Ignition of pyrophoric powders: An entry-level model

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Abstract. Chemically prepared metal nanopowders are normally pyrophoric, i.e. are liable to ignite spontaneously on exposure to air because of high reactivity and developed specific surface. On the other side, reliable theoretical models for spontaneous self-ignition of fine dispersed powders at room temperature have not been suggested so far. A deeper insight into the mechanism of the phenomenon would shed new light on the critical conditions for self-inflammation and thus would provide some clues for optimization of the passivation of fine dispersed powders. In this work, we formulated and analyzed an entry-level model for ignition of pyrophoric powders. Analysis of such a model in terms of the ignition theory gave the following results. Depending on the width of the reaction zone, the ignition may get started in either one or two stages. The duration of each stage was evaluated by using the approximate methods of combustion theory. The parametric limits for the model applicability were derived and the influence of sample length on the ignition process was explored as well.

1. Introduction

The ignition of metallic nanoparticles pressed and backed in vacuum is a very interesting problem for investigators [1, 2], because self-inflammation of such powders in oxidation media can occur (for their high reactivity and developed specific surface) at the relatively low combustion temperatures and even at room conditions [2]. Traditionally for the porous samples inflammation it is conventional to assume that the reaction rate of gaseous oxidant with a material is limited by its diffusion through the condensed product layer for the low values of the diffusion coefficients [3–5], being more less than the temperature conductivity of the material. This assumption allows neglecting temperature distribution over the sample and considering only a single-temperature model. Sometimes it is also proposed, that the oxidizer diffusion rate in gaseous phase is sufficiently larger, than its diffusion rate through the oxide layer on the particle surface. In the case it can be proposed that the oxidizer concentration into the sample pores equals to the concentration in an environment and this approach allows using analysis the results, obtained in the single particles inflammation studies [3] for the porous samples ignition.

These assumptions about the porous samples inflammation often are not satisfied, as is seen from [6], where the inflammation of samples (pressed from zirconium and titanium powders) in air or oxygen after a preliminary thermal-vacuum treatment (PTVT) was investigated. The studies showed that for these samples an inflammation depends on the PTVT treatment temperature and can occur at low temperatures, which in models, premising some interaction through the product layer, seems impossible. The experiments demonstrated a strong dependence of the self-inflammation temperature on oxygen content and concentration, the PTVT treatment temperature, the tablets porosity after PTVT, etc. It follows from these
experiments that for the samples after PTVT the inflammation process limiting process stage is a gaseous reagent supply into the sample by diffusion from external medium. Such situations appear to be applicable for pyrophoric powders, where the filling (charge) inflammation occurs even at room temperature [2]. Authors [6] consider, that this fact is connected with the initial protective oxide film dissolution under PTVT, that sharply increases the samples reactivity. Based on the results and the private data of one author of this work, who had observed the samples of iron nanoparticles (produced by a chemical-metallurgy method) inflammation at room temperature, we can formulate a certain simplified model of a porous sample inflammation in the oxidative environment.

2. Statement of the problem

It is supposed in this model that there is a semi-infinite plane layer of some porous condensed substance, being able to contact and react with an oxidizer in the ambient gas, having the same initial temperature \( T_0 \). It is supposed also, that this porous substance reaction with oxidizer is limited by a diffusion oxidizer supply from the outer media and the interaction products are condensed. Moreover, it is supposed, that the temperatures of porous media and gas in pores are the same (a single-temperature model). For a model generalization the diffusion into such massive layer of the porous condensed substance will be described by an effective diffusion coefficient \( D_{ef} \), defined in such a manner, that the diffusion equation in volume porous materials takes usual form [7]. Moreover, we consider that heat removal from an active zone (i.e. zone with the oxidizer) is carried out due to the heat conduction into the inert part of the sample, which allows neglecting the heat losses into ambient medium and we do not account for the burned-out porous substance during the inflammation. This supposition is based on a high exothermicity of the metal reactions with nitrogen and oxygen. For example, in [8] was shown, that for zirconium burning in nitrogen the formation of solid solution is sufficient \( \theta \) (with low nitrogen content in metal) for both inflammation and burning processes. A mathematical model, describing this process (in dimensionless variables, generally used in combustion theory) has the form:

\[
\frac{\partial \theta}{\partial \tau} = \frac{\partial^2 \theta}{\partial \xi^2} + (1 - \eta)^n \exp \left( \frac{\theta}{1 + \beta \theta} \right),
\]

(1)

\[
\frac{\partial \eta}{\partial \tau} = L_e \frac{\partial^2 \eta}{\partial \xi^2} + \gamma (1 - \eta)^n \exp \left( \frac{\theta}{1 + \beta \theta} \right)
\]

