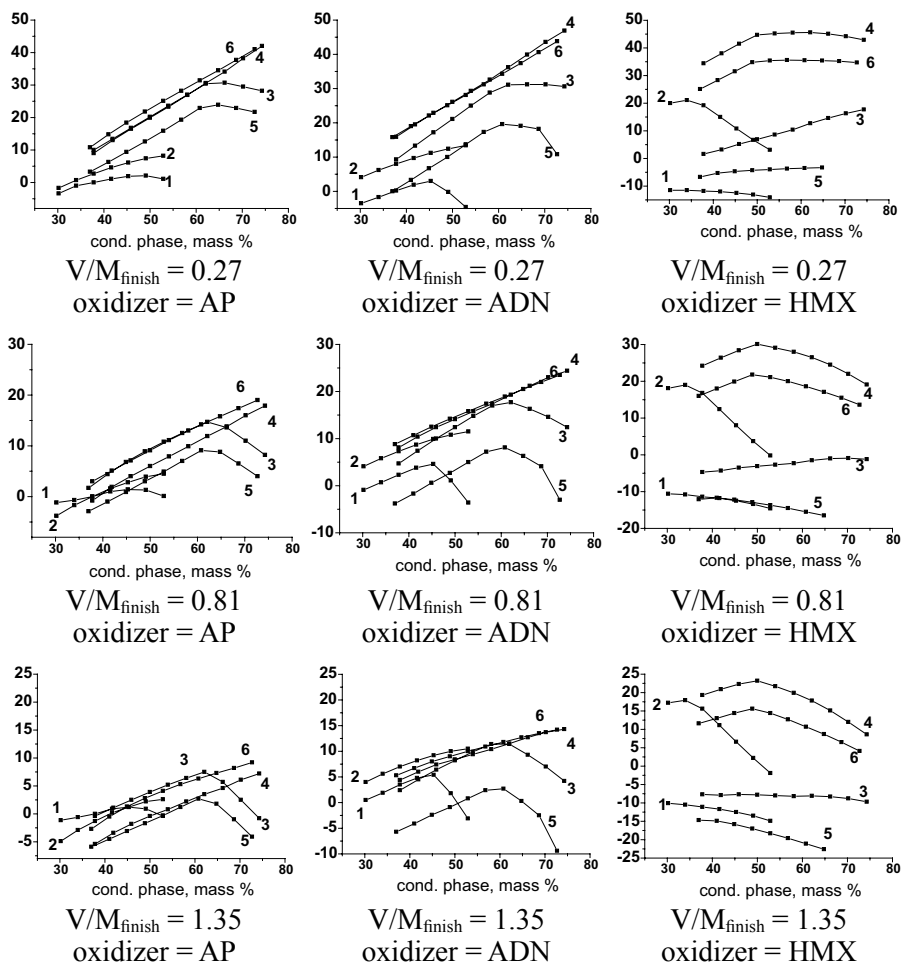


Figure 3. Growth of I_{ef} (ΔI_{ef} , Y-coordinate) as function of the energetic component nature, its content, binder and oxidizer nature, and V/M_{finish} value. X-coordinate is the content of condensed phase (Al_2O_3 or ZrO_2) in combustion products.

- 1) Al+20 vol.% CHB + oxidizer.
- 2) Al+20 vol.% AB + oxidizer.
- 3) Zr+20 vol.% CHB + oxidizer
- 4) Zr+20 vol.% AB + oxidizer.
- 5) ZrH₂+20 vol.% CHB + oxidizer.
- 6) ZrH₂+20 vol.% AB + oxidizer.

Table 3. The best formulations for missiles with $V/M_{\text{finish}} = 0.27$ and 0.54 L/kg. ($M_{\text{start}}/M_{\text{finish}} = 1.5$ and 2.0). Everywhere the binders content is 20 vol. %

Formulation	d	Tc,K	Metal oxides in condensed phase, %		Isp	$V/M_{\text{finish}} = 0.27$		$V/M_{\text{finish}} = 0.54$	
			mass	vol		Ief	Δ Ief	Ief	Δ Ief
20% Al +AP+CHB	1.847	3605	37	17.5	250.9	250.9	0.0	250.9	0.0
46%Zr+AP+CHB	2.571	3820	62.1	27.9	215.9	281.2	30.3		
46%Zr+ADN+CHB	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
37%Zr+ADN+AB	2.390	3844	50.0	20.9	225.1	277.0	26.1	269.6	18.7
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 +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 missiles with $V/M_{\text{finish}} = 0.81$ and 1.08 L/kg. ($M_{\text{start}}/M_{\text{finish}} = 2.5$ and 3.0). Everywhere the binders content is 20 vol. %

