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Temperature and phase transitions of laser-ignited single iron particle

Dao guan Ning, Yuriy Shoshin, Martijn van Stiphout, Joreon van Oijen, Giulia Finotello, Philip de Goey

Department of Mechanical Engineering, Eindhoven University of Technology, the Netherlands

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A B S T R A C T

The combustion behavior of single laser-ignited iron particles is investigated. Transient particle radiant intensities at 850 nm and 950 nm are measured by post-processing recorded high-speed camera images using an in-house developed particle tracking program. Then, the time-resolved particle temperature is obtained based on two-color pyrometry. A plateau-like stage shortly after the ignition is repeatedly observed, and identified as iron particle melting by the measured temperature and the estimated melting time. Besides, an abrupt brightness jump near the end of combustion is observed for most burning particles, while a small portion of the particles (<10%) show a second plateau-like stage instead. The particle temperature right after the brightness jump (1880 ± 70 K) is almost identical to that during the second plateau-like stage. This temperature corresponds to two phase-change temperatures in the Fe-O phase diagram: i) L2 <→ Fe3O4 (s) at 1869 K (congruent melting) and ii) L2 <→ Fe3O4 (s) + O2 (g) at 1855 K (eutectic reaction), where L2 represents a liquid iron oxide. Based on this, the presence of the brightness jump (spear point) is explained by a sudden solidification of supercooled iron oxide droplets with an atomic O/Fe ratio larger than or close to 4/3. Particles’ near-peak temperatures are also measured based on time-integrated spectra. The results indicate that the near-peak temperature increases first fast and then slowly with an increase of oxygen concentration. At higher oxygen concentrations, smaller particles have a slightly lower temperature. The effect of particle size on the near-peak temperature is negligible at lower oxygen concentrations due to weaker radiation. The morphology of combusted particles is examined by microscopy. Some burned particles appear as hollow thin-shell spheres at all adopted oxygen concentrations. Additionally, nano oxides are found at 13–51% oxygen concentrations. Less traces of nano oxides were observed at reduced oxygen concentrations. The nano-oxide formation mechanisms are analyzed based on thermochemical equilibrium calculations.

1. Introduction

To reduce greenhouse gas emissions, new combustion technologies and fuels are needed. Recently, metal-fuel cycles have been proposed as clean power generation methods for several reasons [1–3]. First, metal powders have a higher energy density compared to hydrocarbon fuels and liquefied hydrogen, which is an advantage for storage and transportation. Second, there is no CO2 emission during combustion of metals, which can significantly benefit the environment and relieve global warming. Third, combustion products, i.e., metal oxides can be deoxidized to metal powders by using green energy sources such as wind and solar, which makes metal powders ideally recyclable energy carriers. Aluminum, boron, and magnesium, which are traditionally used as propellants or additives due to their highly energetic reactions, are possible candidates for the metal-fuel cycles. On the other hand, the less energetic iron is considered as a more promising metal fuel because its availability, affordability, flame temperature, and heterogeneous combustion.

Knowledge on iron combustion is barely developed, and literature on this topic is very scarce on both theoretical and experimental sides. Only very recently, systematic experiments on flame propagation, quenching distances, and flame temperatures of iron aerosols were conducted by researchers at McGill University [4–7], although pioneering work on iron dust flames performed by Sun et al. [8–10] started about three decades ago. Meanwhile, using iron powders as a recyclable fuel starts to gain attention of other researchers as well [11,12]. Since iron dust flames consist of individual burning particles, the combustion characteristics of a single iron particle play a crucial role in the flame properties.

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Relevant experimental works on single iron particle combustion are even less available than that on iron dust flames. Tóth et al. [11] studied the combustion behavior of single sponge iron particles in a low-number-density aerosol ignited by hot products of methane/air flames. From recorded high-speed microscopic shadowgraphs, near-instantaneous melting of a particle was observed, which was speculated as FeO melting. However, this argument is questionable because iron particles cannot near-instantaneously oxidize to FeO before melting due to the limitation of oxygen mass diffusion. Wright [13] measured the burn time of a single particle ejected into a hot argon/oxygen mixture for two types of iron particles with different purity. For impure particles, the combustion process was always terminated by a micro-explosion. Contrarily, pure particles combusted smoothly from ignition to burnout, and brightness jump occurs near the end of incandescent particle streak for the majority of particles. In our previous work [14], which aimed at systematically measuring laser-ignited particle burn time at room temperature in nitrogen/oxygen mixtures with various oxygen concentrations, two phenomena similar to that reported in the two above-mentioned works were also observed: (i) a plateau-like stage on the particle brightness profile shortly after ignition, which was hypothesized as melting; (ii) an abrupt brightness jump near the end of a burning particle streak (cf. Fig. 8), which was speculated as sudden solidification of the supercooled iron oxide droplet or one of other phase transitions of the iron-oxygen binary system.

