

New Generation of High-Energy Chemical Propellants Based on Nano-Components

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Abstract

A possibility of designing propellant, in which the energy of intermolecular interaction in addition to chemical energy can be used, is considered. Application fine nano-components (clusters) in similar propellants is supposed. The method, which is based on positions of nanothermodynamics, is developed for determination of thermodynamic functions of similar particles (enthalpy, chemical potential, chemical affinity in relation to various environments etc.). It is considered that for set of particles positions of classical and statistical thermodynamics are to the full right. Application of optimizing procedure is discussed. The standard system of readout, ideology of «supramolecule» and principles of statistical thermodynamics are applied to searching nanoparticles thermodynamic functions. The comparative analysis of this method and the method of quantum chemistry is carried out. Efficiency of the suggested method is demonstrated. Results of calculations have allowed drawing a conclusion that use of fine nano-components allows increasing essentially an energy potential of the propellants. High activity of fine nanoparticles results in rather high probability of coagulation of these particles and their interaction with environment. It is obvious that realization of this phenomena leads to sharp falling of a store of fine nanoparticles energy. Thus, a considerable problem at developing propellants on the basis of the specified components is stabilization of nanoparticles. The analysis of various ways of this problem solution is carried out. It is shown that the method of steric (polymeric) stabilization of nano-particles is preferable. The estimation of stabilized nanoparticles characteristics and of stabilizing polymer weight is carried out. It is shown that application of polymeric coverings insignificantly reduces an energy potential of nanoparticles. The results obtained allow estimating the possibilities and operation conditions of different propellants.

1. Introduction

At present the chemical propellants are classical type propellants used in various motors including rocket ones. For years of development of rocket techniques, many substances, which can be components of this kind of propellants, have been investigated [1–4, etc.]. It is possible to ascertain that now the energy potential of chemical propellants is almost exhausted. The increase in energetic efficiency of these propellants is connected only with perfection of intrachamber processes which is focused on reduction of any losses of energy at functioning of motors. Therefore the interest to exploring the possibility of using in addition to chemical energy other kinds of energy is absolutely justified.

One the of possible solutions is application of fine nanoparticles, which represent one of the

products of nano-technologies, i.e., the technologies providing procedure of assemblage of various objects, which consist of the limited quantity of submicroscopic particles (atoms, molecules, ions). Change of energy of intermolecular interaction provides a store of energy, which can be transformed to useful work.

Let's note basic difference in properties of considered particles from those particles, which usually name nanoparticles. Usually these are particles with the sizes, which not exceed 100 nanometers. However unique properties of particles are shown only in that case when the quantity of microscopic particles in their composition does not exceed value of several hundreds, and the size – a little nanometers. Larger particles can be considered as high-disperse phase, for which the approaches developed by J. Gibbs can be applied [5].

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Indispensable condition of designing the propellants on the basis of new components is determination of thermodynamic functions of these components. Considered components are peculiar objects of the nature, and the problem of determination of their thermodynamic functions is absolutely not trivial problem. Actually, the very fine nanoparticles possess strongly pronounced dualism of properties. On the one hand, they are capable to participate in Brownian motion, pressure developing, i.e., they behave as microscopic particles. On the other hand, these particles can be considered within the concept of "phase". The analysis of possible approaches to determine the thermodynamic functions of fine nanoparticles (clusters) is given in monographs [6–7]. It is worth to note an absence of reliable calculating methods for determination of characteristics of such particles.

Obvious problem in developing the propellants on the basis of fine nano-components is stabilization of nanoparticles properties in order to provide elimination or minimization of interaction between original particles and with other components of propellant at the stages of manufacturing and propellant storage. This problem is considered in a number of works [7–8] and one may consider it as a key problem in developing propellants under discussion. "Price", which should be paid for stabilization realization, is extremely important also. It is expressed in terms of degree of energy potential degradation of nanoparticles.

The purpose of the present work is working out the design principles for new generation of chemical propellants on basis of fine nano-components. Following problems must be solved for realization of this purpose:

- development of a calculated technique for determination of thermodynamic characteristics of fine nanoparticles and propellants on their basis;
- working out a method for fine nanoparticles stabilization;
- determination of characteristics of stabilized nanoparticles.

The solution of the specified problems is described below.

2. Calculated determination of characteristics nanoparticles and propellants on their basis

Essentially, there are various two approaches to the description of nanoparticles: quantum – chemical and the approach, which is based on the classical mechanics and use of experimental data on interaction between microscopic particles.

