

# Effect of Heat Transfer Peculiarities on Ignition and Combustion Behavior of Al Nanoparticles

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## Abstract

Nanoenergetic materials have some advantages against micrometric and bulk materials. This is due to enhanced surface area and intimacy between reactive components that leads to increase in the reaction rate and decrease in the ignition delay. However, till now there is very limited understanding of fundamental physical processes that control reaction and combustion wave propagation. The heat transfer in the case of nanoparticles is characterized some specific features which determine the sometime unusual ignition and combustion behavior. The paper is focused on discussing the ignition and combustion of nano Al particles in conditions of a shock tube and in a plastic tube. It is shown that tiny metal particles at high temperatures and pressures become “thermally isolated” from ambient gas environment and experimentally observed ignition delays may be two order magnitudes longer of those calculated without accounting real energy accommodation and sticking coefficients. When going to conditions of reaction propagation in a plastic tube, some different ways for heat transfer have to be carefully analyzed. Actually, there are no evidences for unique dominant process which may provide propagation of combustion wave with observed speed through the loose Al/CuO particles mixture. It can be stated that the process comprises 2 stages with very fast ignition, releasing large amount of heat and propelling hot gas and condensed material in direction of unreacted mixture followed by more slow reaction of remaining metal with evolved in oxide decomposition oxygen. Common conclusion is that further detailed studying the fundamental properties of nanoenergetics materials and their reaction behavior may open ways for purposed control of the combustion behavior and for effective use of nanoenergetics in practical applications.

## 1. Introduction

The works in nanochemistry opened a bottom-up approach in the architecture of matter, from the atom to millimeter scale. The main idea in energetics is to enhance the surface area and intimacy between reactive components in order to increase the reaction rate and decrease the ignition delay. For the case of nanoenergetic materials, until last time it was limited understanding of fundamental physical processes that control reaction and combustion wave propagation. In many ways, these challenges are direct consequences of the advantages which appear when passing from traditional to nanoscale materials. In particular, the diagnostic tools used must have fast response and high temporal resolution. Actually, there are large difficulties

in performing experimental observation of the nanoscale changes occurring in nanoenergetic materials on the very short time scales associated with the rapid heating rates and high temperatures. Several authors stated that the exact mechanisms for nano Al particles ignition and combustion are currently unclear. The main reason is the lack of available commercial experimental techniques because it is difficult to design experiments with recording physical changes occurring with particles of nano sizes at heating rates reaching  $10^6 \div 10^8$  K/s and more, which correspond to conditions in propagated combustion waves.

Nanopowders are often used [1] to produce so-called metastable intermolecular composites (MICs). These are mixtures of nanosized reagents which are stable under normal conditions and

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capable of interacting with each other with the release of large amounts of energy after activation by a triggering stimulus (thermal, mechanical, or electrical). Examples of such MICs are mixtures of nanoparticles of metals such as Al, Mg, Zr, Hf, etc., and nanoparticles of metal oxides ( $\text{Fe}_2\text{O}_3$ ,  $\text{MoO}_3$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{MnO}_4$ ,  $\text{CuO}$ ,  $\text{Bi}_2\text{O}_3$ , and  $\text{WO}_3$ ). It is known that in the case of classical micrometric thermites, the combustion reaction is slow due to the relatively slow diffusion process. When the reagents are in the nanoscale, the diffusion path is much shorter and the reaction rate is increased significantly as compared with the reaction rate of conventional thermites. Additives of polymer materials or binders or gas generating agents to metal and metal oxide based MICs are able to provide the necessary working body during combustion. An area of particular interest is the use of MICs in microscale motors. This is related to the development of microscale propulsion systems and the use of these energetic materials in micromotors and even small spacecrafts. Supposedly, such mixtures could find application as the gas generating compositions. They can combine high energy characteristics with unprecedented stability, safety, and an opportunity to precisely control the burning rate in a wide range through the regulation of granulometric composition. In the case of nanothermites, due to fast reactions the energy losses to the combustor wall are negligible. For example, the burning rate of  $\text{MoO}_3$ -Al nanothermite, prepared by mechanical mixing of 79 nm aluminum particles and  $30 \text{ nm} \times 200 \text{ nm}$   $\text{MoO}_3$  flakes reaches 790 m/s in a metal tube of 0.5 mm diameter. This composition is considered a promising base for microscale rocket propellants [2].

