# Thermal Theory of Metal Particle Ignition

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A set of equations of metal particles, oxidation kinetics, and thermal balance is considered. Critical conditions for ignition are investigated. It is shown that, in the general case, ignition is not necessarily connected with melting of oxide film and can occur as a result of self-accelerating temperature increase by the thermal explosion mechanism. It is found when the Friedman-Macek theory is valid. Ignition of the titanium-nitrogen, aluminum-oxygen, and tantalum-oxygen systems has been studied by heating a metallic wire with electrical current of constant power in a gas flow. The experiments permit checking the conclusions of the theory.

## I. Introduction

ACCORDING to the ideas developed by Friedman and Macek, as well as by Mellor and Glassman,[1,2] ignition of metal particles of aluminum type in gaseous oxidant occurs when an initial oxide film loses its protective properties, which usually takes place on melting. Heating of the particle up to the melting temperature of the oxide film $T_*$ is realized mainly at the cost of heat supplied from the outer source (hot gas) and partly as a result of self-heating from an oxidation reaction. Friedman and Macek have developed the theory of self-heating using the assumption that the rate of heat release depends on the temperature only. It has been shown that critical ignition temperature $T_{o\,crit}$ is close to $T_*$, and the dependence of the $T_* - T_{o\,crit}$ difference on the parameters was calculated.

In the studies of the present author carried out together with B. I. Khaikin, V. N. Bloshenko, Yu. M. Grigorjev, Yu. A. Gal'chenko, A. P. Aldushin, and S. L. Kharatyan,[3-8] a different and more general viewpoint was developed regarding the mechanism of metal ignition. The mathematical theory of the process was created and the theoretical conclusions were verified experimentally. This paper presents some results of these studies.

## II. Statement of the Problem

A metal particle of a definite form (for simplicity, symmetrical) is in a gaseous oxidant, resting or moving. The initial particle temperature is either much lower than the gas temperature or equal to it. In the first case, a "cold" particle is introduced into the heated gas; in the second case the particle and the gas are heated simultaneously during times much shorter than the duration of the process under consideration. The first case usually takes place in the laboratory experimental conditions, while the second occurs under the real conditions for combustion of metallized propellants. The gas temperature and pressure do not change with time.

The following scheme of the process is considered. Upon chemical interaction of a metal with an oxidant there forms a film of a solid product which separates reagents. The reaction rate is determined by the processes of reagent transfer through the film and depends on the properties and thickness of the film. Since the processes of transfer are activated in solids, the reaction rate greatly increases with increasing temperature.

Heat release on metal oxidation, which depends on the thermal effect and reaction rate, may lead to fast self-heating of the metal particles at high temperatures. Metal ignition as well as the thermal explosion of explosive systems[9-12] occurs as the result of thermal self-acceleration of the chemical reaction whose conditions for appearance depend on the relation between the rates of heat supply and heat removal. In some cases, the heat released at oxidation of particles has time to be removed into the surroundings, ignition does not take place, and after short self-heating the particle assumes the temperature of the ambient gas. In other cases, heat release in the particle leads to self-acceleration of the oxidation reaction and to related progressive growth of the particle temperature which culminates in ignition.

For the general case, the critical conditions for ignition are not related to $T_*$ and are characterized by break of thermal equilibrium between the particle and environments. Melting of the oxide film leading to intensification of the transfer processes and sharp increase in the rate of heat release, is usually a sufficient (but not necessary) condition for ignition. (The role of $T_*$ will be considered in Sec. V.)

In the mathematical description of the process the usual assumptions were taken into account of the absence of temperature distribution in the particle, of the quasi-stationary character of heat- and mass-transfer processes in the gas, and of the constancy in particle sizes and physical properties during the process. The last assumption is possible because small degrees of substance conversion during the induction period are always characteristic for the ignition processes.

The model under consideration is shown in Fig. 1 and can be described by the following set of equations. The equation of thermal balance of the particle is

$$cm \times \frac{dT}{dt} = Qm\frac{d\eta}{dt} - \alpha S(T - T_o) - \varepsilon\sigma S(T^4 - T_o^4) \qquad (1)$$

where $cm(dT/dt)$ is the rate of heat buildup, $Qm(d\eta/dt)$ is the oxidation heat, $\alpha S(T - T_o)$ is heat lost by conduction or convection, and $\varepsilon\sigma S(T^4 - T_o^4)$ is heat lost by radiation.

The equation of oxidation kinetics is

$$d\eta/dt = F(\eta, T) \qquad (2)$$

where the initial conditions are $t = 0$, $\eta = 0$, and $T = T_i$. $T$ is the temperature of the particle; $T_i$, the initial temperature of the particle; $T_o$, the gas temperature; $\eta = \Delta m(t)/m$, the degree (depth) of metal particle conversion into the product; $\Delta m(t)$, the quantity of metal reacted during time $t$; $m$ and $S$ are particle mass and surface, respectively; $Q$ is the heat of reaction per gram of metal; $\alpha$, the heat transfer coefficient; $\varepsilon$, the degree of blackness; and $\sigma$, the Stefan-Boltzmann constant.

