

Analytical Model for Size Effect of Activation Energy of Zirconium and Aluminum Particles

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Abstract: A theoretical model for calculating activation energy by ignition temperature of metal particles was proposed. The critical condition of ignition temperature was that the heat generation rate of combustion reaction and the heat loss rate to the surrounding reach a heat balance. The heat loss rate was controlled by the Knudsen number. The heat generation rate of aluminum particle combustion was calculated using the simplest Arrhenius-type model. The heat generation rate of zirconium particle combustion was calculated by diffusion model. And the activation energy corresponding to the ignition temperature of metal particle was obtained by iterative calculation. The results show that the activation energy of aluminum particles and zirconium particles increases with the increase of particle size, which is linear with the logarithm of particle size. In the larger size range from nanometers to micrometers, a single theoretical model is not enough to describe the size effect of activation energy of metal particles. The polynomial model based on data fitting is more universal.

Key words: activation energy; ignition temperature; zirconium; aluminum; nanoparticles; micron particles

The physical and chemical properties of metal particles change significantly compared with bulk metal^[1-5]. The specific surface area is considered to be the key factor of the above changes. The decrease of metal particle size means that particles may easily collect sufficient oxygen to combust and more atoms are located on the surface. Since atoms located on surface have fewer bonds and neighboring atoms, they require less energy to get rid of the solid phase^[6]. Therefore, the decrease of metal particle size improves its activity, which is manifested by the decrease of activation energy.

Assuming that the size effect of the preexponential factor is negligible, the activation energy of metal particle is considered to be directly proportional to its melting temperature. And the ratio of melting temperature of metal particle to melting temperature of bulk metal is approximately equal to the ratio of cohesive energy of metal particle to cohesive energy of bulk metal. A commonly used efficient model deduces the ratio of melting temperature through the bond energy, and then the relationship between activation energy of metal particle and particle size can be obtained^[7,8]. A more general polynomial model is also obtained through the

algebraic transformation^[9]. However, the accuracy of melting temperature calculation is only verified by some experiments and simulation data at nanometer scale. The applicability of the model and the accuracy of activation energy calculation need further study.

The activation energy of metal particles has an important influence on the ignition temperature, which is the key parameter to control the Arrhenius-type combustion kinetic model of metal particles. The relationship between ignition point and particle size of metal particles can be established by the heat balance between heat generation rate of metal combustion reaction and heat loss rate to the surrounding. Based on the principle of heat balance, a theoretical model to calculate the corresponding activation energy from the ignition temperature of metal particles was proposed. Taking zirconium and aluminum as examples, the relationship between the activation energy of combustion reaction and particle size was studied, and the parameter selection and application scope of the relevant theoretical model were discussed.

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1 Establishment

1.1 Activation energy

Assuming that the metal particles are spherical, Shandiz et al^[7,8] believe that the activation energy ratio of metal particle to block metal is approximately equal to the cohesive energy ratio of metal particle to block metal. The size dependent activation energy calculation model is deduced by calculating the cohesive energy of metal particle:

$$\frac{E_p}{E_\infty} = \left[1 - \left(1 - \frac{Z_p}{Z_\infty} \right) \frac{N_s}{N_T} \right] \tag{1}$$

where E_p is the activation energy of metal particles, E_∞ is the activation energy of bulk metal, Z_∞ is considered to be the coordination number of atoms in the lattice for the bulk, Z_p is the coordination number for the particles, N_s is the number of surface atoms, and N_T is the total atom number of atoms of the particle. N_s/N_T can be calculated by follows^[1,6-8]:

$$\frac{N_s}{N_T} = \frac{4f_s}{f_v(d_p/d_a) + 2f_s} \tag{2}$$

where f_s is the packing fraction of the surface (ratio of the area occupied by atoms to the total area of the surface plane), f_v is the lattice packing fraction (the ratio of the volume occupied by atoms to the total volume of the unit cell), d_p is the particle diameter, and d_a is the atomic diameter.

