## Low temperature oxidation of nanopowders in the structures of energy composites:
# I. About the mechanism of low temperature oxidation of nanosized Al particles in gas phase oxidants

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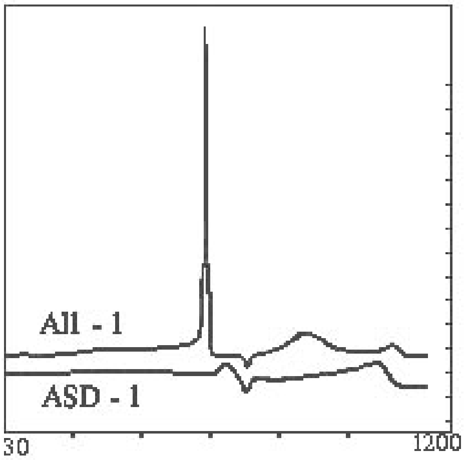
## Abstract

The usage of Al nanoparticles in composition of high energy materials (HEMs) can reach the full oxidation of metal at temperatures lower the melting point of Al for nanopowders with average size lower the critical value depending from the type of oxidizer. It is true for nanoparticles passivated with the Al oxide, carbide and nitride surface coatings and for gaseous oxidizers forming Al oxides (oxygen, $CO_2$, water vapor). The experimental data shows that the critical size is in the range 20-40 nm. The thermophysical analysis confirms the regularities observing experimentally for “low temperature” oxidation of nanopowders and shows that possibility and conditions of aluminum low temperature oxidation process depend on the size of oxidizable particle and that different mechanisms of thermal oxidation processes of aluminum are possible.

## 1. Introduction

Metal aluminum is a chemically active element with high thermal oxygenizing effect. These two characteristic features make it a good energy accumulator. Dispersed aluminium (flakes and powders) is widely used as a high energy material (HEM) for fuels [1], explosive and pyrotechnic substances production [2, 3].



Fugure1: Structure of heat evolution (DTA curves) for the samples of Al nanopowder (Al1-1) and micron sized Al powder (ASD-1) heated linearly up to 1200°C in air flow.

Curves of heat evolution of aluminum particles heated in oxidative atmosphere of air or oxygen [4], carbon dioxide [5], water vapor [6] have the same shape and structure and show a number of heat evolution maximums. Catastrophic breakdown (collapse) of passivating coatings (PC) covering the surface of Al particles occurs at these maxima temperatures. PC collapses present processes of avalanche-type formation and development of through defects, probably, cracks. Fig. 1 shows the structure of heat evolution for nanosized and micronsized aluminum powders heated in air steam, obtained by means of a differential thermometry (Derivatograph-C device, MOM, Hungary). First low temperature maximum of heat evolution (LTMHE) occurs at $T_{LTM}$ (low temperature maximum) which is lower than the metal aluminum melting temperature ($T_M$). Al oxide PC regenerates in the intervals between heat evolution maxima, which leads to metal oxidation slowdown.

The decrease of aluminium particles’ average size from micron (ASD type powders) to submicron and nanosized leads to considerable changes in powders oxidation process heated in gas-phase oxidative environment [4, 5, 7]. As Fig.1 shows it is mainly appears in the decrease in the detected values of start temperature of metal oxidization and $T_{LTM}$ as well as in redistribution of heat produced during aluminium oxidation between the heat evolution maximums. The origin of aluminum particles’ low temperature oxidation process and heat evolution maximum observed in its course appear to be interesting for studying fundamental aspects of “aluminium oxide-metal aluminium” system performance and properties as well as for practical use of aluminium and its alloys. For detailed analysis of ultra fine aluminum particles oxidation in gaseous oxidizer the quasi-isolated nanoparticles oxidation

(QINPO) method was proposed and put into practice [4]. According to this method Al nanoparticles are spread on the surface of aluminium oxide micron particles in a number less than necessary for mono layer formation on micron particles surface. In this case each nanoparticle may be considered as a quasi-isolated one and its behavior on conditions of external impacts free from other particles behavior. Thus "assembly effect" is avoided. Along with this, all-particles cumulative response to outside influence may be ensure quite high and exceed threshold of measurement method.

The use of QINPO method in derivatography permits to determine the dependence of several parameters of ultra fine aluminum particles oxidation process (such as oxidization start temperature and heat evolution maximums temperature, metal oxidation percentage at various temperatures etc.) depend on the investigated powders particles average size, type of PC protecting the particles surface, ways of particle surface chemical modification and other parameters of the examined powders, as well as on used gaseous oxidizer property.