In work [9], comparative analysis is carried out with use of Hartree-Fock method ("ab initio" quan-

tum chemistry method) and the method of nanothermodynamics developed by authors [10]. Results of the analysis for particles, which can become potential propellant components and incorporate more than ten microscopic particles – n , have allowed one to establish the following. The nanothermodynamics method possesses more split-hair accuracy, provides possibility of obtaining the exhaustive information about nanoparticles and does not demand redundant computing resources. It is necessary to notice that when the number n increases, the characteristics of considered nanoparticles approach corresponding characteristics of a disperse phase.

2.1. Nanothermodynamics method

Let's give a short description of nanothermodynamics method. This method is based on the principles of classical and statistical thermodynamics. The dualism of properties nanoparticles is considered as follows.

Within the limits of applicability of a thermodynamic method, determination of conditions of a steady equilibrium state of nanoparticles and character of their interaction with environment can be carried out traditionally. The equilibrium state corresponds to a minimum of some thermodynamic function, and the direction of interaction and its speed are determined by a sign and absolute value of chemical affinity. It is natural that for use of a thermodynamic method the presence of the means for search of thermodynamic functions of nanoparticles, and products of their interaction with various environments is necessary. Obviously that determination of these functions is based on knowledge of the size and structure of nanoparticles.

Accepted assumptions are traditional for this group of methods:

- between microscopic particles only the central forces operate, and potential energy of their interaction is described by pair potential of interaction;
- the pair potential of interaction depends only on the properties of microscopic particles.

Search of structure and size of nanoparticles is based on use of optimizing procedure. In its frameworks for a solid state as criterion function the potential energy serves, and for liquid – Helmholtz energy. Varied parameters for a solid state are co-ordinates of microscopic particles, and for a liquid state – the geometrical size of a particle.

Determination of thermodynamic functions is carried out at use of the standard system of readout, "supramolecule" ideology [11–12] and search of statistical integral for set of particles in composition of nanoparticles. Accuracy of search of nanoparticles characteristics is defined by correctness of used

pair potential of interaction and actual accuracy of the optimizing problem solution.

Use of nano-sized components as a part of chemical propellants is expedient as compared with the substances, which are introduced as a part of a disperse phase, for example, metal fuel.

The structure of aluminum nanoparticles consist-

ing of various quantities of atoms is shown in Fig. 1.

Values of potential energy of these particles and enthalpy of formation as well as chemical potential of these particles are given in Table 1.

Let's note a high value of fine nanoparticles energy. This circumstance gives the grounds for their use as potential high-energy components of propellant.

Table 1
Nanoparticles characteristics

n	13	20	40	60
R_{np} , m	$0.3 \cdot 10^{-9}$	$0.458 \cdot 10^{-9}$	$0.552 \cdot 10^{-9}$	$0.645 \cdot 10^{-9}$
u_{np} , J/kg	$-3.51 \cdot 10^6$	$-4.03 \cdot 10^6$	$-5.12 \cdot 10^6$	$-5.66 \cdot 10^6$
$\Delta H_{f,np}^0$, J/kg	$8.70 \cdot 10^6$	$8.18 \cdot 10^6$	$7.09 \cdot 10^6$	$6.55 \cdot 10^6$
$G_{\mu,np}^0$, kJ/mol	188.1	176.61	127.2	121.2

n – number of atoms in nanoparticle, R_{np} – conditional radius of nanoparticle (sphere radius, on which surface there are centers of peripheral atoms), u_{np} – specific potential energy of nanoparticles, $\Delta H_{f,np}^0$ – standard formation enthalpy of nanoparticles, $G_{\mu,np}^0$ – chemical potential of nanoparticles (standard Gibbs energy).

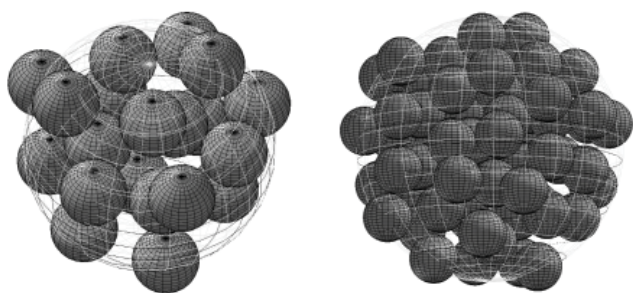


Fig. 1. Structure aluminum nanoparticle consisting from: 20 atoms (a) and 60 atoms (b).

2.2. Characteristics of propellants on the basis of nano-components

The example of propellants, in which fine nanoparticles can be used, is solid rocket propellant (SRP). A traditional component of high-energy SRP is aluminum. The analysis of energy characteristics of SRP at use of powders of aluminum of various sizes including nano-sized aluminum has been carried out.

