

On the Critical Conditions for Thermal Runaway of Fine Iron Particles

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1 Introduction

Iron is an excellent fuel for long-term storage and long-distance transport of clean energy owing to its carbon-free nature, high energy density, and potential for non-volatile combustion in air [1]. For developing practical energy-conversion technologies based on iron fuel, a better understanding of the fundamentals underlying the combustion process of fine (i.e., micron- to hundreds-of-micron-sized) iron particles at elevated temperatures is required. The full oxidation process of an iron particle in a combustion system consists of three major stages: (1) Preheating and ignition leading to a thermal runaway; (2) a rapid oxidation process of a molten droplet at elevated temperatures until iron is completely oxidized; (3) a slow further oxidation process of the lower oxidized products, i.e., from FeO or Fe₃O₄ to Fe₂O₃, upon cooling.

The objective of the current study is to theoretically seek a quantitative answer to the question under which fine iron particles can be ignited. To ignite an iron particle means that a set of critical conditions (e.g., gas or particle temperature) is satisfied to trigger a thermal runaway—the rate of energy release due to iron oxidation exceeds the rate of heat loss to the surrounding. There is yet no experimental measurement of the critical particle or gas temperature required for triggering thermal runaway (referred to as “ignition temperature” in the remainder of this paper) of an isolated particle, or a suspension of iron particles, in a flame. The experimental data of iron ignition temperature in the literature, as partly summarized by Breiter *et al.* [2], are widely scattered owing to the difference in experimental conditions, specimen properties and morphologies, and definition of “ignition temperature”. Khaikin [3] proposed a generic ignition model for reactive metal particles considering the obstructing effect of an oxide layer on the reaction rate, but did not apply it for quantitatively estimating the ignition temperature of iron particles.

The current study aims to develop a model to quantitatively capture the ignition characteristics of fine iron particles. To this end, a physics-based kinetic model of solid-phase iron oxidation—a parabolic rate law reflecting that the oxidation rate is controlled by the lattice diffusion of Fe cations through oxide layers—is considered in the current ignition model. The values of the kinetic parameters were calibrated against the experimental measurement of growth rates of iron-oxide scales over a temperature range from 973 K to 1523 K obtained by Païdassi [4]. Using this model, the effects of initial particle size, initial oxide layer thickness, inert gas species, radiative heat loss, and collective heating in a particulate suspension on the ignition characteristics of iron particles are examined.

2 Model description

2.1 Iron oxidation kinetic model

Microscopic cross-section views of a solid-phase oxide scale grown on iron under isothermal conditions (over a range in temperature from 973 K to 1523 K) in air were first obtained by Païdassi in the 1950s.[4] Figure 1(a) is a sample image from Ref. [4] showing that an iron-oxide scale consists of three compact layers of hematite (Fe_2O_3), magnetite (Fe_3O_4), and wüstite (FeO) stacked from the gas-oxide interface to the oxide-iron interface. The relative thicknesses of the Fe_2O_3 , Fe_3O_4 , and FeO layers with respect to the total thickness of the oxide scale are 1%, 4%, and 95%, respectively. The processes underlying solid-phase iron oxidation are conceptually illustrated in Fig. 1(b).

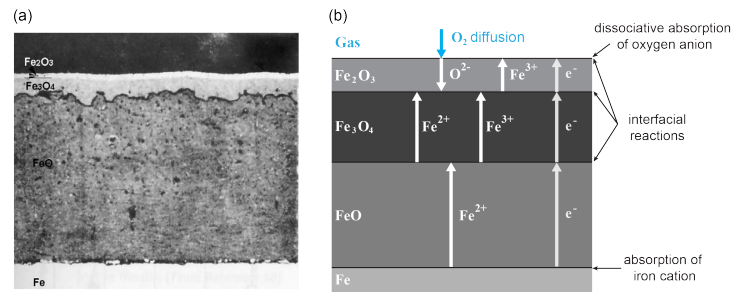


Figure 1: (a) A sample cross-section view of a multilayered oxide scale grown on iron as shown by Païdassi [4]; (b) a schematic illustration showing the key processes underlying solid-phase iron oxidation.