In fact, the coordination number Z_p of metal particles changes with the change of particle size. With the increase of particle size, the ratio of surface atoms decreases and Z_p increases. And it approaches to the coordination number Z_∞ in the metal lattice of block metal. Phuoc et al^[6] think that for the nanoparticles, $Z_p=1/4$ is appropriate, and for the larger metal particles, $Z_p=1/2$ is more suitable. The activation energy of metal particles is calculated by Eq.(1) and Eq.(2), and the required parameters are listed in Table 1.

Table 1 Packing factors and coordination number for different lattice structures^[6]

Lattice structure	f_s	f_v	Z_∞
fcc	0.91	0.74	12
bcc	0.83	0.68	8
hcp	0.91	0.74	12

Substitute Eq.(2) into Eq.(1) and expand by McLaurin series at d_p :

$$\frac{E_p}{E_\infty} = \frac{a}{b} + \sum_{i=1}^{\infty} \left[(-1)^{i-1} \frac{1}{b^i} + (-1)^i \frac{a}{b^{i+1}} \right] d_p^i \tag{3}$$

where

$$a = \left(\frac{4Z_p}{Z_\infty} - 2 \right) \frac{f_s}{f_v} d_a, \quad b = 2 \frac{f_s}{f_v} d_a$$

Without losing generality, Eq.(3) is written as the high

power form of d_p , and the polynomial model of activation energy of metal particles can be obtained^[9]:

$$E_p = A_0 + A_1 d_p^1 + A_2 d_p^2 + \dots + A_i d_p^i, \quad i \rightarrow \infty \tag{4}$$

where $A_0, A_1, A_2, \dots, A_i$ are constants related to material properties, which can be obtained by fitting experimental data.

1.2 Heat loss

When a metal particle is heated by a heat source, its temperature increases and then oxidation reaction occurs. If such a heating process continues, the particle will ignite and burn. When the heat generation of oxidation reaction is in balance with the heat loss to the surrounding, even if there is no heat source, the metal particles can self-sustain combustion. The critical temperature of self-sustaining combustion of metal particles is the ignition temperature, and the mathematical expression of the criterion is^[10]

$$Q_{chem} = Q_{radi} + Q_{conv} \tag{5}$$

where Q_{chem} is the heat generation rate of combustion reaction; Q_{radi} and Q_{conv} are the radiation and convection heat transfer rates, respectively. For micrometers and nanometers particles, the heat transfer to the surrounding is controlled by the Knudsen number K , which can be given as follows^[6]:

$$K = \frac{\lambda}{r_p} \tag{6}$$

where r_p is the particle radius, λ is the mean free path of gas molecules. In order to simplify the model, the temperature gradient of the gas around the particle is ignored, which is uniformly expressed as the ambient temperature T_e . The average free path λ can be calculated by^[10]

$$\lambda(T_e) = \frac{4k(T_e)}{5P} \sqrt{\frac{m_g T_e}{2k_B}} \tag{7}$$

where k is the thermal conductivity of the gas, P is the pressure of the gas, m_g is the mass of a gas molecule, and k_B is the Boltzman constant. When the metal particles are small enough and $k>10$, the heat convection regime is free molecular regime, and the heat transfer rate depends on the collision probability between metal particles and air molecules^[6,10,11]:

$$Q_{FM} = \pi r_p^2 \frac{P}{2} \left(\frac{8k_B T_e}{\pi m_g} \right)^{1/2} \frac{\gamma^* + 1}{\gamma^* - 1} \left(\frac{T_p - T_e}{T_e} \right) \tag{8}$$

where T_p is the particle temperature, and γ^* is the average adiabatic index of gas, defined by follows:

$$\frac{1}{\gamma^* - 1} = \frac{1}{T_p - T_e} \int_{T_e}^{T_p} \frac{1}{\gamma - 1} dT \tag{9}$$

When the metal particles are large enough and $k<0.01$, heat convection regime is continuum regime^[6,10]:

$$Q_C = 4\pi r_p k^* (T_p - T_e) \tag{10}$$

where k^* is the average thermal conductivity, which is defined as^[10]

$$k^* = \frac{1}{T_p - T_e} \int_{T_e}^{T_p} k dT \tag{11}$$

In most cases, k is between 0.01 and 10. The heat transfer regime is transition regime, and the heat convection rate can be defined as^[6]:

$$\frac{1}{Q_{\text{conv}}} = \frac{1}{Q_C} + \frac{1}{Q_{\text{FM}}} \quad (12)$$