Phase transitions are important for understanding metal particle combustion [15]. It is thought as the reason for some unique phenomena observed during metal particles combustion, such as the temperature jump occurring for many metals including steel, by Dreizin et al. [16]. For steel particle, they briefly explained it by mentioning that ‘phase transformations occurs at 1424 °C and 1457 °C in which Fe₂O₃ and FeO are formed’. However, this unique phenomenon is still not fully understood and no further research has been reported for iron particles to the best of our knowledge. In this work, time-resolved temperatures of single burning iron particles are measured using two-color pyrometry, by which the plateau-like stage and the brightness jump that have been observed in few independent works are explained with more compelling and comprehensive evidences. Moreover, the effects of particle size and oxygen concentration on near-peak temperature are systematically studied. Finally, the morphology of combusted particles is briefly discussed, and the formation mechanisms are analyzed based on detailed thermochemical equilibrium calculations.

The paper is organized as follows. The material and experimental methodology are presented in Sections 2 and 3, respectively. The overview of the iron particle combustion process is described in Section 4.1. The particle temperature during the first plateau-like stage, the near-peak temperature, and the temperature near the brightness jump are elaborated in Sections 4.2, 4.3, and 4.4, respectively. The morphology of combusted particles and thermodynamic analysis of nano-oxide formation are discussed in Section 4.5, and finally the main conclusions are summarized in Section 5.

2. Material

Spherical particles within four narrow size fractions with arithmetic mean diameters of around 26 μm (A), 39 μm (B), 45 μm (C), and 54 μm (D), which were mechanically sieved from a commercial iron powder produced by TLS Technik GmbH & Co. (20–50 μm nominal particle diameter, 99.8% purity), were used in the current experiments. Figure 1 shows a scanning electron microscope (SEM) image of the unsieved powder. As can be seen, the shapes of most particles are approximately spherical, and there is no trace of nanoparticles. Particle size distributions were measured by taking images through a calibrated optical microscope and processing them using the ImageJ software [17]. As shown in Fig. 2, the width of the particle size distribution of each fraction spans around 10 μm. The arithmetic mean diameter and the standard deviation of each fraction are calculated and labeled in Fig. 2, which shows that the standard deviation of each fraction is approximately 10% of its mean diameter, and the gap between two consecutive fractions is about 10 μm.

3. Experimental method

3.1. Apparatus

The experimental setup is illustrated schematically in Fig. 3, which consists of three main components: (1) a particle generator, (2) a laser ignition system, and (3) an optical diagnostics setup for both time-resolved and near-peak temperature measurements. The particle generator and the ignition system have been described in
Fig. 3. Schematic of experimental setup (top view). The 2-inch cubic beam splitter is mounted 24 cm away from the particle generator with its bottom matching the burner tip. The high-speed cameras are triggered by a signal generator. The focusing direction of the collimating lens is normal to the laser beam. The spectrometer has a field of view about 2 cm in the vertical direction.

our previous work [14], such that only a brief description is given here for completeness. The particle generator is capable of producing mono-dispersed stream of single particles employing high voltage (~3 kV) to aerosolize metal powders within an enclosed chamber between two horizontal electrodes. Dispersed particles are carried out of the chamber through a small hole at the center of the top electrode by a gas stream (central jet), then vertically move up through a 10 cm long bronze capillary tube with the inner diameter of 0.45 mm. A 70 W, 915±10 nm infrared diode laser (by Changguang Rays Technology Co. Ltd), internally coupled with a 1 mW, 650±10 nm aiming laser, was adopted to ignite iron particles. The laser radiation is transferred via a 100 μm diameter single-core fiber-optical cable and focused at around 1 mm above the burner tip using a set of lenses assembled in a lens tube. The focal spot has an elliptical shape with horizontal (major) and vertical (minor) axes of ∼530 μm and ∼180 μm, respectively. The output power of the laser was set to 24 W, which was selected to minimize the effect of laser heating on particles’ combustion. Iron particles were reliably ignited when crossing the focused laser beam, while at lower powers, the ignition of a portion of particles failed. The ignited particles burned in a shroud flow with compositions identical to the central jet, which isolated the burning particles from ambient air and supported them to move vertically upwards. The velocities and compositions of both flows were regulated by mass flow controllers (Bronkhorst). During experiments, the velocity of the shroud flow was set to 70 cm/s, while the central jet velocity was controlled around 21–43 cm/s in order to keep the burning particles in the field of view of the high-speed cameras. The compositions of both flows were simultaneously adjusted in a range of 13–51% volumetric oxygen concentrations diluted by nitrogen. Combusted particles were collected during cooling down by a microscope slide mounted at 3 cm above the burner tip with a small magnet put on top of it. Burning particle streaks were recorded using a color camera working at a long-exposure mode. Particle temperature was measured by the optical diagnostics setup, which will be described in detail in the next section.

3.2. Optical diagnostics

3.2.1. Time-resolved temperature

To measure the temperature evolution of burning particles, a two-color pyrometer was built based on two synchronized Photron SA3 high-speed cameras (model 60K-4 GB). Light emission from a burning particle was split into 50%-50% portions using a cubic beam splitter (Thorlabs BS032) and then projected towards the high-speed cameras. Both cameras are equipped with an Irix 150 mm f/2.8 macro lens. Two near-infrared bandpass interference filters, with central wavelength of 850 nm and 950 nm and full width at half maximum of 10 nm, were chosen for the pyrometer. The filters wavelengths were selected for the sake of improving the signal intensity at lower temperatures and reducing the dynamic range of images.

