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Influence of silicon on micro-sized iron powder combustion

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Abstract

Long-term energy storage and transportation are essential for a successful transition to renewable energy sources. Metal fuels offer a promising solution, thanks to their high volumetric energy density and stability under ambient conditions, making them strong candidates for CO₂-free energy carriers. In the form of micron-sized powder, iron combustion and the reduction of its oxides can deliver and store energy, respectively. The understanding of pure iron powder combustion is gradually improving thanks to a growing number of studies. From an economical and sustainable perspective, the combustion of iron powder containing impurities is interesting, expanding metal sources and limiting refining costs. In the present work, the influence of silicon is studied, with 20-63 μm powder containing 92.7 wt.% of iron and 7 wt.% of silicon (Fe-7Si). Metal cyclonic combustor (MC2) was used to examine the combustion performance of Fe-7Si powder compared to pure iron in similar conditions. An increase in the preheating temperature to 930 °C was required to sustain a partially stable flame of Fe-7Si. Isothermal thermogravimetric analyses (TGAs) of oxidation with air from 540 °C to 1200 °C show slower oxidation kinetics compared to pure iron. Silicon oxidizes first to SiO₂, as predicted by thermodynamics, but hematite and fayalite formation occurs before silicon is fully oxidized. After combustion in the MC2 and oxidation with TGAs, the resulting oxidized powders were analyzed with a scanning electron microscope (SEM) equipped with an energy dispersive spectrometer (EDS), as well as an X-ray diffraction (XRD) system. Based on the results, a model of iron-silicon particle ignition was developed, predicting an increase in the ignition temperature from 810 °C for pure iron to 947 °C for Fe-7Si.

Nomenclature

λ	Equivalence ratio
$\nu_{x/y}$	Stoichiometric mass ratios
Fe_2O_3	Hematite
Fe_2SiO_4	Fayalite
Fe_3O_4	Magnetite
FeO	Wüstite
SiO_2	Silica
ρ_x	Density of x
A_p	Area of particle
D_a	Area diameter
E_a	Activation energy
h	Internal energy
H_p	Particle energy
h_p	Convection coefficient
k_p	Parabolic grow rate
m	Mass
q_x	Formation energy of x
T_g	Gas temperature
T_p	Particle temperature
W	Molar mass
Z_x	Oxide layer thickness
BET	Brunauer–Emmett–Teller
BSE	Backscattering electrons
EDS	Energy dispersive spectrometer
Fe-7Si	Iron-silicon powder containing 7 wt.% of silicon
ICP-OES	Inductively coupled plasma optical emission spectrometry
MC2	Metal cyclonic combustor
SE2	Secondary electrons
SEM	Scanning electron microscope
TGA	Thermogravimetric analysis
XPS	X-ray Photoelectron Spectroscop
XRD	X-ray diffraction

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Chapter 1

Introduction

To break free from fossil fuels, researchers are exploring alternative energy sources. Several options have already been investigated, including renewable energy such as biomass, hydropower, geothermal energy, solar, and wind.

For biomass, the problem of local emissions persists because the energy is mainly generated by burning complex organic fuels, which release CO_2 , NO_x , and SO_x as by-products of combustion. To reduce as much as possible pollutant emissions, filters and carbon capture technologies can be used. In addition, biomass resources must be managed sustainably to avoid biodiversity destruction. Today, because of its association with deforestation and direct pollutant emissions, despite filters, carbon capture development, and sustainable management, biomass has a poorer reputation compared to other renewable energy sources.

Hydropower and geothermal energy offer many advantages, but in Europe, most of the optimal sites have already been exploited. As a result, their further development is generally limited to specific locations, with local-scale impact and relatively low power output.

Intermittency is one of the major problems with solar and wind energy. However, both solutions appear to be the most commonly used worldwide as they are installed in large capacities. The challenge is to ensure access to energy at all times of the day and throughout the year to prevent potential blackouts or other major electricity problems, as it was the case in Spain and Portugal in April 2025. Transitioning to full production of renewable energy requires the development and large deployment of storage technologies. During high-energetic production and low-demand periods, energy could be stored to be used later.

In a very short term, machinery inertia, flywheels, and automatic regulation are mostly sufficient to sustain network stability. Storage can be reliable on a daily basis since solar panels cannot produce electricity at night, for example. To achieve this, home-sized batteries, V2G (vehicle-to-grid), and various other solutions have already been developed or are in use.

However, long-term storage also represents a significant part of the challenge. One potential solution, in addition to existing pumped-hydro storage, could be the transportation of renewable energy from areas with abundant resources, such as regions with more sunlight, stronger winds, and other favorable conditions. In such a scenario, a ship of empty batteries is sent to recharge them and send them back to the energy-lacking country.

Lithium or lead batteries could provide a solution, but they require a lot of space, are expensive and heavy, and raise environmental concerns.

An alternative for energy transportation in ships is chemical storage using synthetic fuels. One of the widely developing solutions is the production of hydrogen by water electrolysis with the excess of renewable energy. H_2 has a great combustion capacity with a huge gravimetry energy density, about 142 [MJ/kg]. In reality, the volumetric energy density is very small, about 0.011 [MJ/L], and the conditions to keep H_2 in transportable conditions are extreme ($T = \sim 20$ K). Transforming H_2 into alternative fuels facilitates easier storage and handling, thereby improving the cost-effectiveness of on-board applications. The objective is to utilize green hydrogen in combination with nitrogen to synthesize ammonia (NH_3), or with carbon dioxide to produce methane (CH_4) or methanol (CH_3OH). However, these fuels may still generate carbon or nitrogen oxides (NO_x), resulting in localized emissions. Moreover, significant challenges persist regarding maritime transport and production efficiency.

Hydrogen, which is widely used in metallurgy, also has excellent properties for metal reduction, since it effectively extracts oxygen from metal ores. In fact, once a metal is heated to a certain temperature, it readily oxidizes, releasing energy in the form of heat. To facilitate rapid and self-sustaining oxidation, metal fuels are reduced to micro- or millimeter-sized powders, maximizing their surface area and contact with air. In this sense, metal fuels could serve as energy carriers because they are stable under normal conditions and have a high volumetric energy density, making them well-suited for ship transportation, see Figure 1.1. Iron is also an attractive metal fuel due to its abundance and low cost.

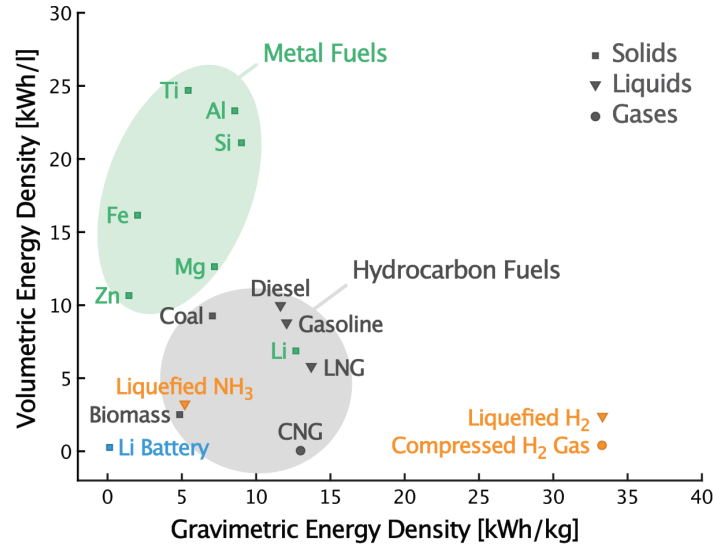


Figure 1.1: **Comparison of volumetric and gravimetric energy densities.** Metal fuels exhibit a higher volumetric energy density compared to other fuels such as hydrogen (H_2), [1].