The $\alpha$ coefficient can be found from the expressions obtained in the theory of heat transfer. There are formulas for various situations which in the general case can be represented as

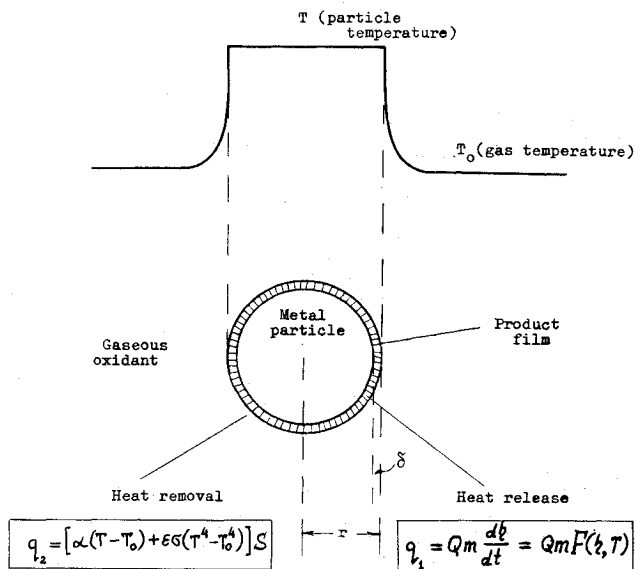$$\alpha = (\lambda/r)\Phi(Ra, Re, Pr)$$

**Fig. 1 Graphical interpretation of the model for metal particle ignition.**

where $r$ is characteristic particle size; $\lambda$, the thermal conductivity coefficient; and $Ra$, $Re$, $Pr$ are the Rayleigh, Reynolds, and Prandtl numbers, respectively. In the simplest case (a spherical particle of radius $r$ in the resting gas), $\Phi \equiv 1$.

To state the problem correctly, the shape of function $F(\eta, T)$ is to be determined as it is done in the theory of thermal explosion. The literature contains many various forms of representing the kinetic equations of metal oxidation.[13-15] A kinetic equation is usually expressed as a relation between the rate of growth of oxide film thickness, on the one hand, and film thickness, oxidant temperature, and concentration at the surface, on the other. Such a relation can be readily presented in convenient form, Eq. (2), taking into account that for the case of small degrees of conversion which is of interest to us, $\delta = \delta_o + \eta f$; $f = vm/S\rho_o$, where $\delta$ is the oxide film thickness by moment $t$; $\delta_o$ the initial thickness of the oxide film; $\rho_o$ the oxide density; and $v$ the weight stoichiometric coefficient of the reaction product for metal.

Various empirical and theoretical forms of kinetic equations exist which describe one or another oxidation regime. In most cases they can be presented in the following form: $d\eta/dt = K(T)C_o{}^p\Psi(\eta)$. Here $K(T)$ is the reaction rate constant of usual Arrhenius type, $K(T) = K_o \exp(-E/RT)$. $C_o$ is the concentration of oxidant at the particle surface (taking into account that a general rate of the process at ignition is limited by the reaction rate, and that the concentrations at the surface and far from it may be considered to be equal); $p$ is the reaction order for oxidant concentration; and $\Psi(\eta)$, the kinetic function.

This paper is concerned with two radically different forms of $\Psi(\eta)$ which are of the most significance for the general theory of metal ignition:

1) $\Psi(\eta) = (\eta_o + \eta)^{-1}$: parabolic law. This law takes place when the process is defined by diffusion of one of (or both) the reagents through the oxide film at the diffusion coefficient which does not depend on the film thickness. The dimensionless value $\eta_o$, which limits the initial reaction rate, takes into account the existence of the initial oxide film $\delta_o$ and defines its diffusion resistance. It can be shown that $\eta_o = \delta_*/f$ where $\delta_* = \mathscr{D}/\mathscr{D}_o\delta_o$; and $\mathscr{D}_o$ and $\mathscr{D}$ are coefficients of diffusion of the transferred reagents through initial and grown films, respectively. If the chemical nature and structure of initial and growing films are the same, then $\mathscr{D}_o = \mathscr{D}$ and $\delta_* = \delta_o$.

2) $\Psi(\eta) = \exp(-\eta/\eta_o)$ exponential law. This law according to the ideas of Evans[15] takes place at fast growth of the film when the appearing mechanical imperfections in the form of smallest bubbles and cracks impede the diffusion and lead to a severe decrease in the rate as the film thickness grows.