Recent studies of nanoaluminum particles combustion [3] revealed some peculiarities of heat transfer indicating the overestimation of heat losses from nanoparticles in surrounding gas during combustion. For nano-scale particles the Knudsen number ( $Kn = 2\lambda/d$ , where  $\lambda$  is the mean free path of the molecules in the gas and  $d$  is the particle size) effects have to be taken into consideration when this number becomes equal  $Kn > 10$ . In such conditions the non-continuum heat transfer expressions must be used to describe heat losses from particle to ambient gas. However, it was found that formal application of these expressions gives the burning time values which are essentially shorter of experimentally observed. This finding means that in description of heat transfer of nanoparticles it is necessary to use the correct energy accommodation coefficient and reasonably low sticking probability for collision of oxygen molecules in reaction with the aluminum surface. In particular, in the shock

tube experiments [3] with nano aluminum particles of 80 nm size the measured burning time was equal to 124  $\mu\text{s}$  instead of 1  $\mu\text{s}$  estimated by formal calculations. It was concluded that at high ambient temperatures existing in the shock tube experiments, the nano sized metal particles experience a sort of thermal isolation from the surrounding gas. This effect has to be considered when modeling metal nano particles ignition and combustion.

Another example of possible effects of gas phase chemistry and difficulties of interpretation of experimental data can be demonstrated while analyzing the displacement of the luminescent front in the plastic tubes filled with energetic material. It was shown in experiments [4] with loosely-packed aluminum/copper oxide (Al/CuO) nano thermites in acrylic burn tube, composed of fully and partially filled sections, that the velocity of the luminous front in partially filled region approached 1000 m/s and was about 600 m/s in the filled region. In partially-filled region the intermediate and product species expanded forward and completely fill the tube being heated up to a temperature of about 3000 K. In the filled region the temperature first increased to the value of 3200 K and then remained at the level of 3000 K even after the front exits the end of tube. These results suggest that the luminous front maybe not represent the ignition of new material but rather some reacting material part is propelled forward through the tube. Qualitatively similar findings were obtained earlier in the burn tube experiments [5] with  $\text{MoO}_3/\text{Al}$  system. In the case of low density samples of loosely-packed nanoenergetic material the high "burning rate" reaching 1000 m/s was experimentally recorded while for densely-packed samples a moderate rate was recorded comprising  $\approx 1$  m/sec which was also typical of the systems with micron-sized powders. These results indicate that observed very high velocities of luminescent front propagation during combustion of nanoenergetic systems in thin channels are probably caused by the hot gas exhaustion but not by the kinetics of heterogeneous chemical reactions in nanosystems. This shows that the question about significant differences (few orders of magnitude) in the reaction kinetics of nano- and micro thermite systems remains open.

Thus, to construct objective mechanisms of ignition and combustion of Al nano particles it is necessary to examine in detail the peculiarities of heat exchange between nano particles and gaseous environment. The present paper illustrates this issue on the examples of fast reaction of individual Al particles in a shock tube and Al/CuO mixtures in a plastic burn tube.