The heat transfer rate of metal particles to the surrounding through thermal radiation is follows^[10]:

$$Q_{\text{radi}} = \varepsilon \sigma_{\text{SB}} (\pi d_p^2) (T_p^4 - T_c^4) \quad (13)$$

where ε is the radiation coefficient and σ_{SB} is the Stefan-Boltzman constant. The heat transfer regime can be defined by the Knudsen number. According to the corresponding heat transfer regime, the heat release rate of metal particles to the environment during combustion can be calculated.

1.3 Heat generation

For aluminum particles, the simplest Arrhenius-type model is used to calculate the heat generation rate^[6,10]:

$$Q_{\text{chem}} = \pi d_p^2 \Delta H_{\text{ox}}(\text{Al}) A_p \exp\left(-\frac{E_p}{RT_p}\right) \quad (14)$$

where $\Delta H_{\text{ox}}(\text{Al})=6.2 \times 10^7 \text{ J}\cdot\text{kg}^{-1}$ ^[12] is the oxidation heat of aluminum, A_p is the preexponential factor related to particle size, and $R=8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ is the general gas constant. As the effect of exponential term on reaction rate is much stronger than that of preexponential term, the change of A_p with particle size is not considered, and $A_p \approx A_{\infty}=1.6 \times 10^7 \text{ kg}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$ ^[6].

For zirconium particles, due to the lack of credible data of preexponential factor, a more complex solid-gas combustion model is used. The oxidation mechanism of metal particles can be defined by solid-state diffusion of oxygen through the oxide layer and gas-phase transport of oxygen to the particle surface. Assuming that the solid-state diffusion of oxygen through the oxide layer is isothermal and the molar volume is constant, the growth rate of oxide layer can be expressed as^[13,14]

$$\frac{d\xi}{dt} = \frac{\Omega}{\left[1 - \left(\frac{\xi}{r_0}\right)\right]^2 \xi} \quad (15)$$

where $\xi=r_0-r$ is the thickness of the oxide layer, r is the radius of the unoxidized particle, r_0 is initial radius, and Ω is the tarnishing coefficient, which is a function of temperature and can be expressed as follows^[13,14]:

$$\Omega = \Omega_0 \exp\left(-\frac{E_p}{RT_p}\right) \quad (16)$$

where $\Omega_0=4.361 \times 10^{-5} \text{ m}^2\cdot\text{s}^{-1}$. The second mechanism of zirconium particle combustion assumes that the reaction kinetics is controlled by the arrival of oxygen molecules to the external surface of the reacting particle, under which the growth rate of oxide layer is^[13,14]

$$\frac{d\xi}{dt} = \frac{J_g M}{\rho} \left(\frac{r_0}{r_0 - \xi}\right)^2 \quad (17)$$

where J_g is the flux of oxygen molecules sticking on the surface of the metal, M is the molar mass of oxygen, and ρ is the density of oxygen. The oxygen flux that depends on temperature and pressure is described by the kinetic theory of gases^[14]:

$$J_g = f \frac{P_{\text{ox}}}{\sqrt{2\pi MRT_c}} \quad (18)$$

where $f=1$ is the impact coefficient and P_{ox} is the partial pressure of oxygen. Comparing the two mechanisms, the smaller one is the decision mechanism to control the oxide growth rate. From a simple geometric relationship, the expression of the heat generation rate of zirconium particle combustion is as follows:

$$Q_{\text{chem}} = \Delta H_{\text{ox}}(\text{Zr}) m_p \frac{3(r_0 - \xi)^2}{r_0^3} \frac{d\xi}{dt} \quad (19)$$

where $\Delta H_{\text{ox}}(\text{Zr})=1.2 \times 10^7 \text{ J}\cdot\text{kg}^{-1}$ ^[12] is the oxidation heat of zirconium, and m_p is the particle mass.