Here the parameter $\delta_*$ has a meaning other than in the parabolic law and characterizes the reaction deceleration by a growing product layer. The value $K(T)$ expresses the properties of the initial film.

The oxidation laws have not been previously treated in the ignition theory. Their distinguishing feature is that the reaction rate may depend very strongly on the degree of conversion and the retarding effect of reactant consumption has to be a much more serious competitor to the thermal self-acceleration of the reaction than usually.

For convenience, the kinetic laws will be written as

$$d\eta/dt = W_i(T) \times \phi(\eta)$$

where $W_i$ is initial reaction rate. For the parabolic law

$$W_i(T) = [K(T)/\eta_o]C_o{}^p; \quad \phi(\eta) = (1+\eta/\eta_o)^{-1}$$

For the exponential law

$$W_i(T) = K(T) \times C_o{}^p; \quad \phi(\eta) = \Psi(\eta) = \exp(-\eta/\eta_o)$$

## III. Dimensionless Set of Equations

According to the ideas of Frank-Kamenetsky,[10] we shall represent Eqs. (1) and (2) in the following dimensionless form

$$d\theta/d\tau = e^{\theta/(1+\beta\theta)} \times \phi(\eta) - \theta/\partial e - (x/\partial e)[(1+\beta\theta)^4 - 1] \quad (3)$$

$$d\eta/d\tau = \gamma \times e^{\theta/(1+\beta\theta)} \times \phi(\eta) \quad (4)$$

$$\tau = 0, \quad \eta = 0, \quad \theta = -\theta i$$

Dimensionless variables
self-heating

$$\theta = (E/RT_o{}^2)(T - T_o)$$

time $\quad\quad \tau = Q/C \times (E/RT_o{}^2)W_i(T_o)t$

Dimensionless parameters:

$$\partial e = [(Qm/\alpha S) \times (E/RT_o{}^2)] W_i(T_o); \quad x = \varepsilon\sigma ET_o{}^2/R\alpha$$

$$\alpha = (C/Q)(RT_o{}^2/E), \quad \beta = RT_o/E, \quad \theta i = (E/RT_o{}^2)(T_o - T_i)$$

All these dimensionless parameters as well as their role are known from the thermal explosion theory. The Semenov parameter $\partial e$ which represents a relation between scales of heat release and heat removal rates is the main among them. Parameters $\beta$ and $\gamma$ in the metal ignition theory, as well as in the general ignition theory, are small ($\beta = 10^{-2} - 10^{-1}$; $\gamma = 10^{-3} - 10^{-1}$). However parameter $\gamma$ plays a more significant role than usually because of the peculiarity of kinetic oxidation laws. Parameter $\theta_i$ mainly defines the general ignition delay time and slightly affects the critical conditions. Parameter $x$ represents a relation between scales of radiation and convective (conductive) losses. At $x \ll 1$ which takes place for small particles, the role of radiation is slightly expressed.

For simplicity, we shall later consider the case where $\beta \to 0$; $\theta_i = 0$; and $x = 0$, which expresses all the main features of the process, and restrict ourselves to the analysis of the critical conditions for ignition. The role of parameters $\theta_i$ and $x$ is quantitatively analyzed in Refs. 3 and 6, where corrections for the particle warm-up and radiation to the critical condition are obtained.

As can be seen from Eqs. (2–4), the greatest self-heating occurs under the adiabatic regime at full conversion of the particle ($\eta = 1$): $\theta_{ad} = \gamma^{-1}$. As we are interested in small degrees ($\eta \ll 1$), it is convenient to introduce a new variable $z = \eta/\eta_o$, and to write the set of equations in the following form

$$d\theta/d\tau = e^\theta \times f(z) - \theta/\partial e; \quad dz/d\tau = \omega \times e^\theta \times f(z)$$

$$\tau = 0, \quad z = 0, \quad \theta_i = 0$$

Here

$$f(z) = \begin{cases} (1+z)^{-1} & \text{the parabolic law} \\ e^{-z} & \text{the exponential law} \end{cases}$$