The reduction process of the iron oxide is well developed. A key advantage is its cyclability, as illustrated in Figure 1.2: once burned, the resulting iron oxide can be reduced and reused, forming a closed cycle. In this cycle, iron combustion provides heat when renewable energy is insufficient. This heat can be used directly or converted into electricity. The oxidized powder can then be transported to regions with a surplus of renewable energy, where it is reduced back to iron using hydrogen.

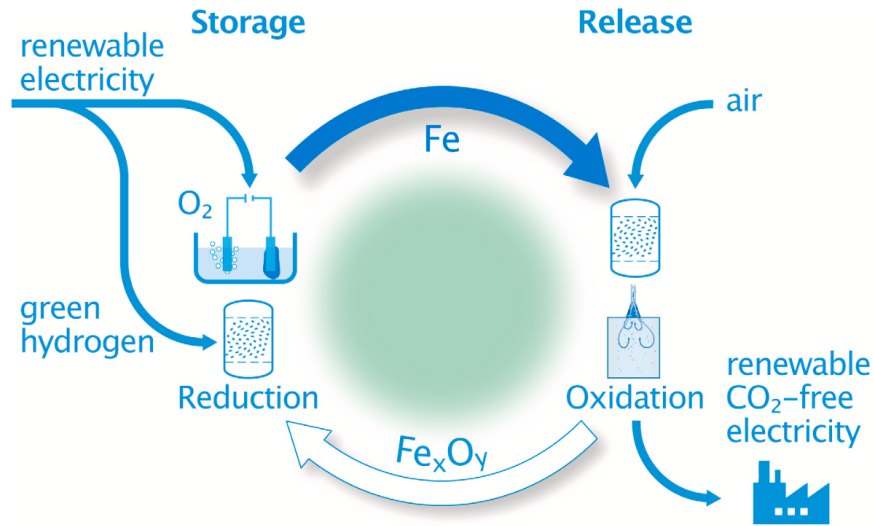


Figure 1.2: **Iron powder cycle**, [1]

Although the iron fuel cycle is promising, it involves losses, such as nanoparticle emissions, residual unburned iron, and thermal NO_x due to the use of air as an oxidizer. Nonetheless, emissions remain far lower than those from fossil fuels. Extensive research, including single-particle combustion studies, has improved the understanding of the fundamental mechanisms to mitigate these effects. Larger-scale experiments, like those in [2], examine particle interactions during combustion.

Another key consideration in deploying this technology is its feasibility and compatibility with existing infrastructure. The energy transition must proceed rapidly, yet building new power plants is costly, time-consuming, and spatially constrained. This is a major barrier to hydrogen implementation: despite growing interest, the infrastructure for using hydrogen as a fuel remains largely undeveloped, posing a significant challenge, though emerging technologies offer some promise.

In contrast, iron offers clear advantages. As a widely used material, its entire supply chain is already established, requiring no fundamental overhaul, which provides a real economic and logistical benefit. While large-scale atomization of iron powder may pose challenges, the powder can be reused over multiple cycles, reducing recurring production needs, as assessed by Prashida et al. [3].

Though dedicated power plants are still in development, burner sizes are steadily scaling up. Importantly, the combustion of iron powder is compatible with existing coal combustion infrastructure, as both rely on pulverized fuel injection. This opens the door to retrofitting coal-fired plants, enabling a faster, more cost-effective transition to carbon-free energy [1, 4].

Although the combustion behavior of pure iron powder is increasingly well understood, producing it at high purity remains a significant challenge for large-scale applications. Consequently, research interest is shifting toward recycled materials or naturally impure iron ores. This study focuses on iron containing silicon, a common impurity in iron ores [5], to assess its usability as a combustible fuel.

Chapter 2

State of the art

This Chapter reviews key findings from studies on using metal powders as energy carriers, followed by an overview of combustion mechanisms, experimental analyses, influencing parameters, and emissions from the pure iron combustion. Finally, oxidation behaviors of pure silicon and iron-silicon mixtures are examined.

Any form of combustion is, in principle, the oxidation of the initial element. In simple terms, during hydrocarbon combustion, carbon (C), hydrogen (H) and dioxygen (O_2) react to form carbon dioxide (CO_2) and water (H_2O), rapidly releasing a large amount of energy. Metal oxidation is a well-known phenomenon, typically something to be prevented or limited to a thin oxide layer. In fact, metal oxidation that occurs at ambient temperatures releases heat, but the process is so slow that it is not considered as combustion. However, by increasing the contact surface between metal and oxygen, using metal powders, and raising the reaction temperature, the oxidation process accelerates significantly. At this point, it becomes known as metal combustion. Metal powders are widely used in fireworks, sparkling candles, etc. Combustion in this case is heterogeneous, fundamentally different from the well-known theory of hydrocarbon combustion, which occurs in the gas phase.

2.1 Pure Iron combustion

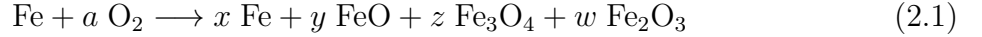
To investigate pure iron combustion, researchers conducted a series of experiments. They began with single-particle combustion tests, allowing them to closely monitor the behavior of an individual particle throughout the entire combustion process. Subsequently, they scaled up to multi-particle experiments using particle batches in a real burner to assess the collective effects and interactions between particles during combustion.

During combustion, particles go through various phases. First, there is the solid-state oxidation; the particle oxidizes and creates some oxide layers. Once the heat released by oxidation is enough, the particle ignites. The particle temperature rises, and the particle becomes liquid; the oxidation is faster. When most of the pure iron is oxidized, the heat released drops, and convective losses become dominant, causing the particle temperature to decrease. During this temperature drop, the particle still oxidizes but at a lower rate, and once the temperature is too low, the particle solidifies, and the process of combustion is finished.

Solid-state oxidation

Focusing on a pure iron particle combustion, it will react with oxygen in the air to form different types of iron oxides. Depending on the level of oxidation, three main iron oxides can be identified: wüstite (FeO), magnetite (Fe_3O_4) and hematite (Fe_2O_3). Wüstite is thermodynamically unstable at low temperature, which means its presence in the final oxide composition is minimal. With further oxidation, magnetite (Fe_3O_4) forms, which is stable. Hematite (Fe_2O_3) is particularly notable for giving iron oxide its characteristic red color; this oxide is stable only in the solid state.

A simplified oxidation equation for solid state can be written as follows:



The formation of oxides is an exothermic process, releasing heat. The enthalpy values associated with each oxide are provided in Table 2.1.

Table 2.1: **Standard enthalpy of formation for various solid oxides**, sourced from the National Institute of Standards and Technology (NIST). The negative values indicate that the formation reactions are exothermic.