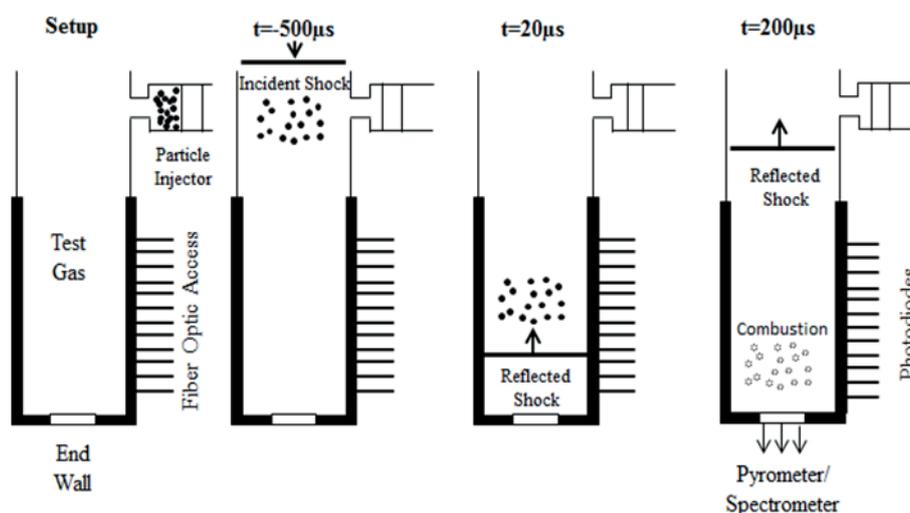


Fig. 1. Schematic of shock tube tests [6].

## 2. Ignition and combustion of nanoAl in a shock tube

Heterogeneous shock tube (Fig. 1) has been used for studying the combustion behavior of Al nano particles [6]. The device is able to produce controlled high temperature (up to 4000 K) and high pressure (above 30 atm) environments with various gas compositions. The reaction behavior of nano-aluminum particles was monitored behind the reflected shock in order to achieve the high pressures desired. The pressure was varied between 3.5–20 atm to determine the effect of the oxidizer concentration on the particle temperature and burn time.

In experiments, the particles of given size were injected from the top in front of the incident shock and passed to the bottom with pushing gas. The particles accelerated quickly behind the incident shock and stagnated instantaneously behind the reflected shock. They were heated in the reflected shock wave, ignited and burned in controlled gas environment. The velocity of the shock was measured using four piezoelectric pressure transducers at different axial locations. The emission of ignited Al nano particles was recorded by a series of photodiodes at the lateral wall of tube and by pyrometer and spectrometer at the end wall of tube.

Emission spectra were collected using an Ocean Optics spectrometer with a 10  $\mu\text{m}$  inlet slit and a 200–550 nm range. The spectral resolution of the spectrometer was approximately 1 nm full-width-half-maximum. It was found that at relatively low shock wave temperature (below 2000 K) only thermal radiation but no significant gas phase emission can be recorded, indicating that the primary combustion mechanism involves mainly surface reactions.

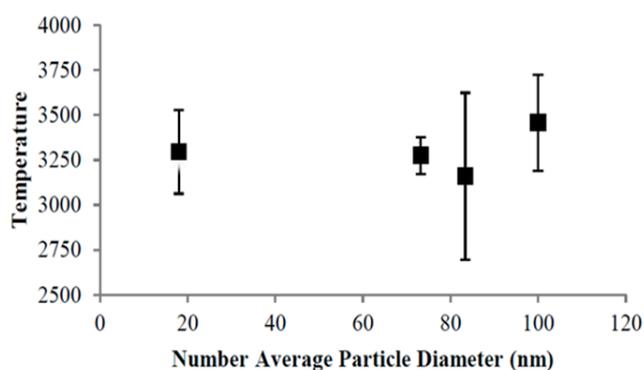


Fig. 2. Maximal particle temperature vs. size at  $1500 \pm 50$  K (20 atm, 20%  $\text{O}_2$ :80%  $\text{N}_2$ ) [6].

The infiltrated photodiode traces of luminosity were treated by using the 10–90% area method to calculate the burn time. Actually, the burning time was defined as the time period between 10 and 90% of the total integrated emission intensity.

The particles temperature was measured with use of a custom built 3-color pyrometer. The time response of the pyrometry system is sub-microsecond. Noise level was typically 10–20% of the signal and the measurement uncertainty had previously been estimated to be  $\pm 150$  K for micron sized particles.

The measured maximal temperatures of Al nano particles of different sizes in an air simulated environment are presented in Fig. 2.

It is seen that the particles maximal temperature remains relatively constant for all particle sizes. The scatter in the measurement is due to the combination of large measurement uncertainty ( $\pm 150$  K), high signal to noise ratio, and short luminosity time scales.

It has to be mentioned that within the framework of classical theory the rapid heat transfer for ultrafine particles results in combustion temperatures that only minimally exceed the ambient temperature. The available experimental data show that the assumptions of classical heat transfer theory do not work in case of nano particle at high gas temperature. Prediction of real particle temperature requires specification of the reaction rate (i.e. heat release rate) in addition to the heat transfer coefficient. The high peak temperatures suggest that the particles are experiencing free molecular regime heat transfer effects.