$$\omega = \gamma/\eta_o \quad\quad\quad \text{a new parameter}$$

## IV. Main Results of the Thermal Theory

The ultimate case of weak kinetic deceleration will be first considered. It takes place at $\eta_o \gg \gamma(\omega \ll 1)$. In this case $\eta_{\text{ind}} \ll \eta_o$,
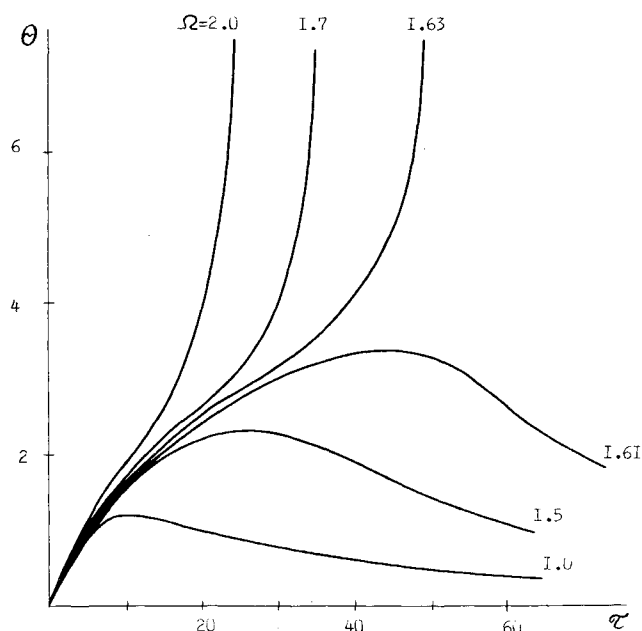
**Fig. 2    Time dependence of heat-up curves at various values of parameter $\Omega$.**



**Fig. 4    Dependence of maximum particle heat-up $\theta m$ on parameter $\Omega$.**

$z_{\text{ind}} \ll 1$ and $f(z) \equiv 1$ for both the laws under consideration (here $\eta_{\text{ind}}$ is degree of conversion attained at the induction period). In this ultimate case interaction between metal and gas is described by the model of a zero order reaction, and the ignition characteristic can be calculated from the solution of the equations[9,16,17]

$$d\theta/d\tau = e^\theta - \theta/\partial e$$

$$\tau = 0, \quad \theta_i = 0$$

As is known from the Semenov theory,[9] the critical condition for ignition is of the form $\partial e_{\text{crit}} = e^{-1}$. At $\partial e < e^{-1}$ a small self-heating of the particle is maintained ($\theta_{st} < 1$); at $\partial e > e^{-1}$ the self-heating progressively increases and leads to ignition. In the general case the picture of ignition is different for the parabolic and exponential laws.
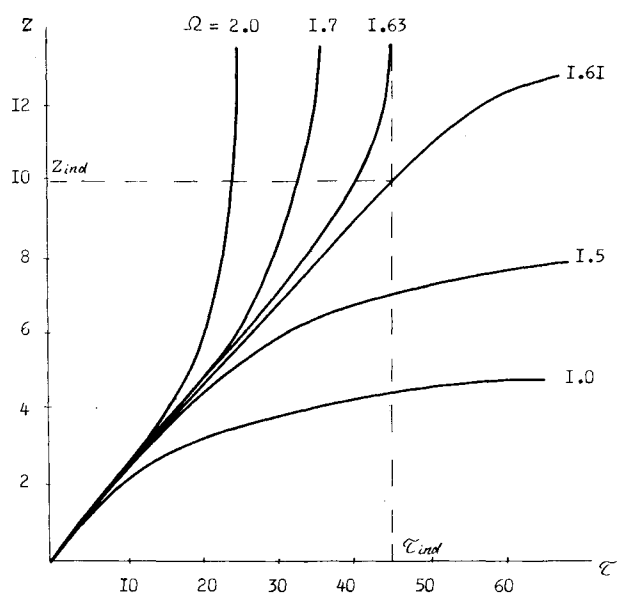


**Fig. 3    Time dependence of conversion degree curves at various values of parameter $\Omega$.**
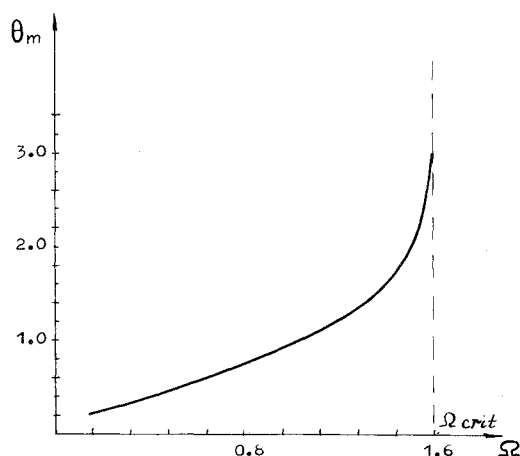
For the parabolic law, there exist an opposite ultimate case $\eta_o \ll \gamma(\omega \gg 1)$. In this case $\eta_{\text{ind}} \gg \eta_o$, $z_{\text{ind}} \gg 1$ and one may assume that $f(z) = (1+z)^{-1} \approx z^{-1}$.

By introducing new values

$$y = z/\omega, \quad \tau' = \tau/\omega, \quad \Omega = \partial e/\omega$$

we obtain

$$d\theta/d\tau' = (1/y)e^\theta - \theta/\Omega$$

$$dy/d\tau' = (1/y)e^\theta$$

$$\tau' = 0, \quad y = 0, \quad \theta_i = 0$$

Only one parameter $\Omega$ enters into this set.