	ΔH_f° (kJ/mol)
FeO	-272.04
Fe_3O_4	-1120.89
Fe_2O_3	-825.50

From Equation 2.1, two additional equations can be derived based on mass conservation. However, with five unknowns, determining the final oxidation state requires additional parameters. Factors such as oxidation kinetics, reaction temperature, and system geometry play a crucial role in estimating the final composition.

To simplify the analysis, a common approach is to assume that the metallic particle is covered by successive oxide layers with decreasing oxidation levels from the centre to the edge, while iron remains at the core, see Figure 2.1. According to Wagner's theory, the growth of the different oxide layers is linked to the movement of ions [6]. Since Fe^{2+} or Fe^{3+} are more mobile than the oxygen anion mainly due to its size, the inner oxide layers (FeO and Fe_3O_4) will grow faster than Fe_2O_3 during the ignition process. The oxide layer FeO is the largest because the diffusion coefficient of Fe in FeO is higher.

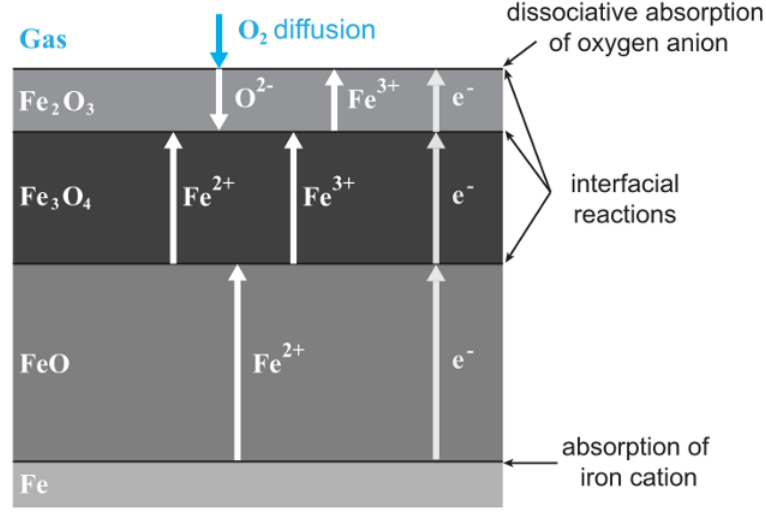


Figure 2.1: **Oxidation layers for pure iron.** The oxidation of the inner layers (FeO and Fe_3O_4) is driven by the mobility of iron cations, while the formation of the outer layer (Fe_2O_3) is limited by the diffusion of oxygen anions, [6].

According to Mi et al. [6], iron oxidation can be divided into several temperature-dependent steps. Initially, dioxygen molecules diffuse from the bulk gas to the surface of the iron particle. At low temperatures, this step is significantly faster than the internal oxidation kinetics, as gas-phase diffusion coefficients are high and largely independent of temperature.

Subsequent stages are governed by the particle's internal kinetics: the adsorption of O^{2-} anions, the migration of iron cations within the growing oxide layer, and the diffusion of electrons and cations through the solid medium. These processes involve overcoming potential energy barriers associated with ionic movement in the crystal lattice. As temperature increases, lattice atoms are activated, facilitating ionic diffusion.

At high temperatures, internal kinetics can surpass the rate of dioxygen diffusion to the particle surface. This transition helps explain why metals are not pyrophoric under ambient conditions. At room temperature, the potential barrier for ion diffusion is too high to allow significant oxidation or combustion. For iron particles to self-ignite, a specific ignition temperature must be reached. This threshold depends on both ambient conditions and powder characteristics.

Ignition

Particle ignition is a key element in the study of combustion. However, the term ignition is quite difficult to describe, as, depending on the type of study, its definition varies.

In optical pyrometry analysis of iron particle combustion in hot air, two definitions of ignition are found in the literature. First, Li et al. [7] define ignition as the completion of the melting phase of the particle. Second, Panahi et al. [8] describe ignition as the first appearance of a luminous particle. Both definitions can be debated for some reasons, first oxidation also occurs in the solid state. This means that heat release through convection or radiation from the particle can occur even if it has not melted completely. In the second

case, the appearance of a luminous particle indicates radiation heat transfer but does not necessarily mean that the particle will sustain combustion on its own. In such studies, the authors often choose the second definition of ignition to compare the effects of specific parameters on single-particle combustion. However, this highlights the need for careful use of the term ignition.

Since iron powder combustion is heterogeneous, the definition of the ignition process also depends on the scale of observation. Considering a unique particle ignition, it can be defined thermodynamically to be the moment at which the heat released by oxidation reactions is greater than the heat lost to the environment by convection and radiation. This phenomenon is also known as thermal runaway. Various elements can influence the ignition process from this point of view, often observed by the ignition temperature, which describes the particle temperature at which thermal runaway will occur. The value of the ignition temperature increases with the size of the protective oxide layer that forms when the powder is stored. The thicker this oxide layer is, the more difficult it is for oxygen to infiltrate and react with the pure iron in the core. The amount of air available around the particle can also interfere with ignition. Finally, the initial size and shape of the particle play a role. The larger the particle, the higher the radiation losses, thus delaying the arrival of the thermal runaway. In terms of particle shape, the aim is to have the largest possible contact surface with oxygen, so spherical particles are ideal, bearing in mind that this type of shape also ensures good particle fluidity for transport [9].

Observing this phenomenon on a larger scale, such as within a particle cloud, the overall temperature in the combustion chamber will rise. In this context, ignition time is defined as the precise moment when the gas surrounding the particle flames begins to heat up and rise. The ignition phenomenon also depends on the properties of the particle cloud. If the particles are too far apart, heat transfer between them will be inefficient, preventing sustained combustion and causing the flame to extinguish before it can sustain for a reasonable time.

Liquid-state oxidation

Once the ignition temperature is reached, the particle temperature increases a lot and reaches the melting temperature of the different oxides. The particle goes from a solid state to a liquid phase. The apparition of liquid at 1377 °C accelerates the oxidation process because the potential barrier disappears and the diffusion process of the ions is faster. Also, as the particle is liquid, the layers mix with each other to form an oxide following the formula Fe_xO_y , where x and y depend on the mixture. If the temperature, the oxygen, and the iron concentration are known, a phase diagram can be a tool to determine which phases are thermodynamically stable and what phases are miscible, see Figure 2.2. When the particles are liquid, the surface tension reforms the particles to become a sphere; this shape is kept during the solidification. Figure 2.3 illustrates the initial powder in picture (a) and the powder after combustion in picture (b). As shown in picture (b), the burnt particles are spherical due to the passage to liquid phase and solidification.