For a sufficiently thick oxide scale, the growth rate of each layer is controlled by the diffusion of ions subjected to the equilibrium activities of Fe and O at the interfaces [5]. Considering the fact that the transport of electrons and the establishment of local equilibria at the interfaces are significantly more rapid than the diffusion of ions across the oxide layers, Wagner's theory [6] relates the oxide growth rate to the diffusivity of ions. The growth of the FeO layer is the most rapid due to the fact that the diffusion coefficient of Fe cations in FeO is greater than that in Fe_3O_4 or Fe_2O_3 . Such a diffusion-controlled growth follows a parabolic rate law,

$$\frac{dX_i}{dt} = \frac{k_{p,i}}{X_i} \quad (1)$$

where X_i is the thickness of an oxide layer, $k_{p,i}$ is the parabolic rate constant, and i is the index of each oxide layer. As the activities of Fe and O at the Fe-FeO , $\text{FeO-Fe}_3\text{O}_4$, and $\text{Fe}_3\text{O}_4\text{-Fe}_2\text{O}_3$ interfaces are fixed by the phase equilibria, the growth of FeO and Fe_3O_4 are barely affected by the ambient O_2 concentration [5]. The temperature dependence of $k_{p,i}$ can be described by an Arrhenius function as follows,

$$k_{p,i}(T) = k_{0,i} \text{Exp} \left(\frac{-T_{a,i}}{T} \right) \quad (2)$$

wherein the values of pre-exponential factor $k_{0,i}$ and activation temperature $T_{a,i}$ for the growth of FeO and Fe_3O_4 layers can be calibrated via line fitting to the plotted data points as reported in Table 1.

2.2 Model of iron particle ignition

In the current analysis, a thermophysical model based on the mass and energy balance equations with the empirically calibrated kinetic model of iron oxidation is used to describe the ignition process of an isolated iron particle and a suspension of iron particles, which are conceptually illustrated in Fig. 2(a)

Table 1: Calibrated parameters for the parabolic growth rate of FeO and Fe₃O₄

-	k_0 (m ² s ⁻¹)	T_a (K)
FeO	2.670×10^{-4}	20319
Fe ₃ O ₄	1.027×10^{-6}	21310

and (b), respectively. The detailed formulation and major assumptions made in this model can be found in [7].

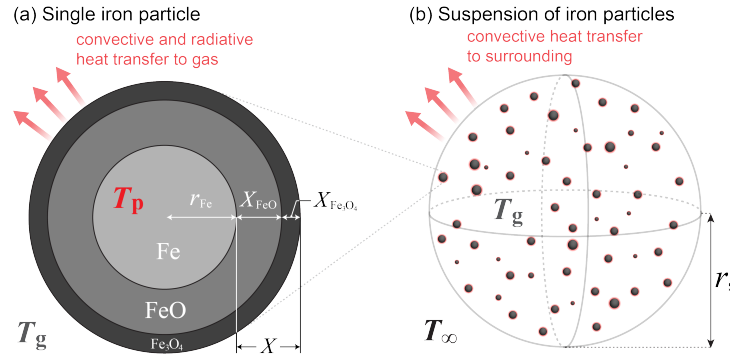


Figure 2: Schematic of the thermophysical model of (a) an isolated particle consisting of a core of pure Fe, an inner oxide layer of FeO, and an outer oxide layer of Fe₃O₄ and (b) a spherical suspension of reacting iron particles.