The pyrometer was calibrated using a NIST certificated tungsten ribbon lamp over a temperature range of 900–2300 °C that was controlled by precisely supplied currents. Multiple images were recorded using different exposure time at each fixed lamp temperature. The average gray value of a selected 10 × 10 pixels area located at the center of the tungsten ribbon, where the brightness is also homogeneous, was calculated using Matlab’s image processing toolbox as a characteristic signal. As a typical example among calibration temperatures, Figure 4 shows that the measured signals increase linearly with an increasing exposure time before image saturation. The slopes of the linearly fitted lines represent the signal intensity per unit exposure time, which can be described as:

\[
S(T) = \alpha \int_{\Delta\lambda} \varepsilon_{1}(\lambda) I_{\lambda, \beta}(T) d\lambda,
\]  

(1)
where \( \alpha \) is the instrument constant, which is a combination of the effective transmissivity of all optical components and quantum efficiency of the photon detector (CMOS) of the camera amongst others; \( \varepsilon_\lambda \) is the spectral emissivity of tungsten, and \( \lambda \) is the spectral intensity of black body radiation, well described by Planck’s law. As the \( \Delta \lambda \) adopted for the two cameras is identical and sufficiently small, the signal ratio between \( \lambda_1 = 850 \) nm and \( \lambda_2 = 950 \) nm can be simplified as:

\[
\frac{S_1}{S_2} = \frac{\alpha_1}{\alpha_2} \frac{\varepsilon_{\lambda_1} I_{\lambda_1,b}}{\varepsilon_{\lambda_2} I_{\lambda_2,b}}
\]

\[
\frac{S_1}{S_2} = 7.645 \cdot \frac{\varepsilon_{\lambda_1} I_{\lambda_1,b}}{\varepsilon_{\lambda_2} I_{\lambda_2,b}}
\]

where \( \frac{\alpha_1}{\alpha_2} \) is a calibration coefficient that can be computed using the measured signal ratio, \( \frac{S_1}{S_2} \), and the theoretical values, \( \frac{\varepsilon_{\lambda_1} I_{\lambda_1,b}}{\varepsilon_{\lambda_2} I_{\lambda_2,b}} \), of tungsten at selected wavelength and temperature. The spectral emissivity of tungsten summarized in [18] was used to calculate the calibration coefficient. Figure 5 shows the measured signal ratios plotted versus the theoretical value. The calibration coefficient was then determined by the slope of the linear fit.

The radiant intensity (integrated gray values of pixels over the whole glowing area of a single particle) histories of the burning particles at 850 nm and 950 nm were recovered by post-processing high-speed camera images using an in-house MATLAB code [14]. Using the measured ratio evolution of radiant intensity between the two wavelengths, and Wien’s approximation, the time-resolved particle temperature can be derived as:

\[
T(t) = \frac{C_2 \left( \frac{1}{\lambda_2} - \frac{1}{\lambda_1} \right)}{\ln \left( \frac{\varepsilon_{\lambda_1} I_{\lambda_1,b}}{\varepsilon_{\lambda_2} I_{\lambda_2,b}} \right) + 5 \ln \left( \frac{\varepsilon_{\lambda_2} I_{\lambda_2,b}}{\varepsilon_{\lambda_2} I_{\lambda_2,b}} \right) + \ln \left( \frac{\varepsilon_{\lambda_1} I_{\lambda_1,b}}{\varepsilon_{\lambda_1} I_{\lambda_1,b}} \right)}.
\]

where \( C_2 \) is the Planck’s second radiation constant. It is difficult to determine the ratio between \( \varepsilon_{\lambda_2} \) and \( \varepsilon_{\lambda_1} \) due to the lack of detailed spectral emissivity of iron and iron oxide at the concerned temperature range. According to the emission spectra of iron dust flames [4,8], when burning iron in high-pressure oxygen [19] and burning iron particles in condition considered in our work that will be given in Section 4.3, no considerable dependency of emissivity on wavelength is observed. Therefore, the gray-body assumption, i.e., \( \frac{\varepsilon_{\lambda_2}}{\varepsilon_{\lambda_1}} = 1 \), is adopted. Normally, this assumption is applicable when the used wavelengths are close to each other.

The measurement accuracy of the two-color pyrometer is evaluated by re-measuring the tungsten ribbon lamp temperatures and comparing with the real temperatures. Figure 6 shows the comparison between the measured lamp temperatures and the real ones in the temperature range of around 1300–2500 K that is similar to the concerned temperature variation of burning iron particles. The root-mean-square error of the measurement is 78 K.

3.2.2. Peak temperature approximation

An infrared spectrometer (by StellarNet Inc.) covering the wavelength range of 877–1755 nm with a resolution of around 1.75 nm was used to measure the time-integrated spectra of burning particles. The spectrometer was calibrated using the same lamp, and calibration coefficients as a function of wavelength were obtained by comparing the measured spectrum with the subtraction of background noises and the theoretical one calculated using Planck’s law and the temperature-dependent spectrum emissivity of tungsten [18]. In the experiments, light emissions from incandescent particles burning within a 2 s duration were collected by a collimator and transferred to the spectrometer via a fiber-optic...
cable. The collimator was mounted 15 cm away from the burner tip, which is identical to the distance from the tungsten ribbon during calibration. The measured raw spectrum was corrected by first subtracting the background noise and then being multiplied by the calibration coefficients. The measured spectra over a wavelength range of 1000–1600 nm, in which the spectrometer has a relatively strong sensitivity, were selected to determine the particle temperature.