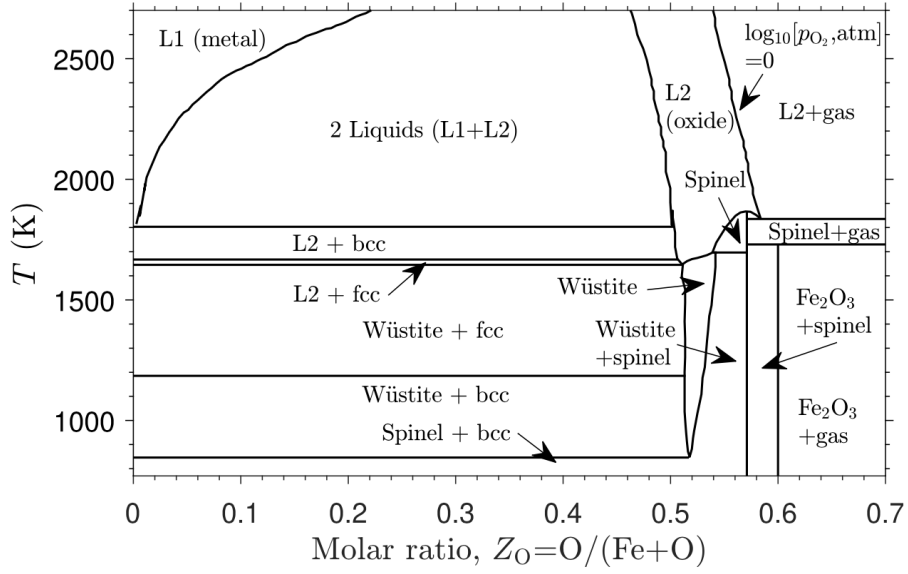


Figure 2.2: **Fe-O Phase diagram.** Link oxygen concentration and temperature to predict the phase of the mixture, [10]

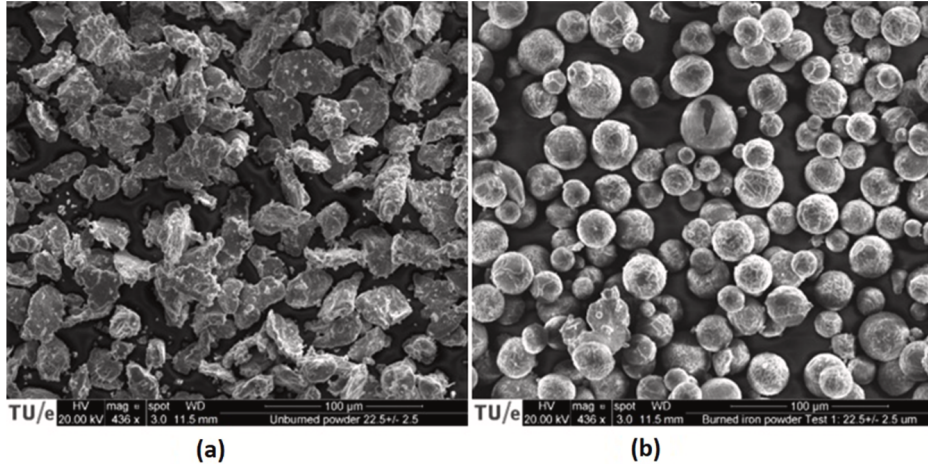


Figure 2.3: **Example of powder (a) before and (b) after combustion.** The powder become spherical after the combustion, [3]

After liquefaction, the majority of the iron oxidises. The particle temperature increases until a peak is reached; after that, the particle temperature drops due to the heat losses. Work of Fujinawa et al. [10] suggested that the oxidation process is not finished after reaching the temperature peak of the particle. In Figure 2.4, the experimental data represented by the dotted red line shows that the oxidation process continues with the cooling because the drop of temperature is not constant.

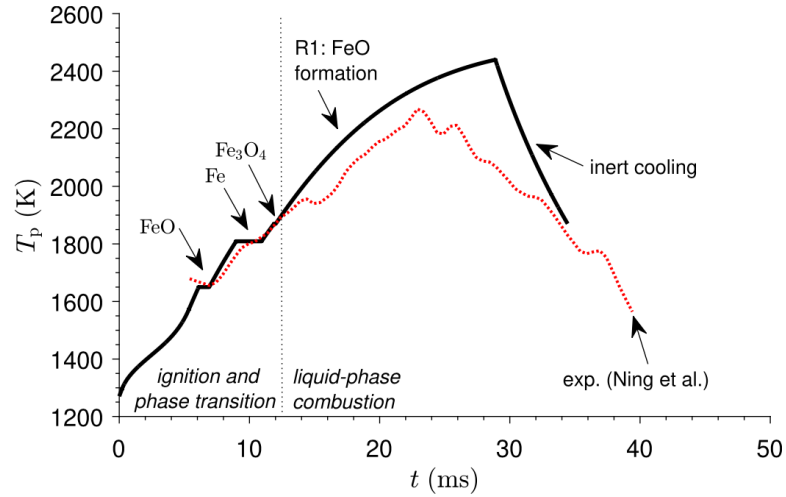


Figure 2.4: **Particle temperature evolution during its combustion.** The experimental data (red dotted line) indicate that oxidation continues during cooling, as evidenced by non-linear temperature drops and stabilization plateaus, [10].

2.1.1 Combustion experiments

All theoretical results presented are based on combustion experiments and numerical simulations. This Section outlines the experiments conducted in the literature to investigate iron combustion.

In the literature, many experiments have been made on one single particle to understand the mechanism of oxidation. After that, the researchers scale up the quantity of particles to analyze real conditions of combustion. During this work, only experiments on a batch of powder have been made, so the one single particle setup has not been described.

Powder flame and burner

To develop a more practical approach to metal combustion, studies focus on experimental burners designed to generate metal powder flames, see Figure 2.5. The flame looks like a tornado because there is a swirling flow inside the burner to increase the residence time of the particles.

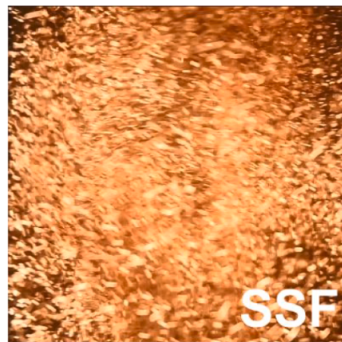


Figure 2.5: **Self-sustainable iron powder flame**, [3].

The increase in particle amounts allows for studying the effect of industrial combustion conditions. Each particle reacts as it did for the single-particle test, but in such a setup, they also react with each other.

The ignition of the powder is due to the high temperature of the surrounding gases, above 1000 K in general. There are different ways to reach this temperature, either by using electric heaters or by using a pilot flame to sustain and/or start the combustion. Both methods have their advantages and drawbacks. With electrical heaters, the heating phase is slow and takes several hours due to convective heat losses. When using gas, for the pilot flame or to preheat the combustion chamber, its combustion emits CO_2 . However, this type of burner offers better controllability compared to electrically heated chambers.

Several studies [2, 3, 11, 12] investigated continuous large-scale combustion in an electrically preheated 5 kW burner, identifying key parameters essential to maintain stable iron flames without external heat support. Their study provides valuable information on how combustion conditions influence nanoparticle emissions and NO_x formation. In addition, they explored the role of particle spacing in sustaining steady combustion. The burner used in their research was also employed in the present thesis, which is why it will be described in more detail in a later Section.

Recently, a significant milestone was achieved at TU/e with external collaborators [13], where an improved demonstrator burner with a power input of 500 kW was developed. In this burner, propane is used to maintain a pilot flame that provides 50 kW at its maximum to the flame. The study demonstrated that scaling up power is feasible while also advancing knowledge on iron recovery, combustion efficiency, NO_x emissions, and particle emissions. They successfully achieved a test duration of 9 hours, effectively limiting powder fouling inside the combustion chamber.