3 Sample results

Figure 3(a) shows the time histories of particle temperature T_p of an isolated iron particle with an initial diameter $d_{p,0} = 20 \mu\text{m}$ subjected to various gas temperatures. For the cases with $T_g \leq 1081 \text{ K}$, as shown in Fig. 3(a), T_p increases to a peak value followed by an asymptotic decrease to T_g . For the case with $T_g = 1082 \text{ K}$, T_p increases monotonically with time as shown in Fig. 3(a). This increase in temperature becomes abrupt after approximately 0.01 s. Sample suspension model results shown in Fig. 3(b) are for the cases with an initial suspension radius $r_{s,0} = 1 \text{ cm}$, particle size $d_{p,0} = 20 \mu\text{m}$, and oxide layer thickness of $X_0 = 10 \text{ nm}$ in air at an equivalence ratio $\phi_{\text{FeO}} = 1$. The particle and gas temperatures of a suspension are initialized to be equal to the surrounding gas temperature T_∞ , and are plotted as dashed and solid curves in Fig. 3(b), respectively. Each pair of T_p and T_g curves correspond to a case with a constant T_∞ . The curve of T_p is slightly above that of T_g for all of the cases. For the cases with $T_\infty \leq 904 \text{ K}$, the resulting temperatures vary non-monotonically over time; for the cases with $T_\infty \geq 905 \text{ K}$, T_p and T_g increase abruptly after a gradual increase over early times.

A gradual increase in temperature followed by a rapid upsurge (as identified in some cases shown in Fig. 3) indicates a particle or suspension undergoing a thermal runaway. The bifurcation between the “go” and “no-go” cases is identified as a critical phenomenon of ignition. Based on the time histories resulting from the isolated particle and suspension models, critical values of T_g and T_∞ above which an isolated particle or a suspension undergoes a thermal runaway, respectively, can be determined. This critical temperature for ignition is referred to as the *ignition temperature* and denoted as T_{ign} . In this study, T_{ign} is used as a metric to probe the effects of various factors contributing to the ignition process of iron particles.

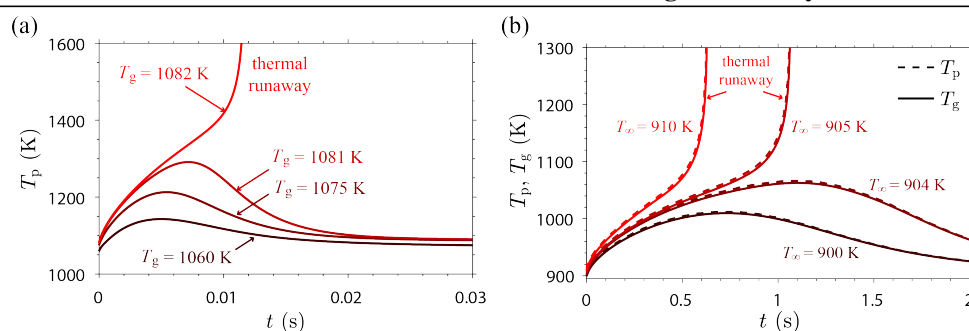


Figure 3: Sample results showing the time histories of (a) T_p of an isolated iron particle at different gas temperatures and (b) T_g (solid curves) and T_p (dashed curves) of a suspension of iron particles subjected to different surrounding gas temperatures with an initial particle size $d_{p,0} = 20 \mu\text{m}$, and oxide layer thickness of $X_0 = 10 \text{ nm}$ in air.