At present, there are few published experimental data on the size effect of activation energy of metal particles, but there are many experimental data on the ignition temperature of metal particles at different particle sizes. Huang et al^[15] summarized the experimental results of the ignition temperature of aluminum particles in the range from 10 nm to 1 mm; Ioffe^[16], Patrikeev^[17], Karpova^[18], Andersen^[19] and Dufaud et al^[20] provided the experimental results of ignition temperature of zirconium particles in the range from 1 μm to 1 mm; Karpova^[18], Ezhovskii^[21], Dufaud^[20] and Pawel^[22] provided the activation energy of the combustion reaction of zirconium particles at certain particle sizes. Therefore, based on the experimental data and theoretical model of the ignition temperature of zirconium and aluminum particles, the corresponding activation energy can be calculated. And the size effect of the activation energy of zirconium and aluminum particles was studied according to the calculation results.

2 Results and Discussion

A brief numerical calculation process for obtaining the activation energy by ignition temperatures is shown in Fig.1a. Firstly, the heat loss rate of the particles is calculated by Eq.(6~13). Let the initial activation energy be a large number, such as $800 \text{ kJ}\cdot\text{mol}^{-1}$, and the heat generation rate of particles is derived by Eq.(14) for Al or Eq.(15~19) for Zr. Secondly, continuously reduce the activation energy, calculate and compare the heat generation rate and heat loss rate of the particles until Eq.(5) is satisfied. The final value of activation energy is the theoretical result for the corresponding ignition

temperature and particle size. Finally, the relationship between activation energy and particle size is obtained according to the ignition temperature of different particle size.

Similarly, the theoretical relationship between ignition temperature and particle size can be calculated numerically according to the change law of activation energy with particle size, as shown in Fig.1b.

Fig.2 shows activation energy of combustion reaction of aluminum particle as a function of particle diameter. The data point is the corresponding activation energy calculated according to the ignition temperature of aluminum particles. The solid line is the fitting result and the dotted lines are the calculation results using Shandiz's model. The shape of metal particles, the surface roughness, the thickness of oxide film and other factors will affect the combustion experimental results, resulting in the scattered data distribution. A large number of relevant experimental data make the fitting results statistically significant. In the range from 10 nm to 1 mm, the activation energy of combustion reaction of aluminum particles increases with the increase of particle size, which is also an important reason for the increase of ignition temperature.

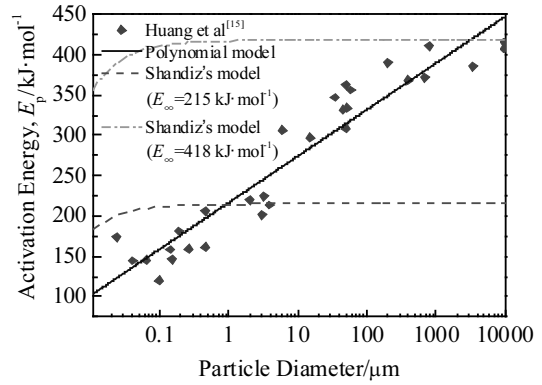


Fig.2 Activation energy of combustion reaction of aluminum particle as a function of particle diameter

The value of E_∞ has a great influence on the calculation results of Shandiz's model. Trunov et al.^[23] summarized the combustion experiments of aluminum particles, and the maximum activation energy measured is 418 kJ·mol⁻¹, which is much higher than 215 kJ·mol⁻¹ used in the calculation of Ref.[6]. Fig.1 shows the calculation of above two parameters. In the range from 10 nm to 1 mm, the calculated results of Shandiz's model are quite different from the experimental data. As shown in Eq.(2), when the particle size of aluminum is around 10 nm, $N_s/N_T \rightarrow 0$ and $E_p \rightarrow E_\infty$, so Shandiz's model cannot effectively calculate the change of activation energy of materials with larger particle size.

It can be seen from the figure that the activation energy and the logarithm of particle size are approximately in a linear relationship, and the linear fitting results are as follows:

$$E_p(\text{Al}) = 57\ 660 \lg d_p + 562\ 600 \quad (20)$$

The parameters of the polynomial model can be obtained by expanding Eq.(20) using the Mclaurin series. The model can describe the relation between activation energy of aluminum particle combustion and particle size well, which is consistent with the experimental data. In the future, more experimental activation energy data of aluminum particles with different sizes are needed to verify the accuracy of the theoretical model.