(2)

with initial and boundary conditions:

\[
\tau = 0: \quad \theta = 0, \quad \eta = 0;
\]

(3)

\[
\tau > 0: \quad \frac{d\theta}{d\xi} = 0; \quad \eta = 0; \quad |\xi| \to \infty: \quad \frac{\partial \theta}{\partial \xi} = \frac{\partial \eta}{\partial \xi} = 0.
\]

(4)

In line with [7], for a transition to the dimensionless variables and parameters we have used the following scaling operations and values:

\[
t_* = \frac{c_e R T_0^2}{E Q \rho_c \rho_g a_0^3 k_0} \exp \left( \frac{E}{R T_0} \right), \quad x_* = \sqrt{t_* \rho_c c_e}/\sqrt{\lambda t_* c_e \rho_c}
\]

\[
\theta = \frac{E}{RT_0^2} (T - T_0), \quad \tau = \frac{t}{t_*}, \quad \xi = \frac{x}{x_*},
\]

\[
\eta = a_0 - a/a_0, \quad \beta = \frac{RT_0}{E}, \quad \gamma = \frac{c_e R T_0^2}{E Q \rho_c \rho_g a_0},
\]
\[
F_k = \frac{c_c \rho_c l_{chem}}{\lambda_c t_*}, \quad a_c = \frac{\lambda_c}{c_c \rho_c}, \quad Le = \frac{D_{ef}}{a_c}
\]

Here \( a_0 \), \( a \) are the initial and current concentrations of the gaseous oxidizer; \( Q \)—the heat effect of the heterogeneous reactions, related to a mass unit of oxidizer; \( n \)—heterogeneous reaction order for oxidizer; \( c_c, \rho_c \)—heat capacitance and density of the condensed phase; \( \rho_g \)—the gas phase density; \( \lambda_c, a_c \)—the coefficients of heat and temperature conductivity of the condensed phase; \( D_{ef} \)—an above given oxidizer effective diffusion coefficient; \( t_{ch} = t_* \)—a characteristic time of the chemical reaction; \( x_* \)—a characteristic length; \( E \) and \( k_0 \)—activation energy and pre-exponential factor of the heterogeneous reaction, related to a unite volume of the porous medium; \( l_{chem} \)—the reaction penetration depth into the porous body (its value will be defined below); \( R \)—the universal gas constant; \( \theta \)—a dimensionless temperature; \( \xi, \tau \)—the dimensionless coordinate and time; \( \eta \)—the oxidizer transformation depth; \( F_k \)—Frank–Kamenetsky criterion; \( Le \)—an analogue of Lewis parameter for oxidizer; \( \beta, \gamma \)—small parameters in the combustion theory.

### 3. Main results

From [7] it is known, that the reaction penetration depth \( L_{chem} \) into the porous body equals (within precision to unit):

\[
L_{chem} = \sqrt{\frac{Le}{\gamma(1 - \eta_{\text{average}}^n(\xi=0))}} \approx \sqrt{\frac{Le}{\gamma}}.
\]  \hspace{1cm} (5)

As follows from [5] the size of the chemical reaction zone (in dimensionless variables) depends on the criterion \( Le \) and a dimensionless reaction thermal effect \( 1/\gamma \). In dimensions, this relation has the form:

\[
l_{chem} = \sqrt{\frac{\frac{D_{ef}}{k_0 a_0^n} \exp(-E/RT_0)^\gamma}{\gamma}},
\]  \hspace{1cm} (6)

i.e. the real value of the reaction penetration depth \( l_{chem} \) into the porous body is defined by the gaseous oxidizer concentration \( a_0 \), an oxidizer effective diffusion coefficient \( D_{ef} \) in the porous body, an effective reaction rate \( k_0 \) and the activation energy of heterogeneous reaction (or the oxidizer dissolution reaction in the condensed phase). This value exponentially depends on the initial temperature \( T_0 \) of the sample.