The optimizing procedure, which is based on use of a thermodynamic method, has been employed for the analysis [13]. As the criterion function and functional restrictions some following parameters can be used: a specific impulse, caloric content of propellant, temperature of combustion products, and mass fraction of various substances as a part of these products. Varied parameters are mass fractions of components as a part of propellant. On these fractions parameters some restrictions can be applied (parametrical restrictions).

Characteristics of conditional propellant on the basis of plasticized isoprene rubber, ammonium dinitramide (ADN), cyclotrimethylenetetranitramine (HMX) and metal fuel – aluminum are given in Table 2. Calculations have been carried out for micron-sized and nano-sized aluminum. Parametrical restrictions are not excess of the binder (11.5%) and metal fuel (26%) content while as the criterion function it was chosen the value of a specific impulse.

The obtained results testify that use of nanoaluminum is capable to increase the value of a specific impulse by ~200 m/s. Besides, an obvious consequence of application of fine nanoaluminum is rising temperature of combustion products. Thus, the expediency of using fine nanoaluminum particles in SRP formulation is obvious.

3. Stabilization of nanoparticles

The energy increase at nanoparticles with decrease in their size leads to growth of their chemical potential (Table1). A consequence of that is the sharp increase in their activity. They easily interact between each other and induce chemical reactions with the substance of environment.

If environment, in which fine nanoparticles are placed, is inert but does not interfere with their moving, the particles coagulation will proceed [14]. As a result of coagulation there is an increase in the size of fine nanoparticles and reduction of their number that leads to reduction of a store of the system energy as a whole.

Table 2
Characteristics of SRP at various type of metal fuel

Characteristics		The size of particles of metal fuel (aluminum)			
		$R = (10-15) \cdot 10^3 \text{ nm}$	$R = 10 \text{ nm}$	$R = 0.7 \text{ nm}$	$R = 0.3 \text{ nm}$
$\Delta H_f^0(\text{Al}), \text{ J/kg}$		0	$1 \cdot 10^6$	$4 \cdot 10^6$	$8.70 \cdot 10^6$
$J_{sp}, \text{ m/c}$		2521.9	2543.1	2635.6	2727.4
Z, %	Binder	11.51	12.75	11.63	11.5
	ADN	60.84	65.45	66.43	66.46
	Al	19.99	19.99	22.43	22.53
	HMX	8.66	2.8	0.5	0.5
$T_0, \text{ K}$		3410.4	3397.3	3657.6	3814.5
α_{ok}		0.4567	0.4461	0.4558	0.46

$\Delta H_f^0(\text{Al})$ – standard formation enthalpy of aluminum; J_{sp} – specific impulse at expansion factor 40/1; Z – mass fraction of SRP components; T_0 – temperature of combustion products in the chamber; α_{ox} – surplus factor of oxidizing elements.

If environment, in which fine particles are placed, is capable to interact with the substance of nanoparticles, following processes are possible:

- heterogeneous reaction on all volume of nanoparticle;
- chemisorption;
- physical adsorption.

Only last type of interaction makes insignificant impact on an energy store of nanoparticles, but the first two types lead to sharp decrease in an energy potential of the particles.

Coagulation of fine nanoparticles and chemical reactions between these particles and environment do not allow keeping the structure and high power characteristics of fine nanoparticles. Thus, for use of fine nanoparticles as a part of chemical propellants, it is necessary to provide their stability.

3.1. Stabilization principles

Electrostatic or steric (polymeric) stabilization is usually used for ensuring the aggregate stability of traditional disperse systems. These approaches can be considered also for fine nanoparticles.

The analysis of electrostatic stabilization of fine nanoparticles carried out by consideration of interaction of nanoparticles-ions [13] has shown that ionization of fine nanoparticles does not provide coagulation elimination. The thermodynamic probability of ionized fine nanoparticles coagulation at presence of contact between them is rather high. There are bases to believe that ionization of particles only somewhat reduces speed of coagulation process. Besides, ionization of fine nanoparticles does not prevent chemical reactions between them and environment.

More perspective way for fine nanoparticles stabilization is steric (polymeric) stabilization [8].

For its realization, the macromolecules of polymer, which form a protective layer, have to be attached on a surface of nanoparticles by chemical or physical adsorption. When the pair of steric stabilized particles approaches, under the influence of intermolecular forces or in the course of thermal movement, to some distance smaller than the doubled thickness of a layer of polymer between polymeric layers the interaction will occur, which leads to occurrence of forces of pushing away the nanoparticles. The closer to each other the particles, the stronger is pushing away force. Thus, this method of stabilization excludes possibility of full merge of particles.