Figures 2 and 3 give curves $\theta = \theta(\tau,\Omega)$ and $z = z(\tau,\Omega)$ obtained by numerical integration of the set (3) to (4) at $\beta = 0.03$; $\theta_i = 0$; $\omega = 10$; $\Omega = \Omega_i$; $x = 0$.

It can be seen from Fig. 2 that at $\Omega$ lower than $\Omega_{\text{crit}}$, the curves of self-heating have a maximum with a small value of $\theta_{\text{max}}$, while at $\Omega > \Omega_{\text{crit}}$ the self-heating of the particle progressively increases with time; fast growth of $\theta$ is considered as ignition. Value $\Omega_{\text{crit}}$ is approximately found from the condition

$$\left. \frac{d\theta_{\text{max}}}{d\Omega} \right|_{\Omega \to \Omega_{\text{crit}}} \to \infty \qquad \text{(Fig. 4)}$$

Thus, the critical condition for ignition in the ultimate case of great $\omega$ is of the form $\Omega_{\text{crit}} = 1.62$.

Figure 3 shows a method for approximate evaluation of $z_{\text{ind}}$. As can be seen, $z_{\text{ind}} \gg 1$, which corresponds to the ultimate case under consideration. Great values of $z_{\text{ind}}$ imply that an oxide film grows significantly during the induction period.

In the general case of arbitrary $\omega$, the critical condition can be represented by the following interpolation formula

$$\partial e_{\text{crit}} \approx e^{-1} + 1.62\omega \qquad (5)$$

For the logarithmic law the ultimate case of great $\omega$ does not exist. At $0 < \omega < 0.3$ the critical condition is of the form

$$\partial e_{\text{crit}} \approx e^{-1} + 3\omega \qquad (6)$$

(Accuracy of the formula is 10%.)

At $\omega > 0.3$ ignition is degenerated. Dependence of $\theta_{\text{max}}$ on $\partial e$ becomes smooth; value $d\theta_{\text{max}}/d\partial e$ does not reach great values, characteristic of ignition at any $\partial e$ (see Fig. 5).

Particle oxidation proceeding even with significant self-heatings does not lead to ignition under these regimes. Thus, ignition of particle by the thermal explosion mechanism is impossible at great kinetic deceleration of the reaction.

The obtained expressions, Eqs. (5) and (6), permit the critical ignition temperatures to be calculated according to particle size and conditions for heat exchange with gas, oxidant concentration, and kinetic parameters of oxidation. It should be remembered in numerical calculations that $k = k'b^{-1}$, where $k'$ is a constant in the kinetic law expressed in terms of oxide film thickness; $l = 1$ for the exponential law; and $l = 2$ for the
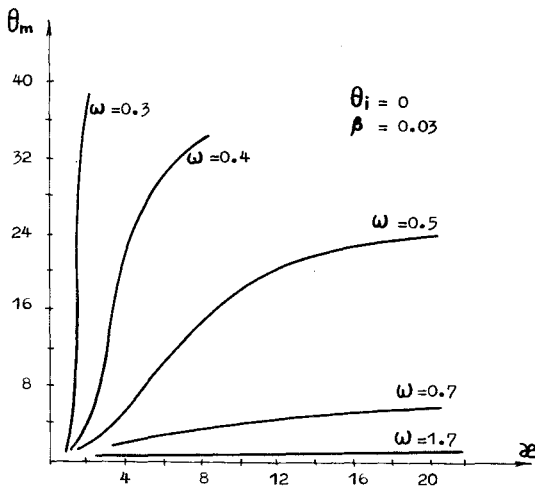
Fig. 5 Dependence of maximum particle heat-up $\theta m$ on parameter $\partial e$ at various values of parameter $\omega$.



Fig. 6 Scheme illustrating different regimes for particle ignition.

parabolic law. As an example, we shall consider a spherical metal particle in the stationary gas. For this case, $\alpha = \lambda/r$ and $f = v(\rho/\rho_0)(r/3)$ (where $\rho$ is metal density).

Neglecting power dependences on temperature in view of the availability of the exponential dependence for both the laws under consideration, the critical conditions may be represented as $r \exp(-E/RT_{o\ crit})/1 + Ar = B$ where $A$ and $B$ are constants independent of particle radius and gas temperature.

From this it follows that the critical ignition temperature first drops as the particle radius grows, and then does not change.[†] For the parabolic law, the region of saturation (the second ultimate case, when the initial state of the film is of no significance) mainly corresponds to the real values of parameters. For the exponential law this region is unattainable since degeneration occurs earlier. Ignition at the exponential law of oxidation may take place only at sufficiently small $r$. Dependence of the critical ignition temperature on oxidant concentration and heat transfer coefficient at $r = $ const is of the form

$$\alpha^{-1}C_o^p \exp(-E/RT_{o\ crit}) = \text{const}.$$

## V. Qualitative Representations of the Generalized Thermal Theory Taking into Account the Phase Transitions in Metal Particle and Oxide Film

So far only the regimes without any phase transitions in the metal particle or oxide film have been considered. Ignition has occurred by the Semenov mechanism due to impossibility of the thermal equilibrium between a reacting particle and environment as a result of progressive thermal self-acceleration of the reaction.