After defining the dimensions of the sample area, where the chemical reaction occurs, for the further analysis of an ignition process it is sufficient to consider a thermal balance of a chemical reaction region. Let’s suppose, that in the reaction zone (i.e. for values \( 0 \leq \xi \leq L_{chem} \)) the temperature changes are low and we can consider \( \langle \theta(\xi) \rangle \approx \theta \). The losses into those sample regions, where the reaction is missing, can be approximately considered proportional to the temperature gradient between an active reactions zone and very far of it (i.e. to the \( \theta \) value). This temperature fall takes place at the distance equal to (at first approximation) \( \sqrt{\tau} \) and the heat flow from the active zone is \( \theta / \sqrt{\tau} \). In accordance to all these approximations, the thermal balance equation for the chemically active zone (for the first order by oxidizer) can be written as:

\[
L_{chem} \frac{d\theta}{d\tau} = L_{chem}(1 - \eta_{\text{average}}) e^\theta - \frac{\theta}{\sqrt{\tau}},
\]  \hspace{1cm} (7)

where \( \eta_{\text{average}} \) is a mean value of the degree of oxidizer transformation in the chemical reaction zone. Dividing the equation (7) on \( L_{chem} \) we have:

\[
\frac{d\theta}{d\tau} = (1 - \eta_{\text{average}}) e^\theta - \frac{\theta}{L_{chem} \sqrt{\tau}},
\]  \hspace{1cm} (8)
By its physical sense the $L^2_{\text{chem}}$ is a relation of the time of the thermal relaxation of the active region ($L^2_{\text{chem}}/a_c$) to adiabatic induction period $t_*$ (for the active region this value is an analogue of Frank–Kamenetsky criterion).

For the induction period a power of the chemical thermal source can be approximately taken as constant and equals to the reaction rate at the initial temperature and mean oxidizer concentration for the active zone (i.e. its value is 1/2):

$$ (1 - \eta_{\text{average}}) \exp \left( \frac{\theta}{1 + \beta \theta} \right) \approx \left( \frac{1}{2} \right)^n \times 1. \quad (9) $$

In this approximation, the induction period is the time, during which the substance in the active zone can be heated on a characteristic interval. This approach is based on the well-known fact: an adiabatic induction period equals the heating time of the substance on a characteristic interval at the initial heat release [9]. This approach allows creating an approximately analytic method to calculate the critical conditions of a spot thermal explosion 10.

Thus for approximated calculation of the porous sample inflammation, we have the equation:

$$ \frac{d\theta}{d\tau} = \left( \frac{1}{2} \right) - \frac{\theta}{L_{\text{chem}} \sqrt{\tau}}; \quad \tau = 0, \quad \theta = 0. \quad (10) $$

From physical considerations, it is clear that a total inflammation process can be divided to two stages. At first stage the heat losses into a sample inert part grow (due to the temperature rise), after which there begins a quasi-stationary period of heating up of an active zone, when the heat release rate is almost equal to the heat release rate. We will analyze the following inflammation process, using by the example the first order reaction (for zero order reaction $n = 0$ below are given only final formulas). For the losses we will consider, that at the inflammation first stage all conditions are near to the adiabatic ones. For the first order reaction, we have equations:

$$ \frac{d\theta}{d\tau} = \left( \frac{1}{2} \right); \quad \tau = 0, \quad \theta = 0. \quad (11) $$

And in this approximation the temperature dependence on time is:

$$ \theta = \frac{1}{2} \tau. \quad (12) $$

Substituting (12) in (10) we determine a time $\tau_1$, when a rate of heat release from active zone becomes equal to a heat release rate:

$$ \tau_1 = L^2_{\text{chem}} = F_k. \quad (13) $$

The heat release rate at this quasi-stationary period of the active zone heating up almost equals to the rate of the heat disposal and thus the temperature rise in this active zone is connected only with decrease in the heat release due to the increase in heated up layer size in the sample inert zone. For the temperature of the heated up sample region, we have equation:

$$ \frac{1}{2} \tau - \frac{\theta}{L_{\text{chem}} \sqrt{\tau}} = 0 \quad (14) $$

and from the $\theta = 1$ we have the time of the active part inflammation:

$$ \tau_{\text{ind}} = \frac{4}{L^2_{\text{chem}}} = \frac{4}{F_k}. \quad (15) $$
which is inversely proportional to, i.e.

$$\tau_{\text{infl}} = \frac{4}{Le^\gamma}. \quad (16)$$

Therefore at $F_k \geq 1$ (for zero-order reaction) at $F_k \geq 2$ (for the first order reaction) only the first stage is realized, i.e. the heating up value $1$ is achieved even at this stage. The inflammation time is near to $1$ or $2$ is achieved even at this stage, i.e. to the adiabatic induction period for the given oxidation regime.