Assuming the emissivity of iron to be independent of wavelength (grey body), the temperature was determined by fitting Planck's law to the measured spectrum based on the least-squares method (i.e., multi-wavelength pyrometry). The time-integrated spectrum is dominated by the radiation of particles near the maximum temperature. Therefore, the spectrometer-measured temperature is close to the peak temperature of particles, and dominated by relatively hot particles.

4. Results and discussion

The general combustion behavior of a laser-ignited iron particle is introduced first. The identification of particle melting, the quantification of peak temperature, and the discussion of the radiation jump (spear point) mechanism follow. Finally, the morphology of combusted particles and thermodynamic analysis of nano-oxide formation are addressed.

4.1. Combustion behavior

Due to the very large temperature variation during the whole combustion process of a burning iron particle (> 1000 K), the recorded images either got saturated near the high temperature stage (c.f. Fig. 7, stage 2) or not detected at the low temperature stages (c.f. Fig. 7, stages 1 and 3). Therefore, the particle temperature during different stages of combustion had to be measured by varying exposure times. For an overview of the burning process stages of an iron particle, the evolution of radiant intensities, obtained by processing images recorded with relatively long exposure time of 0.5 ms and filtered at 850 nm and 950 nm, are shown in Fig. 7. As can be seen, the particle is first detected in the laser beam (red shaded area), and the intensities increase very quickly afterwards. The laser heating time was estimated by matching the vertical position of a burning particle in the images with that of the laser beam upper boundary, which was determined by using the last detected location of a cold particle passing the red aiming laser beam [14]. Shortly after the particle leaving the laser beam, the intensities reach a plateau-like stage at around 2.5 ms. After the plateau period lasting for about 2 ms, the intensities keep increasing until reaching the peak at 20 ms. Some pixels on the recorded particle image get saturated before the peak. Thereafter, the intensities smoothly decrease until 45 ms, where the intensity increases abruptly again leading to a spear-like streak as shown in Fig. 8. Finally, the intensities decrease again until becoming undetectable.

The whole process is divided into three stages based on whether radiant intensity at 850 nm gets saturated or not (c.f. Fig. 7). The particle temperature was measured for each stage separately by adjusting the exposure time of two high speed cameras. These fascinating phenomena, i.e., initial plateau in stage 1 and radiation jump of stage 2, will be explained in the following based on the measured temperature.

4.2. Interpretation of the initial radiant-intensity plateau of stage 1

Figure 9 shows the light emission profile and temperature evolution during stage 1 for two particles with similar diameters of 56 μm and 58 μm burning at 21% and 26% oxygen concentration.
respectively. The particle size is determined from a correlation between particle diameter and time to maximum brightness reported in our previous work [14]. As can be seen from the intensity profiles, the plateau starts at 3 ms and lasts for 3 ms at 21% O₂ and 2 ms at 26% O₂, which indicates that the physical and/or chemical process corresponding the plateau is faster at a higher oxygen concentration. The radiant intensity plateau also suggests that the particle temperature keeps unchanged for a short while. From these features, the process is speculated to be particle melting. The measured temperature fluctuates between 1750 K and 1850 K during the plateau instead of remaining constant, which may be attributed to random errors involved in the measurement. Statistics were conducted for the measured particle temperature during the plateau period. Figure 10A shows a typical histogram for particles burning in 21% oxygen concentration. The average particle temperature is 1777 K, which is very close to the reported melting point of iron (1809 K) [20] and deviates only by 1.8%. As shown in Fig. 10B, the average temperatures measured at various oxygen concentrations show negligible differences as expected for a melting process. Thus, it can be strongly argued that the initial plateau of the radiation emission profile results from iron particle melting.

By assuming diffusion-limited combustion and neglecting iron consumption for simplicity, the melting time, \( t_{\text{melt}} \), of an iron particle can be easily evaluated based on energy balance:

\[
m_p \Delta H = t_{\text{melt}} (\dot{Q}_{\text{comb}} - \dot{Q}_{\text{cond}} - \dot{Q}_{\text{rad}}).
\]

where \( m_p \) is the initial particle mass (in mole); \( \Delta H \) is the enthalpy of fusion during melting per mole of iron, \( \dot{Q}_{\text{comb}} \) is the heat release rate of combustion, \( \dot{Q}_{\text{cond}} \) and \( \dot{Q}_{\text{rad}} \) are the conduction and radiation heat transfer rate, respectively. \( \dot{Q}_{\text{comb}} \) can be calculated by \( \dot{Q}_{\text{comb}} = \dot{m}_{\text{O}_2} \Delta H_{\text{ox}} / S \), where \( \Delta H_{\text{ox}} \) is the oxidation enthalpy (per mole of iron), \( S \) is the oxygen-to-fuel stoichiometric ratio, \( \dot{m}_{\text{O}_2} \) is the oxygen consumption rate (mole per second) limited by diffusion, which can be evaluated by:

\[
\dot{m}_{\text{O}_2} = \pi d_p^2 \rho_b \tau D_{\text{O}_2} (Y_{\text{O}_2,5} - Y_{\text{O}_2,1})/M_{\text{O}_2}.
\]