This method was used for studying an oxidative process in air and carbon dioxide of Al powders with 70-150 nm average size particles [4, 5, 7] producing by metal vapors condensation in flow of neutral gas [8]. In particular, during the investigation of their low temperature oxidation process in air flow it was found that the values of measured temperatures $T_{LTM}$ depend linearly on the value inverse to sample particles average size (Fig. 2).

$$T_{TLM} = 636.1 - 5576/R_o \text{ , где } R_o \text{ – particle's average size, nm} \quad (1)$$

Linear dependence is approximated by simple equation (1) and shows that the average $T_{LTM}$ value goes down when the particles' average size decreases and does not exceed $T_M$ of aluminum value with the increase the particles' average size (transition into flat surface).

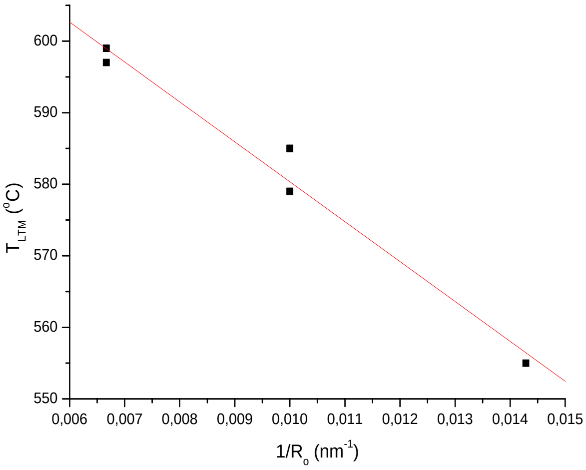


Figure 2: Dependence of $T_{LTM}$ (temperature of low temperature maximum of heat evolution) from the value inverse to sample particles average size R.

This dependence and the dependence of mass of aluminum oxidized at LTMHE on average size of oxidized powder particles' allowed to determine the size of aluminium particles, which can be completely oxidized by its heating to temperatures lower than $T_M$ in gaseous oxidizer formed solid oxidation products - oxides.

The process of aluminium low temperature oxidization (combustion) by gas-phase oxidant that forms aluminum oxides is possible with the use of metal aluminum that was reduced before or is being reduced during oxidization (combustion) to the necessary size particles. This process can be noted for high burning rate, high oxidation completeness, the absence of coagulation of melted metal particles into larger drops (that do not burn down completely) and also absence of agglomeration of solid products during the metal oxidation (burning). The last two factors considerably decrease the burning zone and provide the miniaturization of energy systems that use aluminium as fuel or fuel component.

The goals of this work are: to ascertain factors that make the process of low-temperature oxidation of aluminium feasible; to develop a model that describes a mechanism of low-temperature oxidation of aluminium nano-particles in gas phase oxidant.

## 2. Processes going during low temperature oxidization of nanosized aluminium particles

It is well known that high chemical activity of metal aluminum leads to its surface oxidation under contact with atmospheric air even at room temperature. Aluminium oxides coating formed during such a "soft" oxidization is nonreactive, gas proof, has good adhesion to metal surface and what is important has specific volume close to metal specific volume. Thus this film effectively protects metal under it from oxidation by water vapors, air oxygen, liquid water. According to numerous observations the thickness of such Al surface PC is just 2-4 nanometers [9]. Namely, the formation and development of through defects in this coating at relatively low temperatures (down $500^oC$) made possible the low temperature oxidization of aluminium layers situated under PC. Cracks will be the most significant through defects for oxidation.

As an oxide PC is formed by sequential oxidation of aluminium surface atoms and its thickness is less than ten atomic layers, then its structure and composition will be determined by structure of oxidized and underlying metal atoms.