Phase transitions (melting, polymorphic transformations) of metal and oxide can significantly affect the picture of ignition. Of greatest significance is melting of the oxide film, which intensifies the interaction between metal and gas so substantially that it leads to immediate ignition. Such a mechanism has been first described by Friedman and Macek.[1]

It is evident that the generalized thermal ignition theory should take into account the Friedman-Macek mechanism as well. Solution of the problem may be presented as follows. Based on the above equations, the changes in the particle temperature with time are considered, $\theta = \theta(\tau,\ \partial e,\ \omega)$. It is assumed that ignition occurs when the particle temperature becomes equal to the film melting temperature, viz. $\theta(\tau_{ind},$

$\partial e, \omega) = \theta_*$. Then the critical condition can be represented as $\theta_{max}(\partial e, \omega) = \theta_*$.

At $\theta_{max} < \theta_*$ no ignition occurs. Here $\theta_* = (E/RT_o^2)(T_* - T_o)$ is dimensionless melting temperature. If $\theta_*$ is attained by the explosive way, then the ignition characteristics do not depend on $\theta_*$, and the Semenov mechanism of ignition takes place. The ideas of Friedman and Macek[‡] become significant when $T_*$ is achieved smoothly (under the limit of thermal equilibrium or in the degenerated regimes).

It is convenient to represent schematically various regimes of the process (Fig. 6).

As can be seen, the main problem of the generalized theory is determination of the dependence $\partial e_{crit} = \partial e_{crit}(\theta_*, \omega)$. As is apparent from the analysis of the results of numerical calculations, for the parabolic law in the second limiting region this dependence can be represented as

$$\theta_* = 0.69\Omega_{crit} - 0.35 \ln(1 - 0.62\Omega_{crit})$$

In the present paper the regularities of ignition are analyzed for two kinetic laws of interaction between metals and gases. Similarly, other laws may be treated as well. For instance, the laws of the form $\Psi(\eta) = (\eta_o + \eta)^{-n}$ have been investigated.[3]

## VI. Some Results of the Experimental Check of the Theory

In order to check the theory experimentally, an electro-thermographic method was developed based on the known ways of electrical heating of a metallic wire.[18-20] The method permits us 1) to perform the process at constant electrical power on the wire $P$ making use of the power stabilizer[21]; 2) to study preliminarily the heat exchange between the wire and flow of gaseous oxidant; and 3) to measure the wire temperature during the process. Use of cylindrical particles and electrical

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[†] Account of the correction for radiation leads to the conclusion that $T_{o\ crit}$ begins to slightly grow with further increase in $r$.
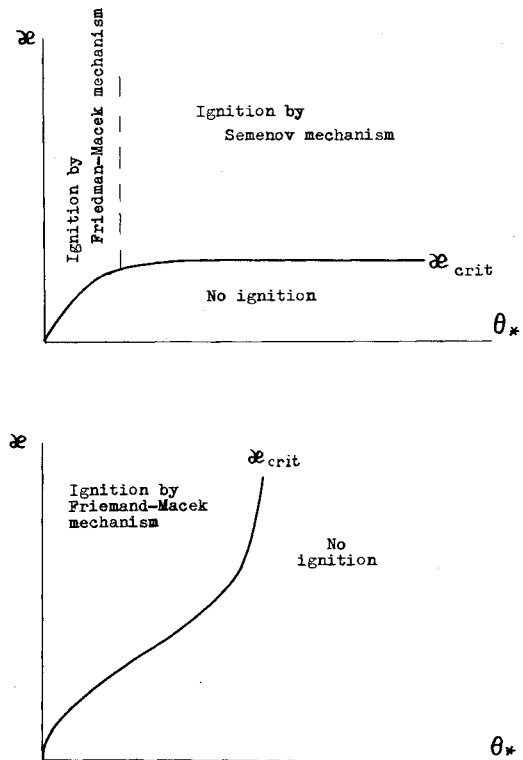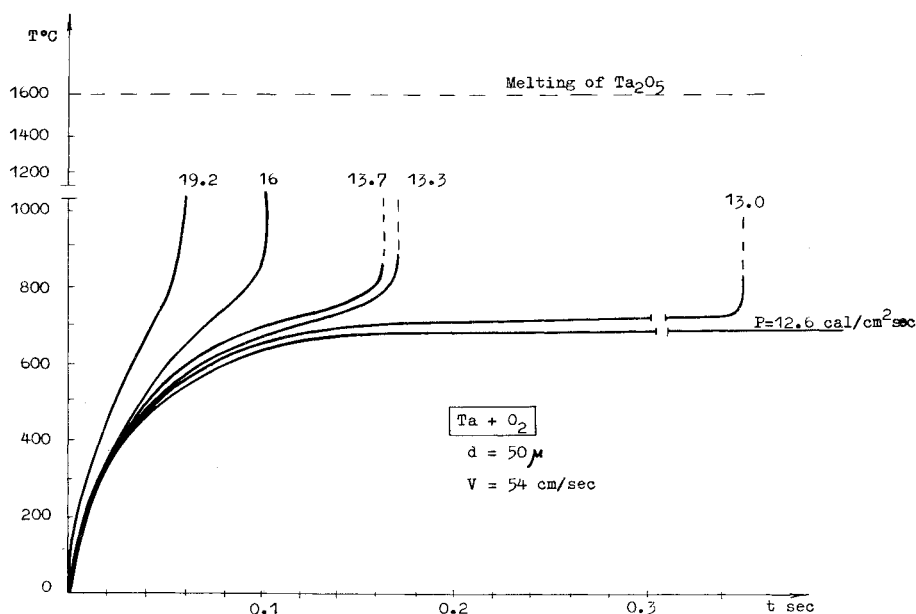
[‡] It should be remembered that the quantitative results of Friedman and Macek are valid only for the linear law of oxidation since they do not take into account the dependence of the reaction rate on the thickness of the oxide film.