The attachment (fixing) of macromolecules of polymer to fine nanoparticle occurs by chemical or physical adsorption of lateral functional groups of a macromolecule.

Stated above allows drawing conclusion that steric stabilization of fine nanoparticles can provide aggregate stability of these particles and prevent interaction of nanoparticles with environment. Besides, end groups of polymer provide connection of nanoparticles with other components of propellant (for example, with softener). This circumstance on the one hand promotes introduction of these particles in propellant composition, but on the other hand – reduces their mobility at a propellant manufacture stage.

3.2. Characteristics of stabilized nanoparticles

For determination characteristics of nanoparticles stabilized by polymer macromolecules, it is possible to use the approach applied to determination of characteristics of individual nanoparticles in work [10] based on determination of potential energy of nanoparticle (U_{np}). Specification of value

of potential energy of nanoparticle is carried out on amendment value (ΔU_{np}) caused by the interaction of polymer macromolecules with nanoparticle.

$$U_{np}' = U_{np} + \Delta U_{np} \quad (1)$$

The amendment value to potential energy of nanoparticle depends on the number of areas on a surface of nanoparticle, to which functional groups of macromolecules (a contact zones) are attached, and also on the potential energy of interaction of nanoparticle and one lateral functional group (u_{ad}). It is defined by a simple equation:

$$\Delta U_{np} = n_{ad} \cdot u_{ad} \quad (2)$$

where n_{ad} – number of contact zones.

Determination of a number of contact zones is based on the solution of geometrical problem consisting in placing an attachment on a surface of nanoparticles of polymer macromolecules (Fig. 2), and calculation of the number of attached to nanoparticle functional groups of macromolecules.

Potential energy of interaction of nanoparticle and one lateral functional group of a macromolecule is calculated by a following equation.

$$u_{ad} = \sum_{i=1}^n \sum_{j=1}^m \varepsilon_{ij} \quad (3)$$

where n – number of atoms in nanoparticle, m – number of atoms of lateral functional group of a macromolecule, ε_{ij} – pair potential of interaction.

For the interaction description between diverse atoms of a macromolecule and nanoparticle, the rule of a combination of pair potential of interaction is used.

The complex of software has been developed for an estimation of nanoparticles characteristics stabilized by polymer. The input data for calculation are the way of joining a macromolecule to nanoparticle (“tail”, “loop” or “echelon”), structure and characteristics of individual nanoparticles [10] and polymer macromolecules.

At use of the developed tools, calculation of characteristics of stabilized nanoparticles (Al_{60}) has been carried out. Stabilization was carried out by physically adsorbed “tails” of macromolecules of polymethylmethacrylate (PMMA).

Results of calculation of nanoparticles characteristics (Table 3) show that the formation enthalpy of nanoparticles stabilized by polymer remains at high enough level (in comparison with individual nanoparticles reduction enthalpy has made ~ 12%).

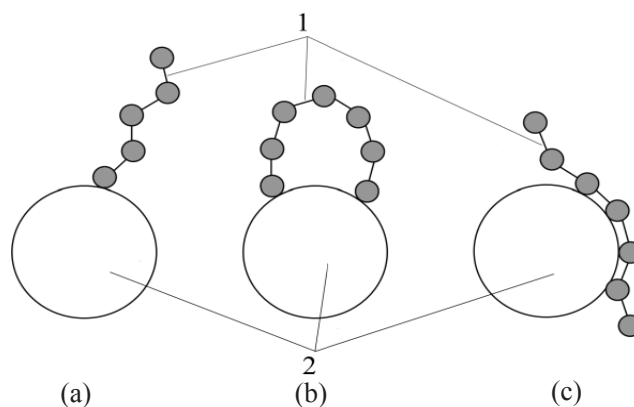


Fig. 2. Ways of joining of macromolecules (1 – macromolecule, 2 – nanoparticles, (a) – “Tail”; (b) – “Loop”; (c) – “Echelon”).

Table 3

Characteristics of individual nanoparticles Al_{60} and nanoparticles Al_{60} stabilized by the “tails” of PMMA

Characteristic	Nanoparticle Al_{60}	Nanoparticle Al_{60} stabilized by PMMA
n_s	40	40
R_{np} , m	$0.6453 \cdot 10^{-9}$	$0.6453 \cdot 10^{-9}$
\bar{u}_p^v , J	$-3.40 \cdot 10^{-19}$	$-3.40 \cdot 10^{-19}$
\bar{u}_p^s , J	$-2.17 \cdot 10^{-19}$	$-2.64 \cdot 10^{-19}$
u_{np} , J/kg	$-5.66 \cdot 10^6$	$-6.46 \cdot 10^6$
$\Delta H_{f,np}^0$, J/kg	$6.55 \cdot 10^6$	$5.75 \cdot 10^6$

n_s – number of peripheral microscopic particles (“surface layer” particles), \bar{u}_p^s – average potential energy of microscopic particles inside of nanoparticle (particles of “a volume phase”), \bar{u}_p^v – average potential energy of microscopic particles of “surface layer”, u_{np} – specific potential energy of nanoparticles.