2.1.2 Impact of the powder

Recently, Prasadha et al. [3] investigated the influence of particle size and oxygen availability (richness) on iron flame stability and related combustion parameters. Their study is particularly relevant, as it was conducted under experimental conditions similar to those used in the present work.

Richness

The richness is quantified by the equivalence ratio ϕ , comparing the combustion conditions with the stoichiometric conditions. This richness has a strong impact on the combustion process.

Reaching a stationary and self-sustainable flame without other energy supply is a key element to limit the dependency on other energy sources. To obtain a self-sustaining flame, fuel-rich conditions (higher powder-to-air ratio than expected at stoichiometry) are more favorable than lean conditions. The reason for the good behavior of the rich mixture is that the particles are near each other, increasing the powder density and flue gas temperature, by improving the heterogeneous flame propagation. The average distance from each particle needs to be less than 1 mm to have a nice flame [3].

In rich conditions, flame stability is achieved, but the trade-off is that the concentration of oxygen is not sufficient to reach the maximum level of oxidation of particles. During combustion, the level of oxidation reaches a threshold, regardless of the size of the particles.

For maximum optimization of cycle efficiency, process-rich combustion is not ideal, but it is very versatile as it decreases the dependency on particle size.

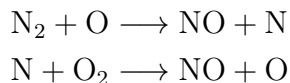
Particles size

By sieving the powder, it is possible to isolate particles within a defined size range. Under identical combustion conditions, smaller particles exhibit a higher degree of oxidation, generate higher gas temperatures, and more readily sustain a self-sustaining flame. Previous studies [7, 14] have shown that the heat necessary to ignite a particle is proportional to its volume. The increase in particle size results in longer ignition and melting delays. These delays increase the time required for a particle to reach its maximal temperature, while its residence time in a combustion chamber is limited. The ideal size range, when burning iron powder in a tornado flame burner (metallic cyclone combustor - MC2), is between 20 and 75 μm [3]. If the particles are bigger, the combustion struggles to reach a self-sustainable flame. In a real industrial process, for a larger burner, the combustion time will increase, allowing the bigger particles to have more time to completely oxidize.

2.1.3 Combustion products

Gas emission: NO_x

The thermal NO_x formation is described by the well-known Zeldovich mechanism, [15]:



It happens at high temperature ($\sim 1400^\circ\text{C}$) (because a lot of energy is needed to break the ternary bond of N_2 into N), when air is used as an oxidizer. In a metallic flame, the NO_x formation is favored by the decrease of particle size, as higher temperatures are reached. However, emissions are reduced in rich conditions, as the NO_x formation requires oxygen, which better reacts with the available iron.

CO_2 emissions are negligible, except in cases where the initial powder contains residual carbon from its processing. In such instances, carbon may be released during the first combustion cycle.

Particles

Recovering the particles after their combustion is a necessity for the cyclability. However, due to the combustion, their shape, size, composition, and aspect change.

The formation of agglomerates is almost unavoidable during the combustion of metallic powder. Agglomeration can occur when particles are projected onto the chamber walls due to centrifugal forces or through collisions between particles. This phenomenon is exacerbated when the particles are in a liquid state, which becomes more likely at higher particle and gas temperatures. To allow for the reuse of the powder, these agglomerates must be broken down to restore the optimal particle size distribution required for efficient reduction and combustion.

In the liquid state, particle explosion is frequent, creating craters and emitting nanoparticles due to local evaporation, see [2]. The explosion of the particles occurs just after

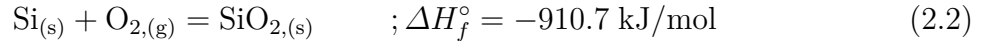
the temperature peak where the difference between the temperature of the particle and the surrounding is the biggest. It results in a slight increase in the internal pressure of the particle [16]. This gradient of pressure can cause an explosion. The evaporation is happening mainly for smaller particles because it is easier to reach the temperature peak. It depends also on the type of mixture; the lean combustion favors the explosion due to a huge amount of oxygen, while a rich mixture is quite safe from this phenomenon, even if higher temperatures are reached. The formation of nanoparticles leads to a net loss of material, thereby decreasing the overall cycling efficiency. Additionally, it necessitates the use of filtration systems, either to protect downstream equipment from clogging or to prevent the release of particulate matter into the atmosphere. However, compared to other metals, iron has a lower tendency to evaporate, which helps to limit such losses.

2.2 Pure silicon oxidation

As the analysis of the pure iron is done, it is important to understand the oxidation of pure silicon, seeing that it is the impurity that is studied in the present work.

Solid-state oxidation

At solid state, the oxidation of the silicon forms silica, which is a protective oxide layer :



The layer blocks the silicon diffusion inside itself, preventing the oxidation [17].

Liquid-state oxidation

For the oxidation in liquid state, the process for pure silicon is different from that for iron, [18]. The oxidation of silicon with oxygen changes from passive to active oxidation depending on the partial pressure of O_2 . The passive oxidation corresponds to the formation of a protective layer of oxide. Related to Figure 2.6, there are three different stages. For the first one, the oxygen partial pressure (P_{O_2}) is so low that the solid oxide is not stable and only the gaseous oxide is stable and follows the Reaction 2.3. As long as P_{O_2} is low $P_{\text{O}_2} < 2.9 \cdot 10^{-4} \text{ atm}$, the oxidation remains active.



After reaching a threshold, $P_{\text{O}_2} = 2.9 \cdot 10^{-4} \text{ atm}$, the first stage moves to stage 2. During stage 2, silicon vapour reacts with oxygen to form SiO_2 , a solid metal oxide named *fog*, see reaction 2.4. The oxidation at stage 2 is active, [18].



The last threshold is, when the partial pressure of oxygen reaches $4.5 \cdot 10^{-3} \text{ atm}$. A protection layer is formed all around the sample, and the oxidation transits to a passive form because the oxygen cannot reach the Si due to the blocking layer.

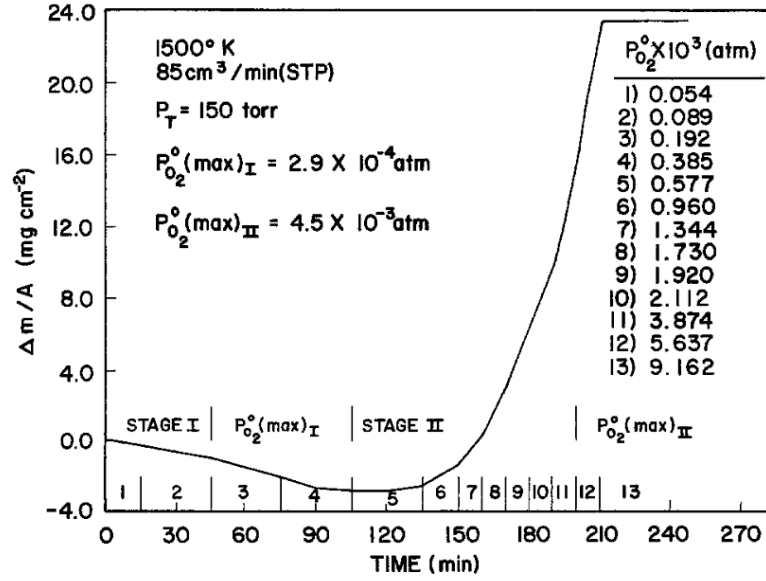


Figure 2.6: **Oxidation of silicon in 3 different stages.** (i) release of SiO in the form of gases resulting of a loss of matter. (ii) oxygen reacts and the mass increases linearly to (iii) finally reach a plateau due to the protection layer, [18].