where \( d_p \) is the particle initial diameter; \( S \) is the Sherwood number assumed to be \( \approx 2 \) for diffusion-dominated mass transport [21], \( \rho_b \) and \( D_{\text{O}_2} \) are gas density and O₂ diffusivity at reference temperature 1040 K based on the 1/2 rule [22], respectively. \( Y_{\text{O}_2,5} \) is the oxygen mass fraction in the bulk and \( Y_{\text{O}_2,1} \) is that adjacent to the particle surface in the gas phase. For the diffusion limited combustion regime, \( Y_{\text{O}_2,1} = 0 \). \( M_{\text{O}_2} \) is the O₂ molar mass. \( \dot{Q}_{\text{cond}} \) can be calculated by:

\[
\dot{Q}_{\text{cond}} = \pi d_p \rho \lambda (T_p - T_\infty).
\]

where \( \rho \) is the density and \( \lambda \) is the gas conductivity at the reference temperature, \( T_p = 1809 \) K and \( T_\infty = 300 \) K are the particle and bulk temperature, respectively. \( \dot{Q}_{\text{rad}} \) can be calculated using the Stefan-Boltzmann law with an emissivity of 0.7 [23]. This term is less important because it is only about 10% of \( \dot{Q}_{\text{cond}} \) at the melting point. As the particles start to melt outside the laser beam, the laser radiation has no contribution to particle melting. Table 1 shows a comparison between the measured and estimated melting time when forming 3 types of stoichiometric iron oxides. The measured melting times are determined by the duration of the initial plateau-like stage of the recorded radiant intensity at 850 nm. The assumption of forming different iron oxides has a small influence on the estimated melting time. This is because the heat release rate is limited by O₂ diffusion, and the heat of combustion is 542 kJ/mol, 561 kJ/mol and 549 kJ/mol when one mole of O₂ is consumed for forming FeO, Fe₂O₃ and Fe₃O₄, respectively. As can be seen, the theoretical analysis overestimates the particle melting time compared to the experimental data. The overestimation might result from several aspects: (1) as oxygen is consumed at the particle-gas interphase, Stefan flow that enhances the mass transfer is induced but is neglected in the theoretical analysis; (2) the convective oxygen mass transfer due to the slip velocity between gas and particle is also neglected; (3) it is possible that FeO formed during solid state oxidization of iron melts already before iron melting. Nevertheless, the estimated and measured melting times show the same trend and the absolute values are reasonably close. This suggests that iron particle is ignited at solid state and burns in a regime close to the diffusion-limited one during melting. In addition, the overestimation does not imply that the particle burns in an intermediate regime where a longer melting duration is expected because of a slower particle burning rate. An accurate prediction for the melting time and the identification of combustion regime for burning iron particle in the solid state require detailed numerical modeling that will take all the above-mentioned aspects into account.

### 4.3. Effects of particle size and O₂ concentration on particle temperature of stage 2

Figure 11A shows typical temperature and light emission evolution in stage 2 for a particle in the size fraction D (mean particle diameter \( < d > = 54.34 \mu m \)) burning at 21% oxygen concentration. The temperature and radiant intensity (in logarithmic scale) have a similar profile. Initially, the temperature increases roughly linearly from around 1700 K to approximately 2400 K near the peak radiant intensity. The temperature then decreases together with the radiant intensity, and no plateau is found in stage 2. Furthermore, based on the observed temperature profile that is approximately linear during particle cooling, heat release from oxidization probably still exists, otherwise the particle temperature would decrease significantly.
smoothened temperature profile is obtained using the moving average filter, “smooth”, in Matlab. Fig. 12 shows peak temperature distributions for four oxygen concentrations. The distribution of measured particle peak temperatures for 21% oxygen is relatively broad, ranging from 2100 K to 2800 K, compared to the distribution of measured melting temperatures (cf. Fig. 10). The broad distribution is thought to be partly related to nano iron oxides (particles) as it will be discussed in Section 4.5, which cannot be assumed as a grey-body and distorts the light emission from the micron-size particle. Because there is only limited information near the 2 wavelengths for two-color pyrometry, any distortion at either wavelength may produce a nonnegligible impact on the measured temperature. A similar broad distribution of iron flame temperatures was also found when nano iron oxides are formed, reported in literature [7]. Similarly, at higher oxygen concentrations, broad temperature distributions ranging from 2300 K to 3000 K are also observed. The average temperature increases from 2440 K at 21% O₂ concentration to around 2600 K at 26–36% O₂ concentrations. The less noticeable temperature difference among 26% and 36% O₂ concentrations could be due to the fact that actual differences becoming smaller than the measurement uncertainty, which can be seen from Fig. 13 (only a 50 K difference between two consecutive O₂ concentrations).