Determination of polymer quantity is based on the analysis of a structure of a polymer layer which provides stabilization of fine nanoparticles. The layer should provide as much as possible full covering of a surface of nanoparticle with polymer macromolecules. It is thus considered that the macromolecule composition includes minimum three links.

Calculations of mass (mass fractions) of fine nanoaluminum (Al_{60} and Al_{120}) and PMMC necessary for their stabilization have been carried out.

Results of calculations, which are presented in Table 4, show that the mass of polymer layer necessary for stabilization of fine nanoparticles considerably surpasses mass nanoparticles.

Table 4
Mass (mass fractions) of fine nanoparticles and stabilizing polymer

Nanoparticle – polymer	Way of attachment of macromolecules	Mass, 10^{-26} kg		Mass fraction, %	
		Nanoparticle	Polymer	Nanoparticle	Polymer
Al ₆₀ – PMMC	“tail” (three links)	268.82	1695.71	13.68	86.32
Al ₆₀ – PMMC	“echelon”	268.82	1263.47	17.54	82.46
Al ₁₂₀ – PMMC	“echelon”	537.64	2327.44	18.77	81.23

3.3. Use of fine nano-components in the propellant composition

The carried out research has allowed determining the basic properties of fine nanoparticles as component of chemical propellants. These are the following.

– Nano particles possess a considerable store of energy.

– Their introduction in the propellant formulation demands addition of significant amount of polymer.

This demand makes extremely difficult developing unitary propellants, for example, solid rocket propellants. However this approach can be used with success in non-autonomous motors, and also in hybrid motors which use solid fuel. Plasticized polymer with fine nanoparticles can be a basis for such a fuel. Substantial increase in fuel enthalpy can provide growth of a specific impulse of these motors [4]. On Fig. 3, the scheme of the hybrid motor, in which stabilized fine nanoparticles are used to manufacture a solid fuel, is given.

4. Conclusions

Following basic results are obtained in the present work.

1. The mathematical apparatus providing determination of characteristics of fine nanoparticles (nano-components) is developed.

2. It is shown that use of fine nano-components may lead to increase in energy of potential chemical propellants owing to application of a new kind of energy – energy of intermolecular interaction. An obvious consequence of use of those components is the enhancement of the combustion products temperature.

3. It is established that the most rational way of stabilization of the propellant system based on nano-sized components is polymeric stabilization.

4. Characteristics of nanoparticles stabilized by polymer are determined.

5. It is shown that use of fine nano-components is most expedient for non-autonomous and hybrid motors.

The obtained results allow looking with optimism at the prospects of developing new generation of high-energy chemical propellants using not only chemical energy.

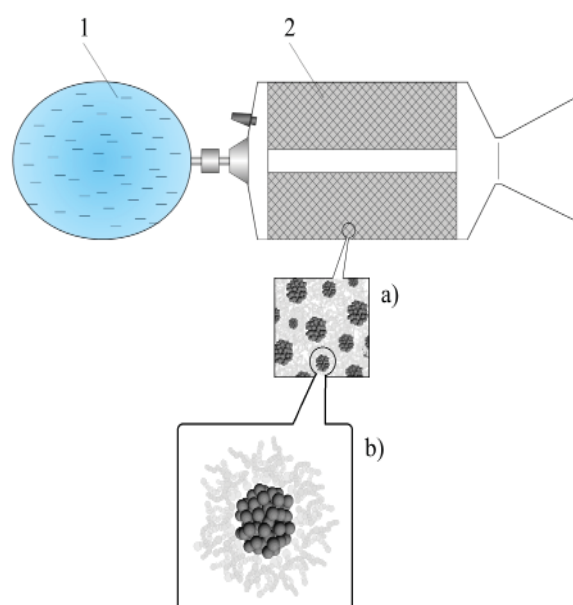


Fig. 3. The scheme of the hybrid rocket motor at use fine nano-components (1 – liquid oxidizer, 2 – solid fuel, a) – plasticized polymer with nanoparticles, b) – nanoparticle stabilized by polymer).

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