As rule aluminium particles consist of microcrystallites "conglutinated" by amorphous aluminium. Thus a particle oxide PC will be like to "quilt" that covers the edges and sides of aluminium microcrystallites formative the Al particle surface and amorphous Al that bands microcrystallites. According to X-ray phase analysis oxide PC formed on ultra fine aluminum particles at "soft" oxidization does not have crystal structure. It is possible to wait that PC formed at "soft" oxidization on aluminum microcrystallites surface have more dense structure than the one formed on amorphous Al surface. For this reason the oxide coating areas over amorphous metal will be the weakest from the point of mechanical characteristics. Structure defects of metal aluminum situated under PC can noticeably to influence its mechanical characteristics. Through defects (particularly cracks) are most likely to appear in these areas. Theoretical investigations of cracks formation of aluminium oxide PC (e.g. $Al_2O_3$) shows that when Al spherical particle temperature grows from set temperature $T_o$ to critical temperature of cracks formation $Tc$ radiuses of particle metal core and oxide coating (PC) increase $\alpha_{Al}(T_c - T_o)$ and $\alpha_{Al2O3}(T_c - T_o)$ respectively. $\alpha_{Al}, \alpha_{Al_2O_3}$ are linear expansion coefficients for Al and $Al_2O_3$. As $\alpha_{Al} > \alpha_{Al2O3}$ then with the temperature grow the metal core expanansion generates the tense state of $Al_2O_3$ coating [10, 11].

As a result of thermal expansion the tensity $\delta$ appears between PC and metal core. The value $\delta$ is equal:

$$\delta = 0.5R(\alpha_{Al} - \alpha_{Al_2O_3})(Tc - T_0), \tag{2}$$

R – typical size of particle [12].

The contact pressure between oxide coating and particle metal core (result of heating) may be estimated by means of Hooke's law of all-around compression [13]:

$$P = \frac{E_{Al}}{3(1-2\mu_{Al})}\frac{\Delta V}{V}, \tag{3}$$

$E_{Al}$ = 71,4 hectopascals – Young modulus, $\mu_{Al}$ = 0.3 – Poisson's constant for Al [14].

The relative change of volume of aluminum particle is estimated by formula:

$$\Delta V \big/ V = \frac{3\delta}{0.5R}.$$

The coating ultimate stress limit is [11]

$$\sigma_{BPAl_2O_3} = P\,R/(4h), \tag{4}$$

$\sigma_{BPAl_2O_3}$ is a value of point of maximum load for $Al_2O_3$ which is equal to 260 hectopascals [10], $P$ – contact pressure, $R$ – PC coating diameter, $h$ – PC thickness.

Critical temperature $T_c = T_0 + \Delta T_c$ is easy to be estimated from (3) и (4) relations, $\Delta T_k$ is a value of critical heating when the crack is formed

$$\Delta T_c = T_c - T_0 = \frac{4h}{(\alpha_{Al} - \alpha_{al_2}\text{o}_3)}\frac{\sigma_{BPAl_2O_3}(1-2\mu_{Al})}{RE_{Al}} \tag{5}$$

The area of crack $S_{cr}$ formed at the critical heating of particle ($\Delta T_k$) is estimated as the difference between increase the surface areas of metal core and oxide coating as a result of thermal expansion:

$$S_{cr} = 2\pi R^2 \Delta T_k(\alpha_{Al} - \alpha_{Al_2O_3}) \quad \text{or using (5),}$$

$$S_{cr} = 8\pi Rh\frac{\sigma_{BPAl_2O_3}(1-2\mu_{Al})}{E_{Al}} \tag{6}$$

i.e., the crack area at critical heating of particle depends on the particle radius, thickness and strength characteristics of coating.

Calculations, which were carried out using the formula (5), showed that the magnitude of critical heating amounts to ~10-30°C for particles with size of 40-150 nm. I.e. in describing experiments the surface oxide coating of aluminum particle is permanently fissuring under its external linear heating. The striping metal is quickly oxidized due to the reaction with surrounding oxidizer and the continuousness of PC will rebuild. At the same time the energy released as a result of oxidation chemical reaction of the particle's striping metal layer dissipates in the surrounding particle medium (matrix) and in the particle volume due to thermal conductivity to a lesser degree due to emission. It is necessary note, that the thickness of oxide PC, which is equal 2-4 nm at room temperature [9,15] rises with the increase of metal oxidation temperature especially at temperature higher the aluminum melting temperature reaching value nearly 200 nm at aluminum oxide melting temperature [16].

It is possible suppose absolutely different thermal processes occurring during particle heating in oxide environment and leading to particle oxidation.

For example, the self cracking process when amount of heating released during metal aluminum oxidation of particle surface striping in result of crack appearance (here and after "reaction zone") caused the thermal metal expansion enough for critical contact pressure creation and consequently new crack appearance. The estimation of oxidation of particles by using thermal balance shows that self cracking of aluminum is possible for particles with diameter less than 13 nm ($D \leq 13$nm) in temperature range 200-650C°.