Figure 13 shows the spectrum-deduced temperatures as a function of oxygen concentration and mean particle diameter. Each measurement point and its error bar originates from 10 to 18 runs under identical experimental conditions. The spectrum-deduced temperatures have a smaller standard deviation of around 3% as compared to the two-color pyrometer, which means that the temperatures measured by the spectrometer are quite close to each other. As the radiant intensity in a wide range of wavelengths is available for determining particle temperature based on an overall intensity distribution, the uncertainty at any individual wavelength has less influence on the temperature determination. Thus, the spectrometer was systematically used to measure near-peak temperatures for distinguishing the effects of particle size and oxygen concentration on particle temperature. As can be seen from Fig. 13, at higher O₂ concentrations, differences among temperatures of different sized particles are more noticeable. A larger particle has a higher temperature, which can be explained by less radiation heat loss due to a smaller surface-to-volume ratio than for a smaller particle. On the contrary, temperature differences among different-sized particles become less significant with de-
creasing O₂ concentrations. This is probably because the radiation heat loss plays a less important role when the particle temperature becomes smaller at a lower oxygen concentration. From an overall perspective, the temperature first increases rapidly with increasing oxygen concentration, while from approximately 31% O₂ is less influenced for all particle sizes. The observed temperature trends versus oxygen concentration can be described by the function: \( T = a - b \exp(-cO₂) \), where \( a, b, \) and \( c \) are coefficients listed in Fig. 13. The less noticeable differences between temperatures of similar-sized particles at relatively high oxygen concentrations can be partially attributed to a stronger radiation heat loss. Additionally, the endothermic dissociation of liquid Fe₂O₄ at around 2600 K could play a crucial role in limiting the particle peak temperature, as will be discussed in Section 4.5.2.

4.4. Mechanism of the radiation jump of stage 3

In order to describe the mechanism of radiation jump (spear point), the temperature evolution in stage 3 is examined, and the temperatures right before \((T_{sp-})\) and after \((T_{sp+})\) the radiation jump are statistically analyzed in this subsection. Figure 14 shows the temperature and radiant intensity evolution in stage 3 for two particles with a similar diameter. Different magnitudes of radiation jump can be observed. As shown in Fig. 14A, the particle radiant intensity decreases first and then reaches a plateau-like stage before considerably decreasing again. No noticeable radiation jump observed for this case. Similar to the trend of radiant intensity, the particle temperature decreases from around 2000 K, which is above the melting points of iron oxides, to approximate 1750 K, and keeps fluctuating between ~1750 K and ~1800 K during the plateau-like stage. By checking the Fe-O phase diagram [25], the particle temperature during the plateau-like stage is very close to two phase-transition temperatures: 1) L2 \(< \leftrightarrow\> \text{Fe}_2\text{O}_4 (s) \) at 1869 K (congruent solidification) and 2) L2 \(< \leftrightarrow\> \text{Fe}_2\text{O}_4 (s) + \text{O}_2 (g) \) at 1855 K (eutectic reaction), where L2 represents liquid iron oxide. This suggests that the particle undergoes the solidification process during the plateau-like stage: phase transition from a molten iron oxide droplet, with atomic O content around 3/4 or more, to solid Fe₂O₄. The very slight decrease of the radiant intensity during the second plateau-like stage can be explained by particle shrinking when it solidifies. As shown in Fig. 14B, the arbitrary radiant intensities of another 55 μm burning particle abruptly jump from 0.6 to 2 at 48.5 ms. The jump can be more clearly observed from the recorded radiant intensity at 850 nm by a relatively strong signal. By increasing the frame rate to 5000 fps, usually, one or two frames can be covered over the jump, which means the jump happens in a timescale of ≤0.4 ms. Furthermore, a considerable temperature change, suddenly increasing from around 1630 K to 1870 K, results in the brightness jump. This abrupt temperature increase cannot be due to a random error because the particle temperature after the jump is systematically higher than before the jump for several milliseconds. A comparable temperature jump from ~1670 K to ~1970 K measured by using a brightness pyrometrical transducer for steel particle is reported by Dreizin et al. [16]. Therefore, the temperature jump eliminates the hypothesis that the radiation jump is caused only by a sudden change of emissivity, and it indeed results from a fast heat release. Similarly, radiation jumps of Zr and Ti particles burning in air, however accompanied with micro-explosion near the end of combustion, were investigated by Molodetsky et al. [26,27]. They hypothesized that this phenomenon is associated with nitrogen gas release from the reaction between metal nitride, formed in the early stage of combustion, and oxygen. By replacing nitrogen with argon in our experiments, the spear point occurs as well, which suggests that the nitrogen release is unlikely the reason for the temperature jump of burning iron particle. From those characteristics, the jump is speculated as crystallization/solidification of a supercooled molten O/Fe droplet, which starts at a temperature below the melting point, and then the droplet solidifies rapidly with fast latent heat release that heats the particle up to the melting point. Another evidence that supports the hypothesis that jump is caused by liquid oxide overcooling comes from comparing the plateau durations for cases when jump is absent and when it is present. As seen in Fig. 14, the plateau is significantly shorter in the second case, which can be explained by the fact that a significant fraction of liquid oxide solidifies during the jump, while in the case of the absence of the jump, solidification begins at the onset of the plateau.