2.3 Iron-silicon mixture oxidation

Most researchers [19],[20],[21] agree to say that the addition of silicon as an impurity in pure iron reduces its capacity to oxidize by creating a protective layer. If the content in silicon is above 3-6 % (regarding different authors) the amount is enough to create a layer that protects iron from oxidation. To go further into details, silicon has a better affinity for oxygen than iron. Silicon will tend to react first with oxygen due to its lower reduction potential, to create two types of oxide phases, fayalite (Fe₂SiO₄) or silica (SiO₂) depending on the concentration in silicon. The layer of SiO₂, the most common, blocks the diffusion as explained before.

Knowing that iron diffusivity is very slow in silica, the coefficient of diffusion $D \approx 8 \cdot 10^{-20}$ cm²/s at 1000 °C [22], there is a massive reduction in oxidation level for the iron-silicon alloys relative to pure iron oxidation level [21].

A first remark to describe the mechanism of oxidation is that silicon does not diffuse (or very limited) inside the silica layer, the result is that the silicon never goes outside the boundary of the initial sample, unlike iron, which forms some oxide outside this initial bound, [20]. During the oxidation process between 900 °C and 1000 °C, three different layers are formed, see Figure 2.7. The first one is the silica layer, only formed by the diffusion of oxygen through the three layers. The second layer is composed of iron oxide with silica present in the interstitial sites. The last layer is hematite induced by the diffusion of the iron cation. As mentioned previously, the size of the oxide layer is proportional to the diffusion capacity, so the silica layer is not big because the diffusion of silicon is very slow.

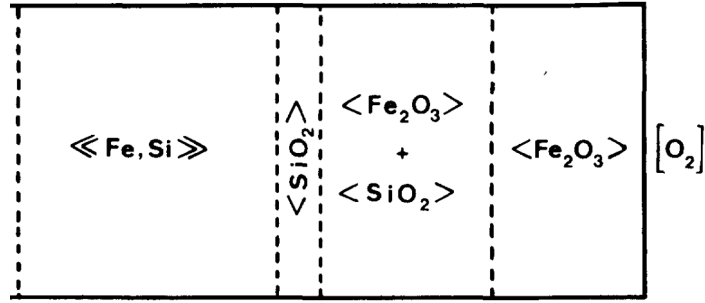


Figure 2.7: **Layer formation during Fe-Si oxidation.** The first oxide layer formed above the solid alloy is a thin silica layer, due to the low diffusion rate of silicon. This is followed by a hematite layer containing silica inclusions, and finally by a pure hematite layer, as silicon does not diffuse beyond the initial layers, [20].

During solid-state oxidation with different layers, some internal stresses can build up due to local density changes. As the oxide layer struggles to deform plastically, the covering layer can crack. These cracks allow oxygen to infiltrate the materials and promote oxidation. Where the silica layer is fractured, and if the concentration in silicon is not enough, the reaction will generate fayalite and wustite.

The main iron oxide formed during oxidation of Fe-Si alloys is Fe_2O_3 . The reason can be explained thermodynamically, as silica plays the role of a barrier, the activity of Fe is low, so equilibrium Fe/ Fe_2O_3 is reached. Finally, the silicon oxide can lead to the formation of either silica or fayalite. As the equilibrium fayalite/hematite is unstable, if the only iron oxide present after oxidation is hematite, it can be concluded that fayalite was not formed, but only silica [20].

To study the particle during combustion, some experiments on one single particle of iron-silicon powder were conducted [14]. The content of silicon varies between 3 and 6 wt.%. It was found that ionic diffusion was not the only rate-limiting step prior to ignition. The diffusion of oxygen in the gas, surface tension, or the chemisorption can be rate-limiting processes. After the ignition, unlike the pure iron, the particles show multiple intensity peaks, see Figure 2.8. All the rising intensities correspond to a rise in temperature and are due to the oxidation process. After the first peak, the intensity dropped because the particle was covered by a thick oxide layer, which reduced the surface chemisorption rate of oxygen and, consequently, the heat release. According to [14], the particle temperature rose to nearly 1900 K after the first peak, which is enough to melt all the oxide layers. But, the melted oxide layer with silicon has high resistance to oxygen diffusion, and so the temperature decreased. During the cooling process, the oxide layer cracked. Cracks can be caused by the presence of surface tension induced by melting, or by thermal dilatations. The presence of cracks created a direct access to oxygen to the core, allowing the iron to oxidize and the temperature to rise again. If the cracks heal quickly, a second small peak appears, but if it is not fast enough, the particle undergoes extensive oxidation, and a large temperature peak occurs. During the experiments, a maximum of two small peaks was observed before having the large one.

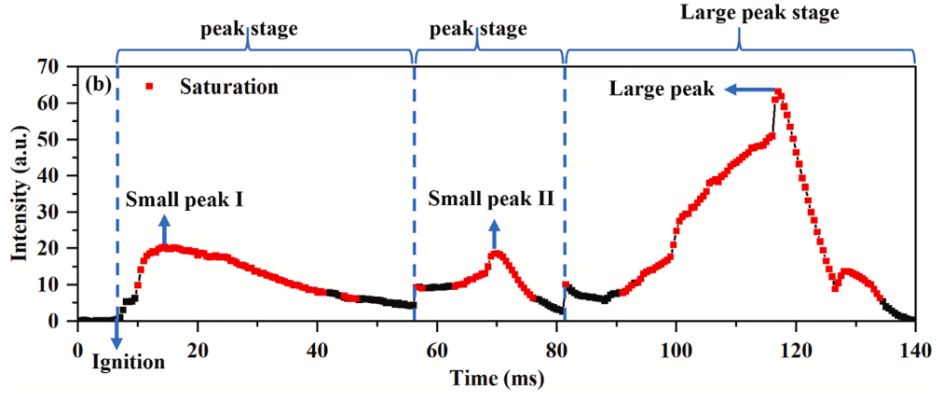


Figure 2.8: **Combustion of one single particle of Fe-Si.** Unlike the iron combustion, there are different peaks with drop of intensity (or particle temperature). The drop after the first peak is due to the diffusion resistance of the layer. During the cooling some cracks appears, allowing the oxygen to oxidize the iron core, increasing a lot the temperature of the particle [14].

There exist some models based purely on thermodynamics to simulate adiabatic combustions of Fe-Si with the software Thermo-calc, [5]. The model considers Fe with 5 wt. % of silicon inside. The simulation allows to follow the different phases of the particle during the combustion, see Figure 2.9.

