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EFFECT OF METAL ADDITIVES ON THE COMBUSTION CHARACTERISTICS OF HIGH-ENERGY MATERIALS

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Abstract. Thermodynamic calculation of combustion parameters and equilibrium composition of HEMs combustion products showed, that at the increase of aluminum powder dispersity the specific impulse and combustion temperature of solid propellants are reduced due to the decrease of the mass fraction of active aluminum in particles. Partial or complete replacement of aluminum by metal powder (B, Mg, AlB_2, Al\Mg alloy, Fe, Ti and Zr) in HEMs composition leads to the reduce of the specific impulse and combustion temperature. Replacement of aluminum powder by boron and magnesium in HEM reduces the mass fraction of condensed products in the combustion chamber of solid rocket motor. So, for compositions HEMs with boron and aluminum boride the mass fraction in chamber is reduced by 24 and 36 %, respectively, with respect to the composition HEMs with Al powder. But the mass fraction of CCPs in the nozzle exit increases by 13 % for HEMs with aluminum boride due to the formation of boron oxide in the condensed combustion products. Partial replacement of 2 wt. % aluminum powder by iron and copper additives in HEM leads to the reduce of CCPs mass fraction in chamber by 4–10 % depending on the aluminum powder dispersity duo to these metals are not formed condensed products at the HEMs combustion in chamber.

1 Introduction

The modern high-energy materials (HEMs) contains an oxidizer (ammonium perchlorate or nitrate), fuel-binder (inert or active polymeric rubbers), nitramines [1–3] and metal fuel (aluminum powder) [4–6], which allows to increase the basic power characteristics of solid propellants at the burning in the combustion chamber. The main characteristics of combustion in relation to the propulsion systems are the dependence of the burning rate versus pressure, combustion temperature of solid propellant, specific impulse [7], which is equal to the increase in the value of thrust implemented with the combustion of unit propellant mass, as well as chemical and particle-size distribution of condensed combustion products (CCPs).

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One way to the increase of HEMs combustion characteristic is the use of combustion catalysts or metal powders and their oxides as a component of solid propellants. The aim of paper is decision possible of metal additives in HEMs with partial replacement of aluminum powder in order of the increase of the combustion parameters propellants and the reduce of the condensed combustion products amount with using a thermodynamic calculation program Terra [8].

2 Combustion parameters

Thermodynamic calculation of combustion parameters and equilibrium composition of the combustion products was carried out for model composition of HEMs [9], which contains ammonium perchlorate of 64.6 wt. %, butadiene rubber of 19.7 wt. % and aluminum powder of 15.7 wt. %. We considered various aluminum powders with different particle size. Mass fraction of active aluminum in composition of powders (brands of ASD and Alex nanopowder) amount from 0.85 to 0.99, depending on their dispersity. The mean particle diameters of aluminum powders of different grades are shown in Table 1. In the capacity of additives were selected such metal powders as: boron, magnesium, titanium, iron, copper, zirconium, aluminum boride and alumino-magnesium Al/Mg alloy. We suggested, that the metal additive is introduced into the model composition of HEM by partial replacement of 2 wt. % aluminum powder.

Table 1. The mean particle diameters of aluminum powder.

Powder brand	d_{10}, μm	d_{20}, μm	d_{30}, μm	d_{32}, μm	d_{43}, μm
ASD-1	10.4	12.0	13.6	17.4	21.9
ASD-4	1.23	1.66	2.28	4.34	7.34
ASD-6	0.85	1.17	1.60	3.01	4.72
ASD-10	0.72	0.90	1.09	1.60	2.11
Alex	0.12	0.13	0.14	0.16	0.18

In the calculations we considered the initial oxidation of aluminum particles. In accordance with the results of our study the active (metal) aluminum Al content in powder of different parties and storage periods, which determined by the chemical analysis methods, we have adopted the average values of active aluminum content (Table 2). The remaining mass fraction of powder ($1-m_{Al}$) is equal aluminum oxide Al_2O_3. For example, Alex aluminum nanopowder is a mixture Al and Al_2O_3 in the weight ratio of 85/15. In the case of powder ASD-10 chemical analyzes are not carried out, and the quantity of active aluminum was calculated by extrapolation of the linear empirical approximation of Al from the value of the specific area of particles surface S_{sp} for powder ASD-1, ASD-4, ASD-6. In this evaluation for ASD-10 we took $S_{sp} = 10000$ cm^2/g. The initial oxidation of the metal additives Ti, Fe, Zr, B, Cu, AlB_2 and Al/Mg alloys we considered equal to zero. The weight ratio of the components in the alloy is assumed equal to Al/B = 0.55/0.45 and Al/Mg = 0.50/0.50.