For particles showing a considerable radiation jump similar to Fig. 14B (for 86% particles), statistics are determined for \(T_{sp-}\) and \(T_{sp+}\), which are temperatures averaged over 1 ms just before and after the brightness jump in order to reduce random errors. Figure 15 shows representative histograms of \(T_{sp-}\) and \(T_{sp+}\) for particles within size fraction D (mean particle diameter \(d = 54.34 \mu m\)) burning at 21% O₂. The average value of \(T_{sp+}\) is about 180 K higher than that of \(T_{sp-}\). Figure 16 shows the measured average \(T_{sp-}\) and \(T_{sp+}\) for fraction D burning at different O₂ concentrations. As expected for solidification, there is no significant influence of O₂ concentration on \(T_{sp-}\) and \(T_{sp+}\).
exact O content can not be determined from the measured temperature as the solidification temperatures of liquid iron oxide with an O percentage of around 3/4 or higher are very close. Based on the measured solidification temperate, FeO can be eliminated for the adopted O2 concentrations due to its relatively low melting point of 1650 K [20]. Additionally, the latent heat release from the entire volume of the supercooled liquid Fe3O4 droplet is more than sufficient to trigger a 600 K temperature jump, which is estimated based on the heat capacity, \( C_p = 200/\text{mol/K} \), and the latent heat of fusion, \( \Delta H = 138K/\text{mol} \), of Fe3O4 according to the NASA Glenn thermodynamic database [28]. Therefore, only part of the supercooled droplet solidifies during the temperature jump up to the melting point, and hereafter the solidification is controlled by heat losses. This is the reason why a plateau-like stage right after the temperature jump (c.f. Fig. 7) is observed.

4.5. Morphology of combusted particles and nano-oxide formation

4.5.1. Morphology of combusted particles

Captured combustion products are examined by an optical microscope and a SEM. Figure 17A1–C1 show optical microscope images of the combustion products captured at 13%, 16%, and 51% O2 concentration, respectively (for 21–36% O2 concentrations, the morphology of combustion products and amount of nano oxide

![Figure 16](image1.png)

**Fig. 16.** Measured \( T_{p-} \) and \( T_{p+} \) as a function of oxygen concentration for the particle size fraction D. The error bars represent the standard deviation of measurement. The red and blue dotted lines indicate the solidification temperatures of \( L_2 \leftrightarrow Fe_3O_4(s) \) and \( L_2 \leftrightarrow Fe_3O_4(s) + O_2(g) \), respectively.

As indicated by the red and blue lines in Fig. 16, \( T_{p+} \) agrees well with the two solidification temperatures of liquid iron oxide with an O atomic percentage of 3/4 (Fe3O4) or higher. However, the

![Figure 17](image2.png)

**Fig. 17.** Optical microscope images (first row) and SEM images (second to forth rows) of combusted particles captured at 13% (A1–A4), 16% (B1–B4) and 51% (C1–C4) O2 concentration. Original average particle diameter is 45 \( \mu \text{m} \).
are similar to the case of 51% O$_2$ concentration, which have been shown our previous work [14]. Spherical particles similar to their original size are found. At the same time, traces of nano oxides are observed. From normal to higher oxygen concentrations, the produced nano oxides are more significant, and the nano oxides present a “hairy” morphology. Sometimes, a thick cluster of nano oxides adhering to a micron-sized particle can be found, which gives a tail-like shape as indicated by the red arrow in Fig. 17B1. This shape can be more clearly seen from SEM images given in Fig. 17A2, C2, and A3–C3. As shown by Fig. 17A2–C2, the combusted micron-sized particles are almost perfectly spherical and have a very smooth surface, which results from the surface tension of a molten particle. However some particles present a cracked hollow spherical shell structure, similar to burned particles of Al [29] and Al/Zr alloys [30,31], as shown in Fig. 17A4 and B4, while Fig. 17C4 shows a fully broken shell. These hollow shells would be relevant to particle micro-explosions happening near the peak temperature for a portion of the particles, which may be due to internal gas release during combustion. If a particle does not explode, the released gases are trapped inside the particle in the form of a bubble in liquid iron oxide. When cooling down, the thin liquid iron oxide film will solidify and form a hollow thin-shell structure. Internal bubbling in burning Al/Zr particles has been directly observed earlier via x-ray phase contrast imaging, which resulted in a micro-explosion during combustion or a hollow sphere [31]. Another possible mechanism is the rapid O$_2$ release during the solidification of supercooled iron oxide droplets as indicated by the eutectic reaction: L2 $\leftrightarrow$ Fe$_3$O$_4$ (s) $\leftrightarrow$ O$_2$ (g) at 1855 K. For iron particles, further studies need to be conducted in order to fully understand the mechanisms of the micro-explosion and hollow sphere formation.