The range of average-sized particles of powders, which were investigated in this work, are 70 - 150 nm. It means that we need to find other mechanisms for describing the nature of the observed low-temperature maximums of heat evolution. At the "reaction zone", as would follow, high-density ( ~400 kW/cm$^2$) heat flows occurred, thus the observed low-temperature maximum of oxidation can be described by the mechanism of metal local overheating with formation of aluminum melt zone and its splash on the particle surface due to effect of stepwise expansion with phase transition (volume jump on 6% by melting), following oxidation of splash melt Al with heat releasing, which lead to melting of new Al portion, splash liquid metal on the surface and in this way till stopping of oxidation process due to blocking oxidizer access to metal surface by generated Al oxide. In accordance with Polezhaev lows [23, 24] the thickness of layer under the melted metal, in which the temperature drops from $T_M$ down to temperature near the mean temperature of particle, is small (less than 6% from the thickness of melted zone). Practically it means that all heat evolving as result of metal Al oxidation spends on the melting of particle metal.

It should be mentioned, as heat evolution under oxidation of mass of Al is 80 times more than required for the same metal mass melting, so 6% metal splash and its oxidation allows to melt new metal mass at 4.8 times greater, than primary melting one. In principle this energy balance allows realized possibility of self-acceleration of aluminum oxidation process if the destruction of oxide layers forming in the result of oxidation of melted Al will ensured because these oxide layers can screen the melted Al surface from gaseous oxidizer.

Formation of low temperature heat evolution maximum observed during aluminium nanopowder oxidation can be completely described if the process of single particle low temperature oxidation is understood. To create the mathematical model of the process leading to low temperature heat evolution it is necessary the formalization of it's following steps:

- crack formation in the oxide PC covering the Al particle and possible form of crack;
- non stationary particle heating by the energy evolved in "reaction zone" during metal Al oxidation;
- destruction of newly created oxide film in "reaction zone" because of the effect of stepwise expansion with phase transition (melting);
- jumping changes in Al density during phase change (melting) its on the particle surface due to
- splash of melted Al through the crack and melt oxidation

The first three steps of Al nanoparticle oxidation process are considered in this work.

Particle oxide PC starts breaking from formation of nanocracks in the PC areas with low mechanical characteristics [17]. Opening along edges of areas with the high mechanical characteristics (areas over microcrystallites sides emerging on particle surface) nanocracks may easily reach triple junctions of boundaries of these areas. As it is shown in [18] areas triple junctions affectively prevent enlargement of nanocracks developed near boundaries. The more the angular opening of edges near triple junctions the less the probability of further crack development is. Thus under other equal conditions nanocrack is supposed to develop along the edge which deviate at the least angle from original direction of crack development. According to [19] during quasi fragile solid body destruction a crack appears when tension at its future top reaches the critical strength value (Griffiths theory). Appeared crack moves on speed of 0,6-0,7 of sound speed in the material and perpendicularly to the top of stretching tensions direction (in this work the top stretching tensions run perpendicularly to the boundaries of PC areas having high mechanical properties). As it follows from above the most probable crack will have characteristic length close to $\sim\Delta$, where $\sim\Delta$ is characteristic size of aluminum microcrystallites that form a particle. One can suggest that the structure of oxide PC for Al powders under research (average particles size 70-150nm, produced analogously by metal vapors condensation and passivated under similar conditions) have similar characteristics of Al microcrystallite.

Estimation of value $\tau_x$ – characteristic time of metal particle local heating by heat generated at oxidation of metal exposed as a result of cracking in PC was based on the following assumptions:

- oxidation of metal takes place as a result of collision of oxygen molecules with metal surface with accommodation coefficient $\beta$ (the probability of stoichiometric reaction with single collision) equals 1.
- collisions of $n$ molecules of oxygen per second with 1m$^2$ flat surface is estimated according to kinetic gas theory formulas:

$$n = \frac{1}{4} NLk_{02} w \ ,$$

where $w$ – highest probable speed of $O_2$ molecules. At the gas temperature about 600°C $w$=700m/sec; $NL = 2{,}7\ 10^{25}$ mol/m$^3$ – Loschmidt number; $k_{O2} = 0{,}23$ – amount oxygen in air.
For these conditions $n$=1.09 $10^{27}$ strikes /sec m$^2$.