Fig. 7 Thermogram of tantalum ignition
in oxygen.

heating not only does not disturb the general character of the results, but even gives possibility of studying the process development during the induction period.

Electrical heating of the wire is equivalent to heating of the gas. The equivalent temperature can be readily calculated from the stationary equation of the thermal balance in the absence of a chemical reaction. A trend of the wire temperature-time curves has been studied in the experiments at varying values of electrical power ($P = 0$ to $150$ cal/cm$^2$ sec), wire diameter ($d = 30$ to $150$ $\mu$), and rate of gaseous oxidant flow at the atmospheric pressure ($V = 0$ to $80$ cm/sec). Based on the analysis of experimental thermograms, the critical values of power, ignition delay periods, and pre-explosion self-heatings have been determined. In some cases, wires hardened just before ignition were metallographically analyzed.

The ignition mechanism of Al in various media ($O_2$, $CO_2$, $O_2 + N_2$) has been studied most comprehensively. The experiments have shown that ignition in $O_2$ and $O_2 + N_2$ can occur depending on conditions both by the Semenov mechanism (the greatest value of $T_* - T_{o\,crit}$ is 400°C) and by the Friedman-Macek mechanism. In $CO_2$ aluminum ignites only by the Friedman-Macek mechanism, the limiting regime being realized

when $T_{o\,crit} = T_*$ and self-heating at $T < T_*$ is completely absent. In the experimental conditions the high-temperature interaction between aluminum and oxygen occurs by the parabolic law (in the second limiting region). Dependence of the critical power on the initial thickness of a specially grown oxide film is not observed at values up to 0.5 $\mu$. At $\alpha =$ const, $P_{crit}$ is slightly dependent on the wire diameter.

Tantalum-oxygen system oxidizes by the linear law. The typical thermogram is shown in Fig. 7. Here one can clearly see a self-accelerating growth of the temperature preceding the ignition. Simplicity of the model makes it possible to determine the kinetic parameters of tantalum oxidation from the experiments on ignition. The calculation schemes are described in papers.[22-24,6] The following parameters of the equation are obtained

$$dQ/dt = k_o'\exp(-E/RT)$$

using the critical conditions $k_o' = 5.8 \cdot 10^3$ cal/cm$^2$ sec, $E = 16.5$ kcal/mole; using the induction periods $k_o' = 6.8 \cdot 10^3$ cal/cm$^2$ sec, $E = 15.6$ kcal/mole.

Of interest are the thermograms of tungsten ignition in oxygen (Fig. 8). It looks as if ignition is defined by the melting