At nano scales, the particle diameter is comparable to or even smaller than the mean free path. The particles behave like the large molecules, and the gas cannot be treated as a continuum medium. Thus, the conductive heat transfer between nanoparticles and gaseous medium has to be described in a free-molecular regime of collisions. The intensity of such a heat transfer is described as [7]

$$\dot{Q}_{cond} = \alpha \pi D_p^2 \frac{p_a \sqrt{8k_B T_a / \pi m_a}}{8} \left( \frac{\gamma + 1}{\gamma - 1} \right) \left( \frac{T_p}{T_a} - 1 \right) \quad (1)$$

Here  $\alpha$  is the energy accommodation coefficient (the ratio of the actual average energy transferred during a collision to the theoretical value under complete energy accommodation),  $D_p$  is the diameter of particle,  $k_B$  is the Boltzmann constant,  $m_a$  is the average mass of the gas molecule, and  $\gamma$  is the ratio of the gas specific heats. The subscripts  $a$  and  $p$  denote the ambient gas and particle, respectively.

In theoretical and experimental works [8, 9] it was suggested that at high particle and gas temperatures, nanoparticles have very small energy accommodation coefficients and become conductively isolated from the ambient gas. Radiation consequently becomes most significant pathway for heat transfer in the low accommodation coefficient regime. With the low accommodation coefficients the heat transfer from the particle via collision with gas molecules becomes inefficient, leading to particle temperatures much higher than those expected using continuum regime expressions.

The particle thermal behavior can be derived from an energy balance (Eq. 2) that assumes a surface-process limited combustion mechanism and heat transfer through conduction to the ambient gas and radiation to the walls of the shock tube (see Fig. 3).

$$m_p C_p \frac{dT}{dt} = \dot{Q}_{gen} - \dot{Q}_{rad} - \dot{Q}_{cond} \quad (2)$$

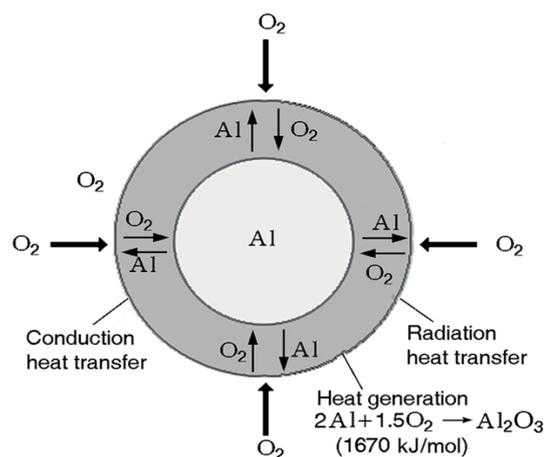


Fig. 3. Physicochemical processes in combustion of nano aluminum particles in oxygen [9].

The influx of heat to the particle is assumed to be due to the chemical reaction between the oxygen and aluminum, which releases  $1.85(10^{-18})$  joules of energy for each collision of oxygen molecule resulting in reaction with the aluminum surface. The rate of chemical heat generation is given by the formula

$$\dot{Q}_{gen} = A_p \phi N_{ox} c q / 4,$$

where  $A_p$  is the particle surface area,  $\phi$  is the sticking probability,  $N_{ox}$  is the number concentration of oxidizer molecules,  $c$  is the molecular speed, and  $q$  is the heat of the reaction. The sticking probability represents the percentage of collisions that react and has a value between zero and one. A sticking probability of zero represents no reaction, and a sticking probability of one indicates each collision results in chemical reaction.

The radiation heat transfer rate is expressed as

$$\dot{Q}_{rad} = \varepsilon_p \sigma A_p (T_p^4 - T_a^4),$$

where  $\varepsilon_p$  is the emissivity of the particle and  $\sigma$  is the Stefan-Boltzmann constant.