Table 2. Mass fraction of aluminum metal and its oxide in various brands of aluminum powder.

Component	Mass fraction of powder components, wt. %				
	ASD-1	ASD-4	ASD-6	ASD-10	Alex
Al	0.995	0.980	0.964	0.947	0.850
Al_2O_3	0.005	0.020	0.036	0.053	0.150

In calculation we used the scheme of solid rocket motor, which shown in fig. 1. The pressures ratio of $p_c/p_a = 4.0/0.1$ MPa was used for gas-dynamic degrees of combustion products flow expansion. The index "c" is marked in the combustion chamber, and the index "a" – at the nozzle exit.

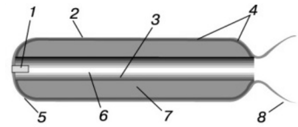

Fig. 1. The design of solid rocket motor: 1 – the igniter; 2 – a motor body; 3 – the burning surface; 4 – an insulation; 5 – a forward head; 6 – a central channel; 7 – the solid propellant charge; 8 – the nozzle.

The main calculated combustion parameters of HEMs such as the enthalpy *I*, the combustion temperature T_{ad}, the equilibrium adiabatic exponent *k*, relative molecular mass of the gas combustion products μ, the coefficient of excess oxidizing elements α, the flow rate of gas products from the nozzle *w* and specific impulse *J* are shown in Table 3.

Table 3. Calculated combustion parameters of HEMs with metal additives.

Metal powder	*I*, kJ/kg	T_{ad}, K	*k*	μ, g/mol	α	*w*, m/s	*J*, m/s
B*	-1841	2215	1.21	19.09	0.335	2228	2482
Mg*	-1841	2603	1.17	18.40	0.422	2289	2509
Al*	-1841	2638	1.18	17.11	0.406	2351	2590
ASD-1	-1854	2636	1.18	17.10	0.407	2349	2588
ASD-4	-1893	2631	1.18	17.07	0.408	2346	2582
ASD-6	-1937	2624	1.18	17.04	0.410	2341	2575
ASD-10	-1979	2617	1.18	17.02	0.412	2336	2568
Alex	-2228	2561	1.19	16.95	0.422	2299	2519
Alex+B	-2179	2366	1.20	18.04	0.409	2285	2517
ASD-4+B	-1886	2408	1.20	18.21	0.397	2329	2571
AlB_2	-1841	2353	1.15	18.97	0.363	2303	2558
Al\Mg (alloy)	-1841	2567	1.17	18.12	0.414	2325	2552
Alex+Cu	-2179	2463	1.20	17.48	0.426	2244	2456
ASD-4+Cu	-1886	2564	1.19	17.32	0.414	2302	2523
Alex+Fe	-2179	2477	1.20	17.53	0.424	2244	2455
ASD-4+Fe	-1886	2576	1.19	17.36	0.412	2303	2523
Alex+Ti	-2179	2530	1.19	17.01	0.422	2278	2496
ASD-4+Ti	-1886	2608	1.18	17.08	0.410	2325	2552
Alex+Zr	-2179	2540	1.19	17.01	0.425	2275	2489
ASD-4+Zr	-1886	2621	1.19	16.99	0.413	2328	2553

*Note: where and in Table 4 B, Mg and Al are not contained metal oxides.

With the increase of aluminum powder dispersity for a number of ASD-4→ASD-6→ASD-10→Alex the specific impulse *J* and combustion temperature T_{ad} of propellants are reduced due to the decrease of the mass fraction of active aluminum in the starting powders. Partial replacement of 2 wt. % aluminum by metal additive (B, Mg, AlB_2, Al\Mg alloy, Fe, Ti and Zr) in the composition of HEMs the values of *J* and T_{ad} are reduced.