- as during “soft” aluminium surface oxidation takes place layer by layer the thickness of oxide coating on the surface gradually reaches 4 nm (about 10 monolayers Al). Therefore, approximately three monolayers of Al atoms (depth 0,61 nm) are expected to be oxidized almost simultaneously during the first (fastest) stage of oxidation. Number of atoms in aluminum layer with area 1m$^2$ and thickness 0,61nm is equal to value $m_{Al} = 1.8\ 10^{19}$, where $\tau_0$ - time of oxidation for Al plate with area 1m$^2$ and thickness 0,61 nm (three monolayers of Al atoms). Then, the value of $\tau_0$ under $\beta=1$ equals the time, required for 3 $m_{Al}$ /4 oxygen molecules striking a plate with area 1m$^2$

$$\tau_0 = \frac{3}{4} m_{A\ell} n^{-1} = 1{,}25\ \ 10^{-8}\ \sec\ = 12{,}5\ \text{nse c}\ ; \qquad (7)$$

Average density of heat flow in “reaction zone” can be estimated, if the value of $\tau_o$ is knowing,: $q = 0{,}61\ \ 10^{-9} \rho_{A\ell} Q_{HA\ell} \tau_0^{-1} = 4{,}08\ \ 10^{9} \frac{W}{m^2}$ , where $\rho = 2700$ kg/m$^3$, $Q_{HAl} = 31$ mJ/kg are density and heat of burning of Al, correspondently;

- oxidation of metal stripped after formation of cracks in PC takes place in direction perpendicular to crack surface to the depth of 0,61 nm (3 monolayers of aluminium atoms) and parallel to the crack boundary (same depth). The total number $N_T$ of Al atoms oxidized in the “reaction zone” at open crack can be estimated as:

$$N_T = m_{Al}\,(S_{cr} + 0.61\ 10^{-9}\, P_{cr}/3). \qquad (8)$$

For oxidation of the required number of Al atoms needs to be transported to “reaction zone” $3N_T/4$ molecules of oxygen. The time of the reaction $\tau_x$ can be estimated

$$\tau_x = \tau_0\,(1+0.61\ 10^{-9}\, P_{cr}/3\, S_{cr}) \qquad (9)$$

The evaluation (under the assumption that microcrystallites length is 5-12 nm) of influence of crack characteristics (length and width) on the average time of local heating of particles, on the average temperature of heating and on the released cumulative metal oxidation energy in “reaction zone” show that the first is (14-18) nc, the second (0.3-1.5)K and the third is (0.7-1.5)$10^{-15}$ J.
It is easy to show that the time of crack creation in PC at the experimental conditions is less than 0,01 nsec, therefore, processes of crack formation shall not be considered connected with the external heating of Al particle. Classic theory of thermal conductivity ignores molecular structure of substance, and considers a particle as continuum, in which thermal field spreads instantaneously [20]. In reality, the speed of thermal expansion is finite and, according to [20] for hard aluminium is equal 2800 m/sec. For the investigated particles the expansion time of thermal field from the "reaction zone" to the furthest point of the particle does not exceed 0,05 nanosecond, which is considerably lower than the average local heating time of the particle, which results from metal oxidation equal to $\tau_x$. The heating rate of experimental sample did not exceed 0.3°/sec., thus, the environment conditions can be considered constant for the time $\tau_x=10^{-8}$ sec.
Particle surface is covered with Al oxide PC, thermal conductivity of which is $\lambda_{Al2O3} = 10$ W/мK and thermal emissivity - $\varepsilon_m = 0.3$ [12,21,22]; thermal conductivity of metal Al exceeds thermal conductivity of PC in more than 20 times. It means that the overflows of heat in PC can be considered as negligible. In general, heat loss on a particle in ambient environment results from heat radiation. It is negligible due to small value of thermal emissivity factor. For this reason the surface of particles can be considered as isolated. In order to solve the problem of thermal conductivity, a particle can be considered as a symmetrical sphere with axis of central symmetry coincident to diameter of sphere passing through the vertex of the spherical surface segment (the “reaction zone”). The area of this “reaction zone” is equal to area of a crack $S_{cr}$, which can be calculated by formula (6).

The process of non-stationary heating of Al particle with energy released from oxidation in the "reaction zone" can be described by solving a classical transient heat conduction problem [20]: a solid sphere with isolated surface is heated with constant thermal flow from the "reaction zone" (flow density 400 kW/cm$^2$ ) during the time $\tau_x$ from the set temperature of the sphere ($T_{med}$) to the temperature (on the surface of the reaction zone) equal to Al melting point (933K).

Boundary problem of thermal conductivity for determination of the temperature at which the LTMHE occurs was calculated by target method using two-dimensional approach.