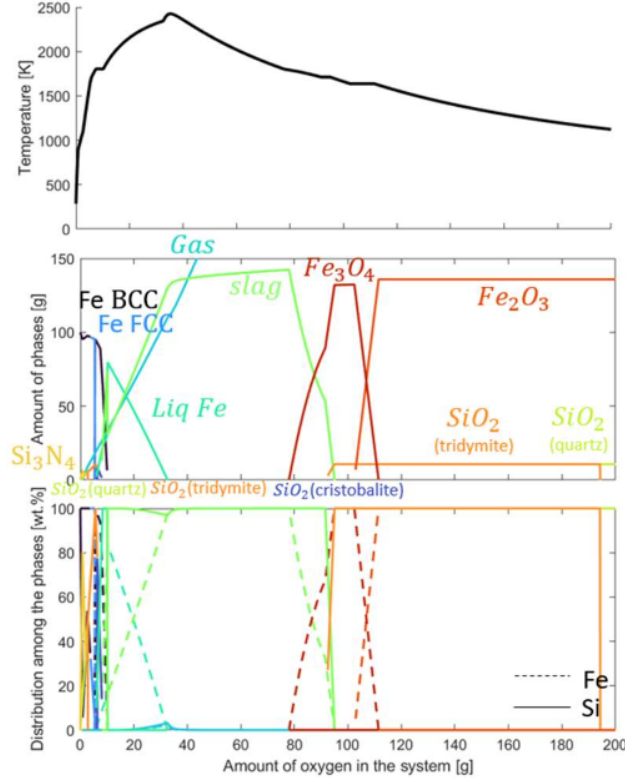


Figure 2.9: **Simulation of an adiabatic combustion of Fe-5Si** [5].

Chapter 3

Methodology

In the present Chapter, the experimental procedures and materials are presented. It begins with a detailed characterization of the metallic powders used. Next, the experimental setup of the metal cyclone combustor (MC2) is described. This is followed by an overview of the isothermal oxidation experiments conducted using thermogravimetric analysis (TGA) and a high-temperature furnace. Finally, a model predicting the ignition temperature of pure iron is developed, serving as a foundation for the ignition model of the iron-silicon. As part of this methodology, equipment such as a granulometer, scanning electron microscope (SEM), and other analytical tools are detailed as the text unfolds. These instruments were first used to characterize the initial powder and later to obtain the results presented in Chapter 4.

3.1 Powder characterization

Two types of micron-sized metallic powder were used during experiments : iron-silicon powder containing 7 wt.% of silicon (Fe-7Si), and pure iron (99.8 wt.% Fe). Both are detailed in what follows, with a focus on Fe-7Si, as the central element of this work.

Fe-7Si

Iron-silicon powder produced with gas atomization by Sandvik was used. First, the powder was sieved to keep the particle size distribution between 20 and 63 μm . The granulometric analysis (SYNC Microtrack flowsync) combines laser diffraction with dynamic image analysis to characterize the particles one by one, from 0.1 μm to 2 mm in diameter, giving information about powder dimension and sphericity. Powder dimension is described by the equivalent diameter of the area (Da), evaluated, as the sphericity, following :

$$Da = \sqrt{\frac{4 \text{ Area}}{\pi}} \quad \text{Sphericity} = \sqrt{\frac{4\pi \text{ Area}}{(\text{Perimeter})^2}}$$

Figure 3.1 (a) presents the typical Da distribution curve for the sieved powder between 20 and 63 μm , further used in Section 4.1 when analyzing the burned powder with the MC2. 92% of the particles are in the expected range, with a median Da at 38.7 μm and an average at 44.5 μm .

For the purpose of the thermogravimetric experiment that will be presented in Section 3.3, 20 μm diameter powder, referred to as Fe-7Si(20), has been used. This powder is the result of a double sieving : the final powder was collected on the upper part of the 20 μm sieving filter when the amount of powder that had first passed through this filter was sieved again. In doing so, the Fe-7Si(20) powder is expected to have a mean diameter close to the filter width, due to sieving uncertainties, which is observable in Figure 3.1 (b), with a median at 17.8 μm .

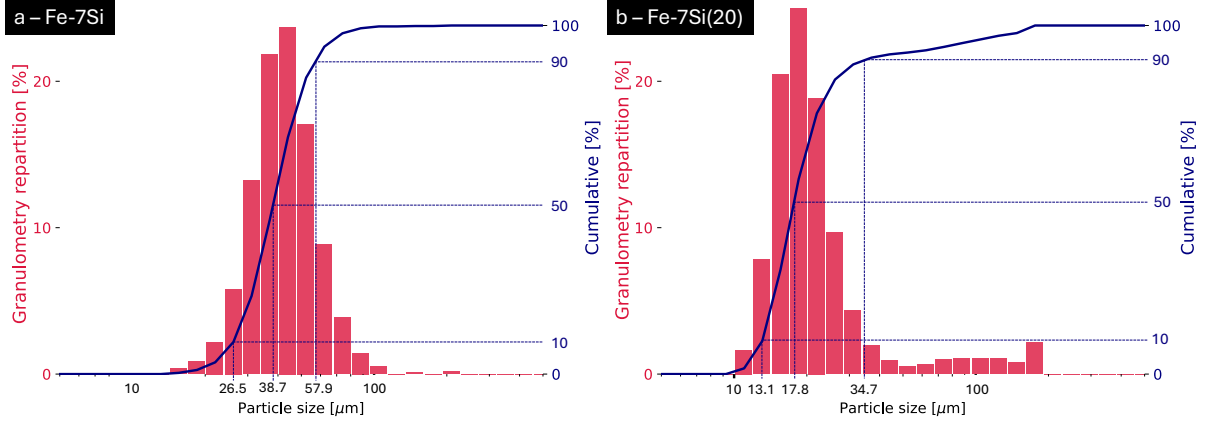


Figure 3.1: **Granulometric analysis on Fe-7Si powder - D_a repartition bar chart and cumulative curve** (a) Fe-7Si powder after selective sieving between 20 μm and 63 μm . (b) Fe-7Si powder after selective sieving around 20 μm (Fe-7Si(20)).

Granulometric measurement gives 0.84 as a median of sphericity, as presented in Table 3.1.

Table 3.1: **Percentiles (D10, D50, D90) of sphericity measurements for the initial powder**

Powder	D10	D50	D90
Fe-7Si	0.695	0.840	0.966

In order to visualize this value, SEM (Zeiss Ultra 55) was used on the initial powder. The microscope operates as follows: a beam of primary electrons is created by heating a cobalt bar and then accelerated by electromagnetic lenses; the electron beam will react with the matter, generating so-called secondary electrons (SE2) and backscattered electrons (BSE) [23]. Dedicated detectors are used to capture SE2, which provide information about surface topography, and BSE, which offer insights into material density and crystallography contrast. SE2 are generated in a manner similar to sand being scattered when a ball hits it. Depending on the orientation of the surface, the signal intensity varies, creating contrast that reveals surface shape and texture. While the BSE signal increases with the atomic number of the targeted element: heavier elements, with more electrons and a denser nucleus, produce a stronger signal. Figure 3.2 shows a global view of the particle surfaces from the initial powder (Fe-7Si and Fe-7Si(20)), which appear mostly spherical due to the gas atomization process used by the manufacturer. Size homogeneity of Fe-7Si(20) powder is also clearly visible.