3 Parameters of condensed combustion products

Table 4 shows the calculated parameters of condensed combustion products at the combustion of HEMs: mass fractions m_c and m_a, the phase composition of condensed particles contained in the combustion products at the pressures $p_c = 4.0$ MPa and $p_a = 0.1$ MPa, respectively.

Table 4. The calculated parameters of CCPs.

Metal powder	m_c, m_a	Phase composition and mass fraction of condensed particles
B*	0.17175 0.37286	$[B_2O_3]_c = 0.01904$; $[BN]_c = 0.13587$; $[B_4C]_c = 0.01684$ $[B_2O_3]_a = 0.19266$; $[BN]_a = 0.13643$; $[B_4C]_a = 0.02746$;$[C]_a = 0.01631$
Mg*	0.19665 0.25803	$[MgO]_c = 0.19665$ $[MgO]_a = 0.25803$
Al*	0.25272 0.29605	$[Al_2O_3]_c = 0.25272$ $[Al_2O_3]_a = 0.28825$; $[C]_a = 0.00780$
ASD-1	0.25325 0.29575	$[Al_2O_3]_c = 0.25325$ $[Al_2O_3]_a = 0.28823$; $[C]_a = 0.00752$
ASD-4	0.25478 0.29460	$[Al_2O_3]_c = 0.25478$ $[Al_2O_3]_a = 0.28798$; $[C]_a = 0.00662$
ASD-6	0.25642 0.29283	$[Al_2O_3]_к = 0.25642$ $[Al_2O_3]_a = 0.28735$; $[C]_a = 0.00548$
ASD-10	0.25787 0.29062	$[Al_2O_3]_c = 0.25787$ $[Al_2O_3]_a = 0.28638$; $[C]_a = 0.00424$
Alex	0.26253 0.27569	$[Al_2O_3]_c = 0.26253$ $[Al_2O_3]_a = 0.27569$
Alex+B	0.20036 0.29253	$[Al_2O_3]_c = 0.20036$ $[Al_2O_3]_a = 0.24039$; $[B_2O_3]_a = 0.02685$; $[BN]_a = 0.02529$
ASD-4+B	0.19089 0.29821	$[Al_2O_3]_c = 0.19089$ $[Al_2O_3]_a = 0.25594$; $[B_2O_3]_a = 0.00045$; $[BN]_a = 0.04182$
AlB_2	0.16798 0.33444	$[Al_2O_3]_c = 0.07914$; $[BN]_c = 0.08884$ $[Al_2O_3]_a = 0.12644$; $[BN]_a = 0.13171$; $[B_2O_3]_a = 0.07629$
Al\Mg alloy	0.20855 0.26815	$[MgAl_2O_4]_c = 0.20611$; $[MgO]_c = 0.00244$ $[MgAl_2O_4]_a = 0.20695$; $[MgO]_a = 0.06120$
Alex+Cu	0.23721 0.25903	$[Al_2O_3]_c = 0.23721$ $[Al_2O_3]_a = 0.24057$; $[Cu]_a = 0.01846$
ASD-4+Cu	0.24307 0.27369	$[Al_2O_3]_c = 0.24307$ $[Al_2O_3]_a = 0.25641$; $[Cu]_a = 0.01728$
Alex+Fe	0.23744 0.24058	$[Al_2O_3]_c = 0.23744$ $[Al_2O_3]_a = 0.24058$
ASD-4+Fe	0.24355 0.25641	$[Al_2O_3]_c = 0.24355$ $[Al_2O_3]_a = 0.25641$
Alex+Ti	0.26037 0.27392	$[Al_2O_3]_c = 0.23207$; $[Ti_3O_5]_c = 0.02830$ $[Al_2O_3]_a = 0.24057$; $[TiO_2]_a = 0.03335$
ASD-4+ Ti	0.25617 0.28128	$[Al_2O_3]_c = 0.23146$; $[Ti_3O_5]_c = 0.02471$ $[Al_2O_3]_a = 0.25541$; $[Ti_2O_3]_a = 0.02442$; $[C]_a = 0.00145$
Alex+Zr	0.26008 0.26759	$[Al_2O_3]_c = 0.23317$; $[ZrO_2]_c = 0.02691$ $[Al_2O_3]_a = 0.24057$; $[ZrO_2]_a = 0.02702$
ASD-4+Zr	0.25954 0.28274	$[Al_2O_3]_c = 0.23283$; $[ZrO_2]_c = 0.02671$ $[Al_2O_3]_a = 0.25555$; $[ZrO_2]_a = 0.02660$; $[C]_a = 0.00059$