Calculations for non-stationary heat conductivity for various diameter particles and $\tau_{x,}$ which is conformable to Al microcrystallite $\varDelta$ = 5 nm are presented in Table 2.

Table 2.

The comparison of experimental and numerical calculated values of $T_{LTM}$ for Al nanoparticles investigated in the work. The size of micro crystallites proposed 5 nm.

| R, nm | 150 | 100 | 70 |
|---|---|---|---|
| $T_{LTM}$, K (calculation) | 849 | 818 | 769 |
| $T_{LTM}$, K (experiment) | 872<br>870 | 858 | 828 |

Qualitative conformity of the estimated and experimental data of the environment temperature is clearly seen. Higher values of experimental data can be explained by a number of factors, such as:

- differences in specific size of a crack. Rectangular crack shape was taken for calculations, while natural shape may be close to elliptical;
- dissimilarity of real accommodation coefficient values $\beta$ from 1;
- heat losses of a particle considered as negligible quantity while in fact heat losses are unavoidable.

Destruction of the oxide coating that was regenerated during the time $\tau_x$ in the crack area can be identified as the problem of determination of critical deflection $W_x$ of rectangular solid plate with the fixed edges [11]. The plate's geometry is equal to the crack's geometry. The plate deflection is result of jump change (6%) in the density of melting aluminium under the plate. Contact pressure between the newly-formed oxide coating and liquid metal can reach its critical value $P_x$, which can be calculated [11, 13], as follows:

$$P_x = \frac{\sigma_{BP_{A\ell_2O_3}} * h_x^2}{6 * \gamma * b^2},$$

where γ – proportionality coefficient: $0{,}05 \le \gamma \le 0{,}08$ for $1 \le \frac{b}{a} \le \infty$ , leading to formation of critical deflection $W_x$ , calculated as: $W_x = \alpha \frac{P_x * b^4}{E_{A\ell_2O_3} * h_x^3}$, where $E_{A\ell_2O_3} = 382 \cdot 10^9$ Pa Young's modulus for corundum ($Al_2O_3$) [10, 14], α – proportionality coefficient $0{,}014 \le \alpha \le 0{,}028$ for $1 \le \frac{b}{a} \le \infty$ [11] or

$W_x = \frac{1}{6} \cdot \frac{\alpha}{\gamma} \cdot \frac{\sigma_{BP_{A\ell_2O_3}}}{E_{A\ell_2O_3}} \cdot \frac{b^2}{h_x}$ , where $0{,}27 \le \frac{\alpha}{\gamma} \le 0{,}34$ for $1 \le \frac{b}{a} \le \infty$ is considered $\frac{\alpha}{\gamma} \sim 0.3$ , leading to the beginning of film destruction.

The value of critical deflection $W_x$ of PC can be estimated as hight of the figure formed in crack volume at the expansion of melted Al. The lower limit of such figure is parallelepiped with the height $W_x$ filled the crack. Numerical evaluation of $W_x$ value permits to evaluate the depth the melted Al under the crack and shows that this depth is considerably lower than single layer of aluminum atoms. So, even the melting of Al atoms monolayer can break the surface oxide film. For this reason the process of oxide film destruction shall be considered as unavoidable on reaching the metal surface temperature equal to $T_M$.

Oxidation process of ultra fine Al powders with carbon dioxide and water vapour has identical characteristics as oxidation with air or oxygen. It is possible to affirm that the above described mechanism of LTMHE occurrence can be applied to Al oxidation in these oxidants.

The use of aluminum nanopowders provide a way for it's low-temperature oxidation, higher percentage of metal oxidation, and decrease coalescence of separate melted particles into larger drops, which can not burn completely during oxidation time (duration of stay in combustion chamber). It should be noted, that oxidation (burning) temperature lowering of aluminium particle reduces agglomeration of solid combustion products [5].

## 3. Conclusions

This study was carried out with supposition that defects (cracks) form and develop in PC because of different temperature expansion coefficients for $Al_2O_3$ and Al. The results show that possibility and conditions of aluminum low temperature oxidation process depend on the size of oxidizable particle and different thermal oxidation processes of aluminum are possible. The complete oxidation of particles by their self-cracking occurs when their size is less than 13 nm. If size is more than 13 nm metal local overheating may start with aluminium melting and its splash to particle surface.

Good correspondence of experimental dependences of temperature of environmental medium causing the appearance of LTMHE from the particle average size and the numerical calculation results obtained by using a single particle non-stationary heating was observed.

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