4 Analysis and discussion

4.1 Effect of initial particle size and oxide layer thickness

The results of T_{ign} are plotted in Fig. 4(left) as a function of initial particle diameter, $d_{p,0}$, with three different initial oxide layer thicknesses for an isolated particle in air. For the case with $X_0 = 0.1 \mu\text{m}$ (the solid red curve in Fig. 4(left)), there is a significant decrease in T_{ign} as $d_{p,0}$ increases from $1 \mu\text{m}$ to approximately $20 \mu\text{m}$; T_{ign} nearly plateaus for further larger particles. Although qualitatively the same trend is identified for the case with a much thinner initial oxide layer of $X_0 = 10 \text{ nm}$ (dashed maroon curve), T_{ign} decreases less significantly with an increase in $d_{p,0}$ and reaches nearly the same plateau value ($\approx 1082 \text{ K}$) as that resulting from the case with $X_0 = 0.1 \mu\text{m}$. For an even thinner initial oxide layer of $X_0 = 1 \text{ nm}$ (dash-dotted black curve), the entire curve of T_{ign} plateaus at 1082 K , independent of initial particle size. This independence of T_{ign} on particle size (for sufficiently large particles) is qualitatively explained as follows: For increasingly large particles, the increase in energy release rate surpasses the increase in the rate of convective heat removal. As a result, larger particles are more prone to ignition. If a parabolic oxidation rate law is considered, however, to heat up larger particles requires a greater amount of energy release associated with a thicker oxide layer grown, in return, impeding the oxidation rate. Hence, a large particle size has both enhancing and hindering effects on the ignition propensity of an iron particle. These mutually compensating effects result in the independence of T_{ign} on particle size for sufficiently large particles governed by a parabolic oxidation rate law. As a comparison, the result of a model (recently proposed by Hazenberg and Oijen [8]) neglecting the impeding effect of an oxide layer on the oxidation rate is plotted as the dotted blue curve in Fig. 4. The resulting T_{ign} persistently decreases as $d_{p,0}$ increases, manifesting only the enhancing effect of an increase in particle size.

4.2 Effect of inert gas species

The current model considers the fact that the kinetics of iron oxidation is controlled by solid-phase diffusion and is independent of gas-phase O_2 concentration (at least, for $p_{\text{O}_2} > 4 \times 10^{-4} \text{ atm}$). The T_{ign} in a gas mixture with O_2 and different inert species is plotted as a function of the mole fraction of O_2 in Fig. 4(right). The result of T_{ign} for the case with N_2 (plotted as the solid curve) does not change significantly as X_{O_2} varies, owing to the fact that the thermal conductivities of diatomic gases O_2 and N_2 are very close. For the case with He , the resulting T_{ign} increases with a decrease in X_{O_2} . This trend

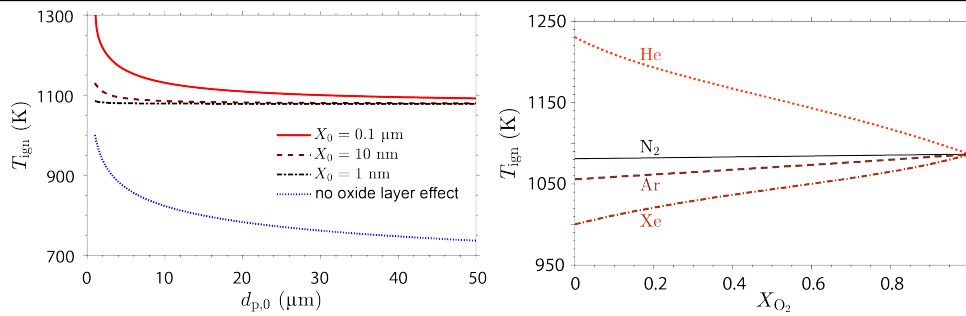


Figure 4: **Left:** Critical temperature for ignition, T_{ign} , as a function of initial particle diameter, $d_{p,0}$, with three different initial oxide layer thicknesses, i.e., $X_0 = 0.1 \mu\text{m}$ (solid red curve), $X_0 = 10 \text{ nm}$ (dashed maroon curve), and $X_0 = 1 \text{ nm}$ (dash-dotted black curve). Results from the current model for an isolated particle in air are compared to the result of a model [8] neglecting the obstructing effect of oxide layer on the oxidation rate (plotted as the dotted blue curve). **Right:** The ignition temperature T_{ign} of an isolated iron particle with $\delta_0 = 10^{-3}$ as a function of mole fraction of oxygen X_{O_2} in a bulk gas mixture with different inert species, i.e., He (dotted), N_2 (solid), Ar (dashed), and Xe (dash-dotted).

is due to the fact that He has a higher thermal conductivity than that of O_2 . On the other hand, the T_{ign} for the cases with Ar and Xe decrease significantly as oxygen mole fraction decreases, since Ar and Xe have an increasingly low thermal conductivity. A reduced thermal conductivity of the ambient gas has a heat preserving effect on a reacting particle, thereby, facilitating thermal runaway.