Fig.3 shows activation energy of combustion reaction of zirconium particle as a function of particle diameter. The solid data point is the corresponding activation energy calculated according to the ignition temperature of zirconium particles, and the hollow data point is the activation energy measured by experiment directly. The calculated results of activation energy of Zr with a particle size of 40 μm are consistent with the experiment results, and other three experiment results with a particle size of 8, 44 and 750 μm go the same with the theoretical curve, which to some extent verify the accuracy of the calculated results. When calculating the activation energy of zirconium particles, the selection of initial oxide thickness

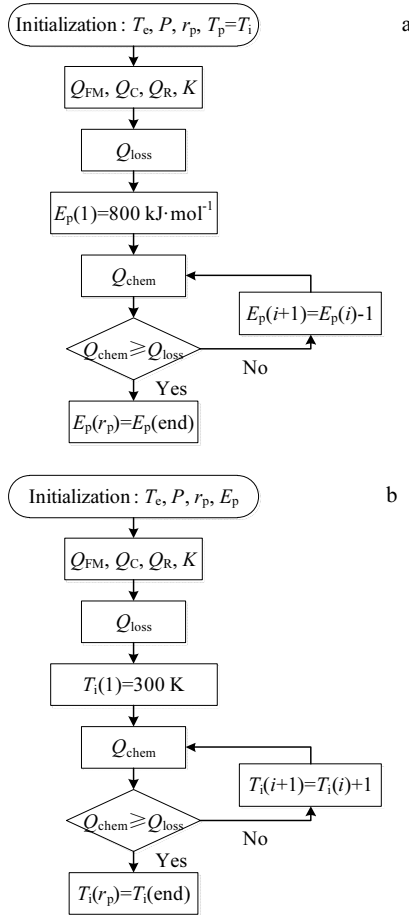


Fig.1 Numerical calculation process of activation energy (a) and ignition temperature (b)

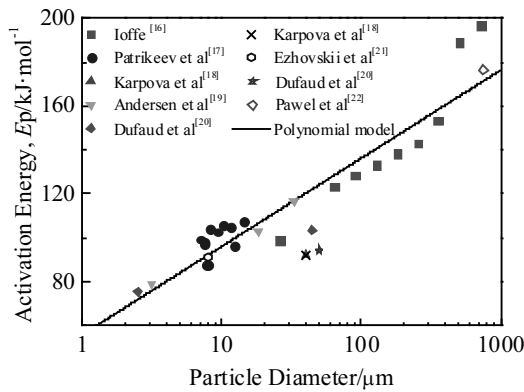


Fig.3 Activation energy of combustion reaction of zirconium particle as a function of particle diameter

ζ_0 has a great influence on the calculation results. Karpova et al [18] studied the ignition temperature and activation energy of 40 μm zirconium particles. Let $\zeta_0=0.2$ nm, the tested activation energy is equal to the calculated activation energy (solid triangle point and fork point in Fig.3). Therefore, in the calculation, $\zeta_0=0.2$ nm is taken uniformly. It should be noted that this will lead to errors, because the initial oxide thickness of zirconium particles is not the same in different experiments. In the range from 1 μm to 1 mm, the activation energy of zirconium particles is approximately linear with the logarithm of particle size:

$$E_p(\text{Zr}) = 36\ 400 \lg d_p + 266\ 200 \quad (21)$$

The model can describe the combustion activation energy of zirconium particles with the change of particle size successfully, which is consistent with the experimental data.

Fig.4 and Fig.5 show the ignition temperature as a function of particle diameter for aluminum and zirconium, respectively. The data points are the experimental results, and the solid line is the ignition temperature-particle size relationship calculated with Eq.(20) and Eq.(21). It can be seen that the calculated results are consistent with the experimental results, and the proposed model can better describe the relationship between ignition temperature and particle size. With the increase of particle size, the specific surface area of metal particles decreases, and the collision efficiency between oxygen molecules and particles decreases, which leads to the increase of ignition temperature. The dashed lines are the calculated results of Shandiz's model, which deviates greatly from the experimental result. With the increase of particle size d_p , the growth rate of Q_{chem} is greater than that of Q_{loss} , which eventually leads to the decrease of calculated ignition temperature, inconsistent with the actual situation.