Another important result follows from the expression for an active zone length $L_{\text{chem}}$:

$$L_{\text{chem}}^2 = F_k = \frac{Le}{\gamma} = \frac{D_{\text{ef}} c_c R T_0^2 \rho_c}{a_e Q E a_0 \rho_g}. \quad (17)$$

The value of $F_k$ turns to be a main parameter of the consideration and it doesn't depend on the chemical reaction rate at some initial ignition temperature as always in traditional problem of the thermal inflammation [11]. It means that by changing of the sample ignition temperature we cant sufficiently affect the Fk criterion value, i.e. to influence on its character (one-stage or two-stage). The situation is related to the fact, that the region size $L_{\text{chem}}$ (used for the Fk criterion calculation) is inversely proportional to the square root of the chemical reaction rate at initial temperature, and thus the main characteristic, determining the Fk criterion value is the value of the effective diffusion coefficient $D_{\text{ef}}$. Notice that in the dimension variables the ignition time is exponentially depending on the sample initial temperature. The assumption about a porous infinite thickness of the porous material layer, that was made at the problem statement, can be broken if the term $l_{\text{chem}}$, is changing, depending on the effective diffusion coefficient, oxidizer concentration in the ambient gas and (exponentially) on the sample initial temperature. This supposition can be used if the porous material layer thickness $L_{\text{sample}}$ is markedly larger than $L_{\text{chem}}$. In opposite limiting case (when the porous material layer thickness is less than $L_{\text{chem}}$) the chemical reaction occurs in the porous body total volume, so in this situation an inner heat drain is missing and in the context of considered model an inflammation can take place at any values of the governing parameters. For the critical conditions consideration it is necessary to carry out a correct account for the heat release into an environment.

The most interesting situation arises when the sample is greater than $L_{\text{chem}}$, but it can not be assumed to be infinitely great one, i.e. the heating up zone for the ignition time (being calculated for an infinite sample) becomes greater than size of the sample inert part. It means that during an ignition delay time the heat exchange conditions at the opposite end of the porous medium can become apparent.

If this opposite end of the porous medium $\xi = L_{\text{sample}}$ is thermally isolated, i.e. $\frac{dT}{d\xi} |_{\xi=H} = 0$, the decrease of the sample size in this parameters region will lead to increase in the ignition time delay, because the heat losses from the active zone to the sample inert part heating decrease.

On the other hand, if this opposite end of the porous medium is supported at a constant temperature, the sample size $L_{\text{sample}}$ decrease in this parameters region will lead to the ignition time growth, because the heat losses from the active zone to the sample inert part heating increase. When during the inflammation the size of the heated up zone becomes equal to the size of the inert part of the sample a further heat flow decrease from the active zone will cease and this flow will grow with the increase in active zone temperature. Thus there an equilibrium between the heat release and heat removal rates can be established. If this equilibrium will be established before the active zone will be heated up to the value $\theta = 1$, an inflammation doesn't take place, in opposite case the inflammation occurs, but the inflammation time is greater than the time, calculated by the formulas (15)–(16). The most urgent is accounting for the sample finite dimensions for the little values of parameter $F_k$, because the effective diffusion coefficient
$D_{ef}$ value has a strong influence on the inflammation regimes and modes. The $D_{ef}$ value can change in wide range (with the porous medium structure changes) and therefore we will discuss its relation with a true oxidizer diffusion coefficient $D$ and its dependencies on the porous body structure parameters. From [7] we have for the simplest porous body model the following connection between $D_{ef}$ and $D$:

$$D_{ef} = D \frac{N \pi h^2}{4 \chi}, \quad (18)$$

where $N$ is a pore number per surface unit of area of the sample, $h$ is a pores mean diameter and $\chi$ is a twisting coefficient (equal to a mean distance along a pore and corresponding to a unite length in direction, perpendicular to the sample surface). In the porous body conventional models $\frac{N \pi h^2}{4 \chi}$ is a body porosity $\Pi$ and thus equation for can be re-written as:

$$D_{ef} = D \frac{\Pi}{\chi}. \quad (19)$$

The effective rate constant $k_0$ can be expressed through the heterogeneous reaction rate constant $k$, related to a unique surface area by equation (7): $k_0 = \chi N \pi h k$.

If we suppose that the pore sizes are correlated with the size of particles, constituting the porous body, then for the very little particles (e.g. for the nanosize particles) the pore diameter can be lesser than the molecule free path length (so called Knudsen region) and at such situation the effective diffusion coefficient is proportional to the pore diameter cube and is equal to the material gas permeability coefficient [7]:

$$D_{ef} = 1.27 \times 10^3 \sqrt{\frac{T}{M}} \frac{N h^3}{\chi}, \quad (20)$$

where $T$ is temperature and $M$ is oxidizer molecular weight.

4. Conclusions
- A model of the porous sample inflammation is proposed, based on an assumption of a limiting role of the oxidizer diffusion into the ignition mechanism.
- It is shown that the inflammation process can have two-stage character.
- The duration of the stages is determined by combustion theory methods.
- The applicability limits of the semi-infinite body model are determined.
- The role of the sample finite size finiteness in the inflammation process is analyzed.

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