For a number of ASD-4→ASD-6→ASD-10→Alex as a result of the assumption of the presence of aluminum oxide in initial aluminum powder, the mass fraction of condensed particles in the combustion products is increased.

It should be noted, that during the HEM combustion with boron in the chamber the quantity of condensed boron oxide is small and boron nitride in the combustion products dominate. Due to the nature of boron and magnesium additives (the ratio of molar masses of elements and oxides, the stoichiometric coefficient of oxidation reactions), a partial replacement of aluminum by boron and magnesium (in the mechanical mixture and alloy) reduces mass fraction m_c of CCPs in chamber. So, for compositions HEMs with boron and aluminum boride AlB_2 mass fraction m_c is reduced by 24 and 36 %, respectively, relative to the composition HEMs with active aluminum powder.

For compositions HEMs with iron and copper additives also have the reduce of m_c at 4–10 % depending on the aluminum powder dispersity. During HEMs combustion in the chamber these compounds are not formed in condensed product. As a result, the combustion products contain less alumina Al_2O_3 and the mass fraction of a condensed phase is decreased. Accordingly, HEMs compositions with iron and copper additives the reduction effect of mass fraction m_c is more pronounced in the case of HEM with Alex aluminum nanopowder, than HEM with microsized aluminum powder ASD-4, due to a larger content of alumina Al_2O_3 in Alex. Additives of titanium and zirconium in the case of HEMs with ASD-4, in opposite, Ti_3O_5 and ZrO_2 oxides make an additional contribution to the condensed products and increase mass fraction m_c.

Analyzing the data calculations pertaining to the nozzle exit, we note an increase of mass fraction of CCPs m_a of 13% for HEMs with aluminum boride AlB_2 due to the formation of boron oxide B_2O_3 in the combustion products. In the case of HEMs compositions with Alex and ASD-4 metal additives reduce the mass fraction of CCPs at the nozzle exit.

4 Conclusion

1. Thermodynamic calculation of HEMs combustion parameters and equilibrium composition of the combustion products showed, that at the increase of aluminum powder dispersity for a number of ASD-4→ASD-6→ASD-10→Alex the specific impulse and combustion temperature of solid propellants are reduced due to the decrease of the mass fraction of active aluminum in powder particles. Partial or complete replacement of aluminum by metal powder (B, Mg, AlB_2, Al\Mg alloy, Fe, Ti and Zr) in HEMs composition leads to the reduce of the specific impulse and combustion temperature.

2. Replacement of aluminum powder by boron and magnesium (in the mechanical mixture and alloy) in HEMs reduces the mass fraction of condensed products in the combustion chamber of solid rocket motor. So, for compositions HEMs with boron and aluminum boride the mass fraction in chamber is reduced by 24 and 36 %, respectively, with respect to the composition HEMs with active aluminum powder. But the mass fraction of CCPs in the nozzle exit increases by 13 % for HEMs with aluminum boride due to the formation of boron oxide in condensed combustion products.

3. Partial replacement of 2 wt. % aluminum powder by iron and copper additives in HEMs leads to the reduce of CCPs mass fraction in the combustion chamber by 4–10 % depending on the aluminum powder dispersity duo to these metals are not formed condensed product during the HEMs burning in the combustion chamber.

4. Additives of titanium and zirconium in HEMs with ASD-4 make an additional contribution to formation of titanium and zirconium oxides in the condensed products and increase the CCPs mass fraction in the combustion chamber.

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