Eq.(20) and Eq.(21) are based on the fitting of experimental data, so its application range should be resulted to the experimental data range, and the improvement of its accuracy needs to be further supplemented by the experimental data. In

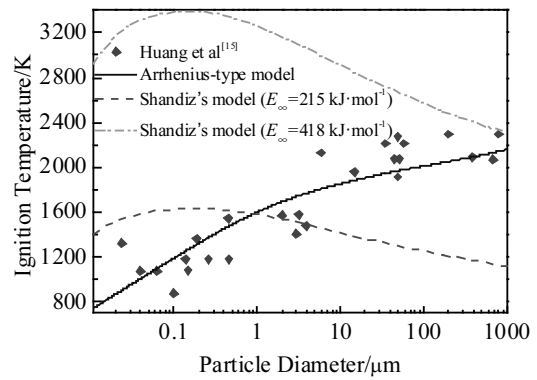


Fig.4 Ignition temperature of aluminum as a function of particle diameter

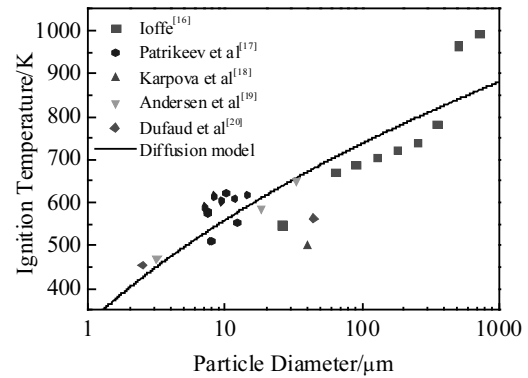


Fig.5 Ignition temperature of zirconium as a function of particle diameter

fact, when the metal particle size reaches the larger size, its ignition temperature changes little with the particle size [15]. The linear relationship between activation energy and the logarithm of particle size is obviously not applicable. The selection of heat generation rate model and parameters also has an influence on the calculation results. In Eq.(14), the preexponential factor A_p is assumed to be a constant, and its change with particle size is ignored, which affects the accuracy of E_p calculation results. The diffusion model, also known as the nuclear contraction model, and closer to the physical nature of zirconium particle combustion, is selected. Dufaud [20] compared the calculation results of several nuclear contraction models, and suggested that the calculation error of the nuclear contraction model is small. However, the selection of ζ_0 also brings some errors to the calculation results, which will be improved in the further work.

3 Conclusions

1) In the range of particle size from 10 nm to 1 mm, the relationship between the activation energy of aluminum

particle and particle size is approximately $E_p(\text{Al})=57\ 660\lg d_p+562\ 600$.

2) In the range of particle size from 1 μm to 1 mm, the relationship between the activation energy of zirconium particle combustion and particle size is approximately $E_p(\text{Zr})=36\ 400\lg d_p+266\ 200$.

3) Experimental conditions, combustion heat generation model and calculation parameters all affect the calculation results. More accurate experimental data, such as the initial oxide layer thickness of metal particles, and more accurate calculation parameters help to improve the accuracy of the model.

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锆、铝颗粒活化能尺寸效应的理论模型

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摘要: 提出了一个通过金属颗粒着火温度计算活化能的理论模型, 着火温度的临界条件为燃烧反应产热率与对周围环境放热率达到热平衡。放热率由 Knudsen 数控制, 铝颗粒燃烧产热率通过 Arrhenius 形式的模型计算, 锆颗粒燃烧产热率由扩散模型计算, 通过迭代计算, 得到金属颗粒着火温度对应的活化能。结果表明, 铝颗粒、锆颗粒的活化能随粒径增大而增大, 与粒径的对数呈线性关系。在纳米至微米的更大尺寸范围内, 单一理论模型不足以描述金属颗粒活化能的尺寸效应, 而基于数据拟合的多项式模型更具有普适性。

关键词: 活化能; 着火温度; 铝; 锆; 纳米颗粒; 微米颗粒

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