The conduction of heat in a free molecular regime to the surrounding gas (last term in the energy balance) is described by the Eq. 1 and plays important role in determining calculated particle thermal behavior. Reasonably good agreement with experimental data was achieved [6] provided that the energy accommodation coefficient and sticking probability were taken to be  $\alpha = 0.0035$  and  $\phi = 0.0009$ , respectively. The former value agrees well with theoretical limit for the energy accommodation coefficient  $\alpha$  [9]:

$$\alpha < \frac{\theta^2}{\left(2\frac{C_V}{R} + 1\right)T_a T_p},$$

where  $C_V$  is the molar specific heat of the gas and  $\theta = 428$  K is the Debye temperature of aluminum.

It has to be noted that extremely low fitting values for energy accommodation and sticking coefficients are the result of processing the experimental data within the framework of proposed complex model involving the processes of chemical kinetics and heat transfer. The precise data on kinetic parameters as well as on experimentally measured values of ignition delay, burning time and maximal particle temperature are not known. However, the available information allows making some definite conclusions about the dependency of the burning time on the particle size and impossibility of explaining the experimental results on the basis of continuum model. Actually, formal application of these expressions gives the burning time values which by 2 orders of magnitude shorter of experimentally observed. As it is mentioned above, in the shock tube experiments with nano aluminum particles of 80 nm size the measured burning time was equal to 124  $\mu$ s instead of 1  $\mu$ s estimated by formal calculations.

Obviously, the above analysis can be extended in the future in order to take account of different factors. For example, in traditional models it is assumed that oxidizer molecules collide and react on a smooth spherical surface of an aluminum particle. In reality, surface roughness and the presence of cracks in the oxide layer may substantially alter the relationship between the particle diameter and the surface area available for chemical reactions. Theoretical analysis [10] exhibited the effect of cracks in the oxide layer on the burning time of aluminum particles. For non-fractal surfaces, the burning time is linearly proportional to the particle size. The burning-time diameter exponent decreases from 1 to 0 as the fractal dimension increases from 2 to 3. The weak effect of the particle size on the burning time of nano aluminum particles may stem from the fractal nature of the surface available for chemical reactions.

Further studies are needed to elucidate the effects of the pressure and the oxidizer type on the burning time of nano aluminum particles. As discussed in the literature [11, 12], the burning behavior of aluminum particles may depend on the heating rate. For heating rates greater than  $10^6$  K/s, the melt dispersion mechanism may become operative (Fig. 4).

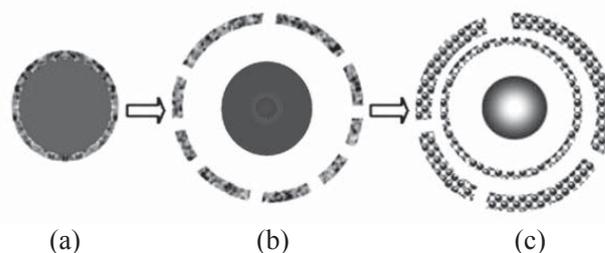


Fig. 4. Schematic of the melt-dispersion mechanism of combustion of nano aluminum particles at a high heating rate ( $>10^6$  K/s) [11]: (a) aluminum core covered by the initial alumina shell; (b) fast melting of aluminum leads to spallation of the alumina shell; (c) unloading wave propagates to the center of the molten core of the Al particle and generates tensile pressure, which disperses small Al clusters.

A number of studies have been conducted to ascertain the validity of that mechanism according to which melting of the aluminum core creates pressures of 1–4 GPa causing spallation of the oxide shell. The ensuing pressure imbalance between the core and the exposed surface results in an unloading wave and disperses small liquid aluminum clusters. The liquid aluminum clusters react fast with the oxidizing gas. The melt-dispersion mechanism was employed to explain the unusual experimental results [13] and its first experimental evidence was provided in [14]. In that work transmission electron microscopy images suggested the rupture of the oxide shell and the presence of small reacted Al clusters. A detailed review of various theoretical and experimental studies on the melt-dispersion mechanism can be found in [15].