4.3 Collective effect in a suspension of particles

The results of T_{ign} for a spherical suspension of iron particles (with $\delta_0 = 10^{-3}$ and a fixed initial particle size of $d_{p,0} = 20 \mu\text{m}$) in air are plotted as a function of ϕ_{FeO} , i.e., the fuel equivalence ratio considering FeO as the only oxide product in Fig. 5(a). As the initial radius of a spherical suspension increases from $r_{s,0} = 1 \text{ mm}$ (dashed curve) to 5 cm (dotted curve), the resulting T_{ign} decreases from approximately 1075 K, which is slightly below the T_{ign} for an isolated particle (indicated by the solid horizontal line), to values below 800 K. This reduction in T_{ign} is due to the collective effect of energy released by multiple particles suspended within a finite-sized volume that is losing heat to the surrounding via its external surface [9]. Analogous to an isolated particle, the convective heat loss rate of a spherical suspension scales linearly with suspension radius as $A_s \propto r_s^2$ and $h_s \propto 1/r_s$. The rate of energy release from the reacting particles in a suspension scales with N_p that is proportional to r_s^3 . The increase in energy release rate thus surpasses the increase in heat loss rate for an increasingly large suspension. This analysis suggests that, as a result of the collective effect, the critical ignition temperature of iron particles within a flame may be lower than that for an isolated particle.

5 Concluding remarks

A model describing the heat and mass balance equations for heterogeneously burning micrometric iron particles was developed. The solid-phase oxidation kinetics described by a parabolic rate law were empirically calibrated using measured experimental data on the time-evolution of the growth of iron-oxide layers. Findings showed that the ignition temperature depends on the ratio between the initial oxide layer thickness and particle size, δ_0 , and is independent of particle size. For isolated iron particles in air, the predicted ignition temperature plateaus at approximately 1080 K, and becomes independent of δ_0 , for $\delta_0 \lesssim 0.003$. The lower thermal conductivity of the gas-phase environment, the lower the

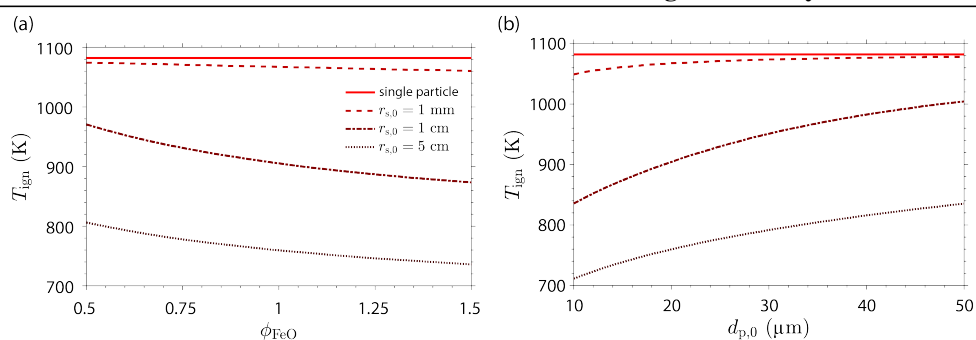


Figure 5: The ignition temperature, T_{ign} , of an iron-particle suspension in air with different initial suspension radii, i.e., $r_{s,0} = 1$ mm (dashed), $r_{s,0} = 1$ cm (dash-dotted), and $r_{s,0} = 5$ cm (dotted), and $\delta_0 = 10^{-3}$ (a) as a function of fuel equivalence ratio (assuming FeO as the only product) with $d_{p,0} = 20 \mu\text{m}$ and (b) as a function of initial particle diameter with $\phi_{\text{FeO}} = 1$. The value of T_{ign} for an isolated particle (with $\delta_0 = 10^{-3}$) in air is marked by the horizontal solid line.

ignition temperature. The ignition behavior was found to be largely independent of radiative heat loss effects. The collective heating effect in burning particle suspensions was shown to significantly reduce the ignition temperature.

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