4.5.2. Thermodynamic analysis of nano-oxide formation

During combustion of molten iron particles, vapor phase iron and oxides may originate from three liquid components: Fe(l), FeO(l) and Fe$_2$O$_3$(l), which contribute to nano-oxide formation. Note that FeO(l) is not present in the liquid phase under normal pressure because it dissociates to Fe$_2$O$_3$(cr) and O$_2$(g) at 1730 K [25]. To evaluate the formation mechanism of nano-oxides, detailed thermochemical equilibrium calculations were performed for pure Fe(l), FeO(l), and Fe$_2$O$_3$(l) at 2000–3500 K (1 atm) using Cantera 2.4.0 [32]. The thermochemical properties of all Fe-containing species were introduced from the NASA Glenn thermodynamic database [28] except for FeO$_3$(g), which was adopted from Goos et al. [33] as it is missing in the NASA database. The computational results show that vapor-phase iron and oxides originate from R1: Fe(l) $\leftrightarrow$ Fe(g) (evaporation), R2: FeO(l) $\leftrightarrow$ O(g) + O$_2$(g) + Fe(g) + FeO(g) + Fe$_2$O$_3$(g) (dissociation), and R3: Fe$_2$O$_3$(l) $\leftrightarrow$ FeO(l) + O(g) + O$_2$(g) + Fe(g) + FeO(g) + Fe$_2$O$_3$(g) (dissociation). Figure 18 shows the equilibrium vapor pressure of all gaseous Fe-containing species generated from Fe(l), FeO(l) and Fe$_2$O$_3$(l), respectively, as a function of temperature at normal pressure, and corresponding boiling/dissociation point. The calculated boiling point of iron is 3140 K, which is in very good close agreement with the value (3133 K at 0.1 MPa) reported in the NIST-JANAF table [20]. Besides, the calculated dissociation point of FeO(l) is 3396 K, which is lower than the values calculated for simpler dissociation reactions: FeO(l) $\leftrightarrow$ Fe(g) + O(g) (3678 K) and FeO(l) $\leftrightarrow$ Fe(l) + O$_2$(g) (3573 K) [34]. Moreover, a higher Fe$_2$O$_3$(l) dissociation point (2603 K) is found than that (2257 K) calculated for the dissociation reaction: Fe$_2$O$_3$(l) $\leftrightarrow$ FeO(l) + O$_2$(g) [34]. As can be seen, below 2603 K, the vapor pressure of Fe(g) evaporating from Fe(l) is more than one order of magnitude higher than that of all Fe-containing species dissociated from FeO(l) and Fe$_2$O$_3$(l) at the same temperature. Therefore, the observed few traces of nano-oxide particles at reduced oxygen concentration conditions are likely formed during the vapor-phase oxidation of Fe(g) evaporated from Fe(l). Once the temperature reaches the Fe$_2$O$_3$ dissociation point, the formation rates of Fe(g), FeO(g), and Fe$_2$O$_3$(g) in R3 increase significantly. The released gaseous Fe-containing species from R3 at the dissociation point have the composition of 45% FeO(g), 34% Fe$_2$O$_3$(g), and 21% Fe(g) (note that the main gaseous product in R3 is O$_2$, about 99.8% of all gaseous species, which is excluded when calculating the composition of gaseous Fe-containing species). Thus, the observed nano-oxides mainly dissociated from Fe$_2$O$_3$(l) at elevated oxygen concentration conditions where particle peak temperatures can reach the Fe$_2$O$_3$(l) dissociation point.

5. Conclusions

Time-resolved temperature measurements are presented for single laser ignited iron particles, as well as near-peak temperatures deduced from time-integrated spectra for various conditions (particle size and O$_2$ concentration). The near-constant brightness stage observed shortly after ignition is indicated as iron melting by measured temperature. Besides, the estimated melting duration of an iron particle based on diffusion-limited combustion assumption agrees well with measurements at two oxygen concentrations, which is another strong evidence for the iron-melting hypothesis. Based on the observation of different degrees of brightness jump and corresponding temperature measurement at the shoulder of the spearpoint, the mechanism of the brightness jump can be well explained as the sudden crystallization of a supercooled iron oxide droplet with O content close to Fe$_2$O$_3$ or higher. In addition, there was no plateau-like combustion stage in the high temperature phase found in the time-resolved particle temperature behavior.

Near-peak temperatures of different-sized particles burning at 13%–51% oxygen concentration were determined by fitting Planck’s law to the measured spectra. The near-peak temperature as a function of oxygen concentration can be well described by an expression: $T = a - b \exp(-cO_2)$ with varying coefficients for different particle sizes used in the present study. At higher oxygen concentration, particle size has an obvious impact on the near-peak temperature due to the more important role of radiation, which leads to a lower temperature for smaller particles. On the contrary, at lower oxygen concentrations, there is no significant difference among the near-peak temperatures of different-sized particles. Furthermore, the dissociation of liquid Fe$_2$O$_3$ could play an important

![Fig. 18. Vapor pressure of released gaseous iron and oxides from Fe(l) evaporation and FeO(l) and Fe$_2$O$_3$(l) dissociation as a function of temperature at a total pressure of 1 atm.](image-url)
role in limiting particle peak temperature at elevated oxygen concentrations.

Com busted particles were captured and examined via an optical microscope and SEM. Some particles appeared as a hollow thin-shell sphere for all oxygen concentrations adopted, which could result from the solidification of a liquid oxide with a bubble inside that formed due to gas release at higher particle temperature or from the eutectic reaction: \(^{\text{L2}} \leftrightarrow \text{Fe}_2\text{O}_4 \ (s) + \text{O}_2 \ (g)\) at 1855 K. Furthermore, small amount of nano-oxides showing a “hairy” structure was still observed at reduced oxygen down to 13%, while at elevated oxygen, considerably more nano-oxides with the same structure was found. The thermochemical equilibrium calculations suggest that minor nano-oxide particles originate from vapor-phase oxidation of \(\text{Fe}(g)\) evaporated from \(\text{Fe}(l)\) below 2603 K, while above the temperature, considerably more nano-oxide particles could be generated from \(\text{Fe}_2\text{O}_4(l)\) dissociation, which matches the experimental observations.

Declaration of Competing Interest

There is no conflict of interest for this work.

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