### 3. Ignition and combustion of nanoAl in a plastic burn tube

Another example of implicating problems arising in exploring and treatment of ignition and combustion of nanoAl is illustrated by experiments in a plastic burn tube [16]. These experiments are comprised of loading a tube with energetic material, igniting from one end, and observing the propagation of the luminous front with high speed video and/or the pressure wave with a series of pressure transducers to determine a flame speed [17]. Such experiments are good examples of high speed diagnostics and exhibit the high heating rates of free combustion. However, even the straight forward and exceedingly prevalent measurement (flame speed) has been shown to be significantly complicated by the challenging nature of these materials. Recent work [18] demonstrated how much is still unknown about this widespread technique. It was shown that the luminous front taken as the

reaction front propagated even faster through unfilled tube. It evidently means that it does not represent the ignition of new material but rather combusting material which is propelled forward through the tube. It was also found that the materials were remaining hot and bright long after the luminous front passed. Consequently, one may expect that significant fraction of unreacted material exists, which continues burning after the initial passage of the luminous front. Thus, the actual physical meaning of flame speed is far from understood in the plastic tube experiments.

One thing that is certain from the burn tube experiments is that nanoenergetic reaction can produce hot material that moves very fast. So, one may conclude that a convective mechanism is dominant. This suggests that the primary tool of heat transport is a convective process [19, 20]. The key evidence from those studies is that the highest flame speeds coincided with low packing densities, high gas production, low initial pressure, and confinement, which are all the conditions that are most conducive to moving gases and material. In comparison, condensed phase conduction would be oppositely affected or insensitive to those parameters. Convection is further supported by the high specific surface area and small sizes intrinsic to nanoparticles, which yield a very low thermal relaxation time. Therefore, it is expected that in a hot gas particles will quickly equilibrate to that temperature.

Despite the attractive simplicity and logics of that assumption, it has to be checked with direct calculations of heating efficiency of hot gases. For this end one can evaluate the heat flow generated by hot gases moving in the tube. Evaluation [21] of the convective heat transfer contribution to the material heating from initial to ignition temperature (conventionally chosen as 1300 K) showed that it provides reaching the burn rate which is orders of magnitude less than those measured in burn tubes and open tray experiments.

Similar treatment can be given to radiative heat transfer [21]. To simplify the problem, the radiative heat transfer is estimated between two black bodies with the temperatures corresponding to the flame and wall conditions. This estimate produces the value of heat flow which is order of magnitude less than that of convective heat transfer and could not provide propagation of reaction front with experimentally observed speed.

Additional option that can be evaluated is the heat transfer based on the flow of hot material. Actually, the amount of gases existing in these systems is unlikely to be able to account for the amount of heat needed for heating the initial particles in tube. According to crude estimates, the hot gas (oxygen)

may provide only few percent of needed heat. Even in the case of vaporized metal that could condense to release additional energy, the amount of generated heat is insignificant because the rising pressure in the tube would effectively suppress the metal evaporation.

It has to be mentioned that most of these estimates are based on exaggerated values and the exhaust of gases from the open end of tube may take increasing the needed amount of heat. However, in addition to above estimations one may consider the movement of hot condensed phase material advected into the unreacted zone. It might be assumed that the existing in combustion wave conditions may facilitate the aerosolization of materials which was really observed in experiments with fuel rich Al/CuO nanoparticles ignited by a wire heated at a high rate [22]. There were detected light-emitting species which were leaving the wire at high velocity as a result of reaction. Possibly, the advective behavior can be also realized via the melt dispersion mechanism, as the molten aluminum fine droplets produced would be propelled at high rates.

Alternatively, condensed phase reactions may play essential role in heat release and propagation of combustion wave. Natural restriction for such reactions is due to oxide shell on Al particles which prevents diffusion of oxygen to metal. It is known that self-diffusion coefficients for bulk  $\text{Al}_2\text{O}_3$  are too low to account for the time scale measured in combustion experiments [23]. In particular, the values just only of  $\sim 10^{-15}$  and  $\sim 10^{-17}$   $\text{m}^2/\text{s}$  for Al and O in alumina are given in [24] for temperature  $\sim 2000$  K. Thus, even with a 2 nm oxide shell, one can evaluate a characteristic diffusion time of 4 ms, which is much slower than the burn times.

However, the kinetics of the diffusion might be significantly accelerated, for example, by an intrinsic electric field to support enhanced diffusion velocity with a Cabrera-Mott mechanism. Therefore, one can expect that an initial diffusion step successfully occurs during ignition, which then creates high temperatures and alternate pathways. This may explain the values of ignition delay observed in some systems.