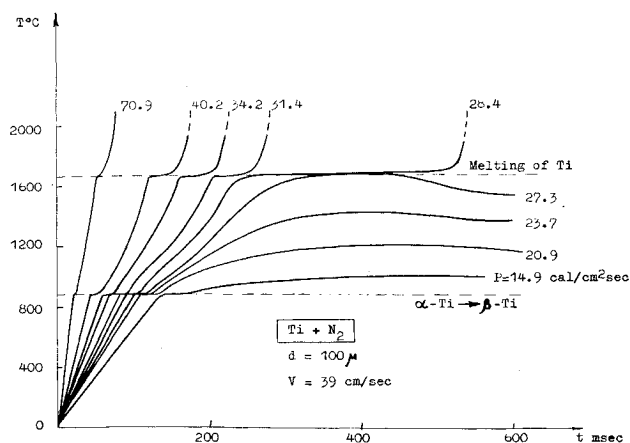

Fig. 8 Thermogram of
tungsten ignition in oxygen.
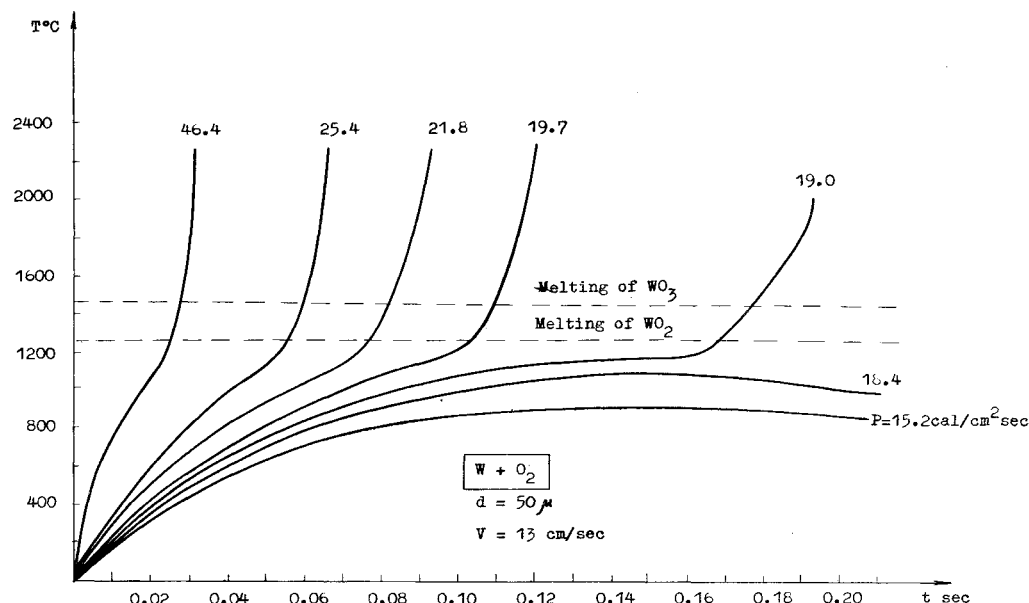
Fig. 9   Thermogram of titanium ignition in nitrogen.

of the film of intermediate product $WO_2$. Ignition of titanium wires in nitrogen is profoundly affected by melting of titanium (Fig. 9), but the latter does not hinder watching of the self-accelerating temperature growth that leads to ignition, and of pre-explosion self-heatings. Figure 10 shows the growth of nitride film thickness at the induction period. Prior to ignition, $\delta$ achieves the values of 3 to 4 $\mu$ at $d = 150 \mu$.

Thus, the experimental studies provide a qualitative support for the main points and conclusions from the thermal theory, viz. 1) the presence of self-accelerating temperature growth and pre-explosion self-heatings (and hence, the reality of the Semenov mechanism); 2) slight dependence of the critical temperature on the particle size and initial film thickness at the parabolic law of oxidation and existence of the second limiting region; 3) considerable growth of the oxide film thickness at the induction period.
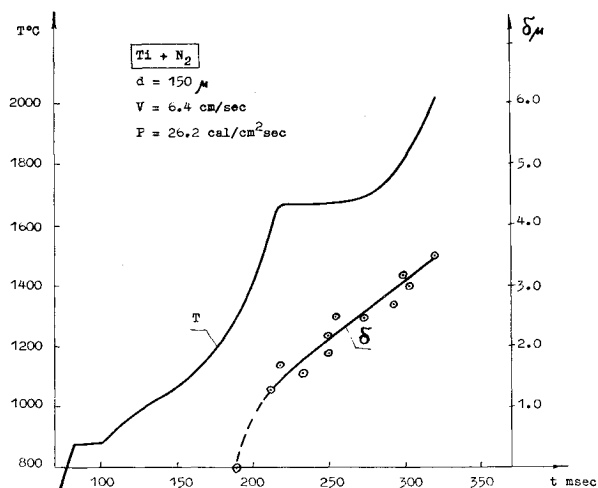
Besides, the experiments have confirmed the conclusion from the generalized thermal theory on the existence of two ignition mechanisms. Rigorous quantitative comparisons are hindered because of the lack of information on the kinetics of high-temperature interaction between metal and gases. The developed theory can be later quantitatively polished and brought up to detailed formulas (both calculation-empirical and analytical). Of interest are experimental studies on ignition of different metal particles to clear up the role of specific factors (melting of metals, presence of intermediate products and others) and creation of efficient methods for studying the kinetics of heat evolution at high-temperature oxidation.

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Fig. 10   Time dependence of nitride film thickness at the induction period of titanium ignition in nitrogen.