Formulation	d	Tc,K	Metal oxides in condensed phase, %		Isp	$V/M_{\text{finish}} = 0.81$		$V/M_{\text{finish}} = 1.08$	
			mass	vol		Ief	Δ Ief	Ief	Δ Ief
20% Al +AP+CHB	1.847	3605	37	17.5	250.9	250.9	0.0	250.9	0.0
46%Zr+AP+CHB	2.571	3820	62.1	27.9	215.9	265.6	14.7	261.5	10.6
43%Zr+ADN+CHB	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
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
37%ZrH ₂ +HMX+AB	2.423	3340	48.9	20.7	229.7	272.7	21.8	269.2	18.3

SCP for especial tasks

There are many especial aspects in SCP application when the ballistic effectiveness may become insignificant and some other parameters may play the main role. These are such like the requirement for environmental safety of combustion products (this problem is described in [8]), possibility of safe conversion of propellants after storage life is over (especial binders based on thermoplastic elastomers have been created for it [9, 10]) and many other.

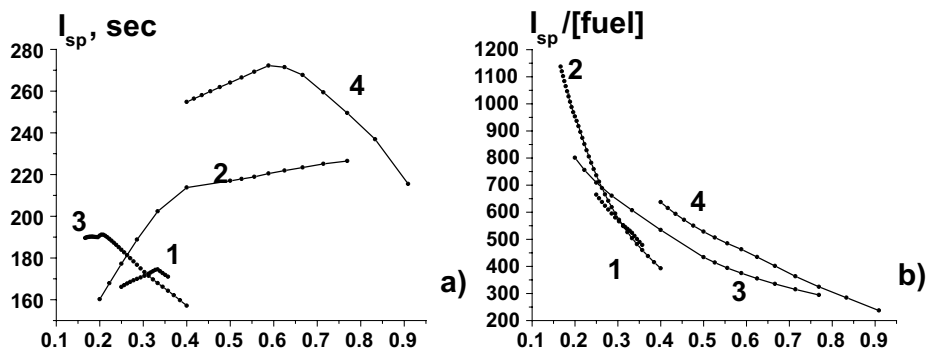


Figure 4. Values I_{sp} and $I_{sp}/[\text{fuel}]$, achieved applying compositions basing on solid compound (fuel: active binder = 85:15) and CO_2 . X-coordinate – portion of the compounds (fuel+AB) being carrying from Earth in the whole formulation with CO_2 . Nature of the mixture (fuel+binder): 1) Al+AB. 2) AlH_3 +AB. 3) Be+AB. 4) BeH_2 +AB

In this paper we'd like to consider one of proposals to use carbon dioxide as oxidizer for homing from Mars [11, 12]. The problem of Mars exploration and, particularly, homing back is very complex and expensive because one has to carry the propellant for homing from the Earth. As there solid carbon dioxide covers the pole Mars areas we could try to use carbon dioxide as oxidizer and to carry from the Earth fuel only charging oxidizer on the Martial surface. As oxidizer occupies more than 50% of propellant mass it means that one should carry to Mars much less loading and it may compensate a rather low I_{sp} values that propellants with CO_2 show. Naturally, as CO_2 is very poor oxidizer it may be used with the most energetic fuels only, such as Be, Al, Mg and their hydrides. Sure among metals Be is the most powerful, then Al, and then Mg. I_{sp} values of the formulations where the solid part of all propellant is the mixture of an energetic fuel with the active binder AB in mass ratio 85:15. It is evident that

basing on Al one can obtain at least $I_{sp} \sim 175$ s, basing on Be ~ 190 s, basing on $AlH_3 \sim 225$ s, and basing on $BeH_2 \sim 275$ s (Figure 4a). For a brief estimation of real effectiveness of this decision we are applying so called value I_{sp}^* , that is I_{sp} reduced to 1 kg of that portion of the propellant that has been carried from the Earth ([fuel]), that is $I_{sp}^* = I_{sp}/[\text{fuel}]$. It is evident on the Figure 4b that these I_{sp}^* values are very high.

The real effectiveness of such an approach (using such *in-situ* resource as carbon dioxide) has to be estimated only taking in account total mass of spaceship starting from the Earth, mass and construction of the spaceship for homing, expected load mass from Mars etc., that is each task may have its own optimal resolution.

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