Based on the available information, it can be concluded that a significant step to nanoenergetic combustion is the breakdown of passivating metal oxide layer. However, cross-barrier diffusion still could be important as a determining factor for ignition delays or as a mechanism responsible for weakening of the oxide shell. The exact nature of the overcoming of the shell is not yet well understood, but it has been observed in a variety of experiments. The break down exposes elemental aluminum that can readily react.

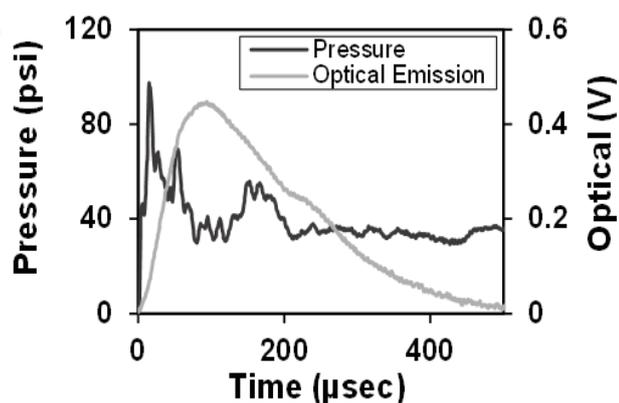


Fig. 5. Al/CuO nanothermite combustion in a constant volume pressure cell (25 mg of reactant in a 13 cc cell) [25].

Now, when discussing the reaction mechanisms of Al nanoparticles one may consider gas-condensed heterogeneous one as well as condensed phase reaction mechanism. As for the gas-condensed reaction mechanism, an interesting information was obtained in special experiments conducted at constant volume pressure cell setup. They showed two distinct timescales [25], as it is presented in Fig. 5.

It is seen that the pressure peak is reached in  $\sim 10$   $\mu$ s that is comparable to the burn tube experiments. However, the optical signal reaches maximum value at  $\sim 100$   $\mu$ s that indicates a two-step process consisting of initial reaction, which heats up original material and reduces the oxidizer followed by heterogeneous burning in the released  $O_2$ . Analysis of additional experimental data obtained with the Bunsen burner and in the shock tube demonstrates that gas-condensed heterogeneous reaction could not ensure reaching the  $\sim 10$   $\mu$ s burn time, but these may become responsible for a slower burning that occurs after the initial fast reaction.

As for the condensed phase reaction mechanism [21] stating that oxidation occurs directly between the condensed phase (i.e., solid or molten) fuel and the condensed phase oxidizer, the main restriction could be very limited interfacial area between the reagents because interface exists only in the points of contact between adjacent nanoparticles of differing components. Recently, there were obtained theoretical and experimental data demonstrating very fast sintering of nanoparticles. The common features of reactive sintering process were described in detail in [26]. Preliminary experimental estimates were obtained in simplified planar geometry with Al/CuO nanolaminates (150 nm thick). In open configuration experiments [27, 28] there were measured relatively high combustion speeds up to  $\sim 80$  m/s which are comparable with the values found for nanoparticle thermites.

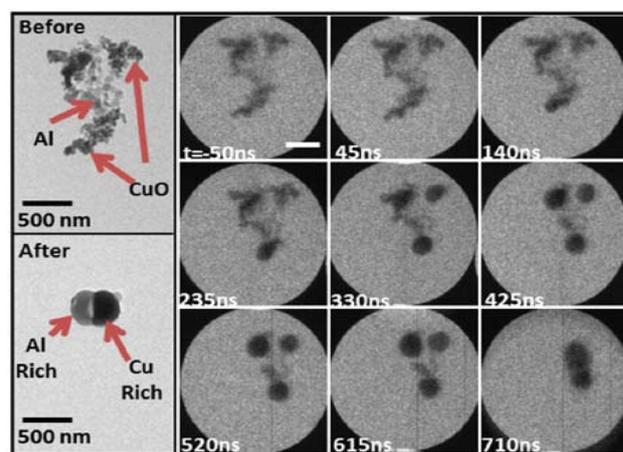


Fig. 6. Results from a DTEM experiment performed on Al/CuO nanothermite [21].

The informative evidences of condensed phase reaction mechanism were obtained in experiments with loose powder nanothermites conducted in vacuum conditions with use of Movie Mode Dynamic Transmission Electron Microscopy (DTEM). This type of microscopy allows direct observing the nanometer scale morphological changes with nanosecond temporal resolution [29]. The technique uses short ( $\sim 15$  ns) electron pulses which generate the images timing with respect to laser heating ( $\sim 12$  ns pulse,  $10^{11}$  K/s heating rate). This allows studying temporal evolution of the material and makes the technique ideal for probing the condensed phase reaction process. In experiments with Al/CuO loose particles, DTEM studies showed temporal behavior involving melting and coalescence leading to the formation of a large inter-component interfaces, see Fig. 6. In this figure the images on the left handside were obtained with traditional TEM imaging and show the aggregates appearance before and after laser pulse action. The images to the right were obtained with DTEM technique using single spaced 95 ns electron pulses. It can be seen that the conformations in Al/CuO aggregates occur in the time periods of 100's nanoseconds order. The completion time vary depending on the size of the aggregates, but generally it comprised  $\sim 0.5$ – $5.0$   $\mu$ s that corresponds well to  $\sim 10$   $\mu$ s time period detected in fast nanoenergetic combustion.

The information discussed clearly show how complex the reaction mechanisms of nano energetic materials and how difficult is to explore it in detail. Summarizing information of this section, one may describe the overall process of combustion in a plastic burn tube as follows. After ignition, the heat is transferred through a convective process in direction of fresh material. The high pressure developed in a reaction zone drives hot solid and molten material forward heating the unreacted metal

particles. The hot metal escapes from the particle shell via fracturing that leads to formation of thin layer of liquid metal interacting with oxidizer and to formation of relatively large particles. The gases evolved from the surface of these particles propel the material forward and the reaction propagates fast. After passing the ignition front, the reaction of the rest of metal with  $O_2$  generated via oxide reduction proceeds further accounting for the secondary timescale found for some nanocomposites.

#### 4. Conclusions

When working with every new class of materials the optimal way to optimize and control their reaction behavior is establishing deep understanding of the fundamental physical and chemical processes under study. In the case of Al nanoparticles some severe challenges arise from its specific reactive nature due to presence of a 2–5 nm shell of oxide material which serves as a barrier to reaction. Recent developments in nanochemistry opened a bottom-up approach in the architecture of matter but practical use of advantages of nanoenergetic materials takes comprehensive knowledge of the mechanisms of heat transfer and physicochemical transformations of the materials. Due to great complexity of the problem a lot of work has to be done in order the mechanisms of aluminum nanoenergetic reaction and propagation can be reasonably explained.

In the paper, some peculiar properties of heat transfer between metal nanoparticles and gaseous environment in a shock tube and in a plastic burn tube are discussed. Apparent thermal isolation of nanoparticles in conditions of shock tube interactions with gas molecules is explained on the basis of analysis of energy accommodation process and sticking properties of the metal surface. In particular conditions of hot gas with 1500 K temperature and pressure in reflected shock wave ca. 20 atm the coefficients are equal to 0.0035 for energy accommodation and 0.009 for gas molecules sticking. Obviously, numerical values of those coefficients could be modified in the future while getting deeper insight into reaction mechanism and improving diagnostic technique.

When going to conditions of reaction front propagation in a plastic burn tube, some different ways for heat transfer have to be carefully analyzed. Actually, there are no evidences for unique prevalent process which may ensure propagation of combustion wave with observed high speed through the loose Al/CuO particles mixture. It can be stated that the process comprises 2 stages with very fast ignition, just releasing large amount of heat and

propelling hot gas and condensed material in direction of unreacted mixture followed by relatively slow reaction of remaining metal with evolved from oxide decomposition oxygen.

Common conclusion is that further detailed studying the fundamental properties of nanoenergetic materials and their reaction behavior may open ways for purposed control of those materials combustion behavior and for effective use of nanoenergetics in practical applications. Hopefully, the collected here information will help to choose the objective directions for future theoretical and experimental researches.

#### Acknowledgement

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