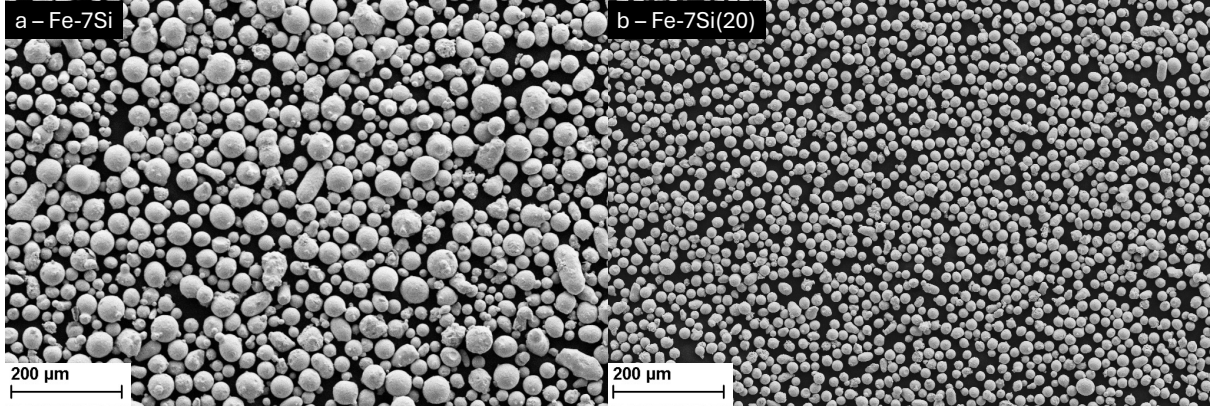


Figure 3.2: **SE2 images of Fe-7Si powder** (a) Fe-7Si powder after selective sieving between 20 μm and 63 μm . (b) Fe-7Si powder after selective sieving around 20 μm (Fe-7Si(20)).

Inductively coupled plasma optical emission spectrometry (ICP-OES) and carbon chemical analysis, measured by combustion method, performed on Fe-7Si powder permits establishing its global composition. The resulting measurements, in Table 3.2, show that iron (92.7 wt.%) and silicon (7.0 wt.%) are the main components of the powder. The high content of silicon will give a good opportunity to characterize the effect of this element on the combustion and oxidation processes. Impurities such as chromium, manganese, copper, cobalt, and carbon are present, but in few quantities (< 1 wt.%). Their effect on the oxidation process is expected to be very limited and will therefore be potentially neglected in subsequent analyses. However, even in small quantities, carbon content could contribute to micro-explosions. The sum of the composition percentages does not equal 100 %, with a missing 0.09 wt.% likely due to measurement uncertainties or unquantifiable oxygen from initial surface oxidation.

Table 3.2: **Fe-7Si composition using ICP-OES and carbon chemical analysis**

Element	Fe	Si	Cr	Mn	Ni	Cu	Co	C
wt.%	92.7	7.00	0.08	0.08	0.02	0.01	0.01	0.01

The SEM is also equipped with an energy dispersive X-ray spectrometer (EDS), which enables the determination of the elemental makeup and composition [23]. To generate characteristic X-rays from a sample, the beam of electrons excites atoms in the material. This excitation ejects an inner-shell electron, creating a vacancy. An electron from a higher-energy shell then fills the vacancy, releasing energy as an X-ray. The emitted X-rays have energies unique to each element, allowing EDS to identify the elemental composition of the sample. The precision of the detector is $\sim 1 \mu\text{m}^3$, due to uncertainties on the interaction location of the electrons. The chemical composition of 40 particle cross-sections was analyzed with EDS, giving 6.89 ± 0.47 wt.% of silicon and 93.11 ± 0.47 wt.% of iron. No other element detected during ICP was detected during this analysis. Furthermore, EDS was performed on 6 points of the cross-section of 1 particle, showing composition of Si and Fe is 6.71 ± 0.13 wt.% and 93.29 ± 0.13 wt.%, respectively. These quantifications indicate a homogeneous chemical composition within individual particle cross-sections, although small variations are observed between different particles.

X-ray Photoelectron Spectroscopy (XPS), a technique used to determine the elemental composition of a material’s surface, was performed on the powder. It operates by analyzing photoelectrons emitted from the sample when irradiated with X-rays. Unlike EDS, XPS is highly surface-sensitive, with an analysis depth of approximately 10 nm, making it ideal for studying the outermost surface layers. The XPS analysis revealed a highly oxidized layer approximately 10 nm thick on the powder surfaces. The composition of this oxide layer is presented in Table 3.3. Surface contamination by carbon was also detected, corresponding to an estimated thickness of about 1 nm. However, the maximum analysis depth of the technique was reached without detecting any unoxidized metallic phase, indicating that the oxide layer may extend beyond 10 nm. The exact thickness of the oxide layer could not be determined, but as it was not visible during SEM or EDS analysis, its thickness is very small ($\ll 1 \mu\text{m}$).

Table 3.3: **XPS on Fe-7Si powder.** Surface mass concentration [wt.%].

Element	Fe	Mn	O	C	Si
wt.%	17.1	1.1	47.4	6.7	27.7

Brunauer–Emmett–Teller (BET) surface area analysis is a technique to measure the specific surface area of materials by physical adsorption of krypton gas molecules onto the surface. By analyzing the amount of gas adsorbed at different relative pressures, the BET equation can be applied to determine the surface area of the material. On Fe-7Si powder, BET surface area analysis revealed a specific surface area of $0.0313 \pm 0.0002 \text{ m}^2/\text{g}$. This result suggests that the particles have a relatively non-porous or densely packed structure with minimal external surface available for gas adsorption, typically observed after gas atomization.

Fe

Pure iron, atomized by Höganäs, was used when performing TGA, in order to calibrate the experimental procedure. As described in Table 3.4 presenting ICP-OES results, the powder is composed of 99.8 wt.% iron. The powder dimensions were taken between $20 \mu\text{m}$ and $63 \mu\text{m}$ after sieving, as the Fe-7Si powder. BET surface area analysis performed on this powder revealed a value of $0.0282 \pm 0.0003 \text{ cm}^2/\text{g}$.

Table 3.4: **Pure iron powder composition using ICP-OES**

Element	Fe	Cr	Cu	Mn
wt.%	99.8	0.01	0.01	0.02

3.2 Metallic cyclone combustor

The initial purpose of this master thesis, the implementation of an experimental 5 kW powder burner inside the UCLouvain laboratories, led to a one-week stay at Eindhoven University of Technology (TU/e) to acquire knowledge about the burner. The described Fe-7Si powder was burnt in the experimental burner, presented in Figures 3.3. This

specific burner is often called the MC2 in the literature [2, 3, 11, 12]. It allows the combustion of metallic powder into hot air, without any other burned products, from methane combustion, for example.

The installation consists firstly of a gas flow control panel, containing the various inlet pipes to vary the oxygen and nitrogen content, as well as the powder injection rate. Bronkhorst[®] mass flow controllers are used to precisely manage the different gas flows.

The gas mixture, at ambient temperature, is injected into the electrically preheated combustion chamber. The burner operates on the cyclonic flame principle: the main flow, containing the powder, is injected from the top center of the chamber, while a swirling motion is generated by two tangentially oriented inlet pipes at the top, creating a cyclone along the chamber wall. The three inlet pipes have a 6 mm inner diameter. The tornado flame allows good circulation of particles within the chamber, increasing the powder residence time and the homogeneity and stability of the flame [2, 24]. According to the same studies, the combination of a main flow of 20.5 L_N/min and a swirl flow of 25.5 L_N/min resulted in a swirl number of 11 within the burner [25].

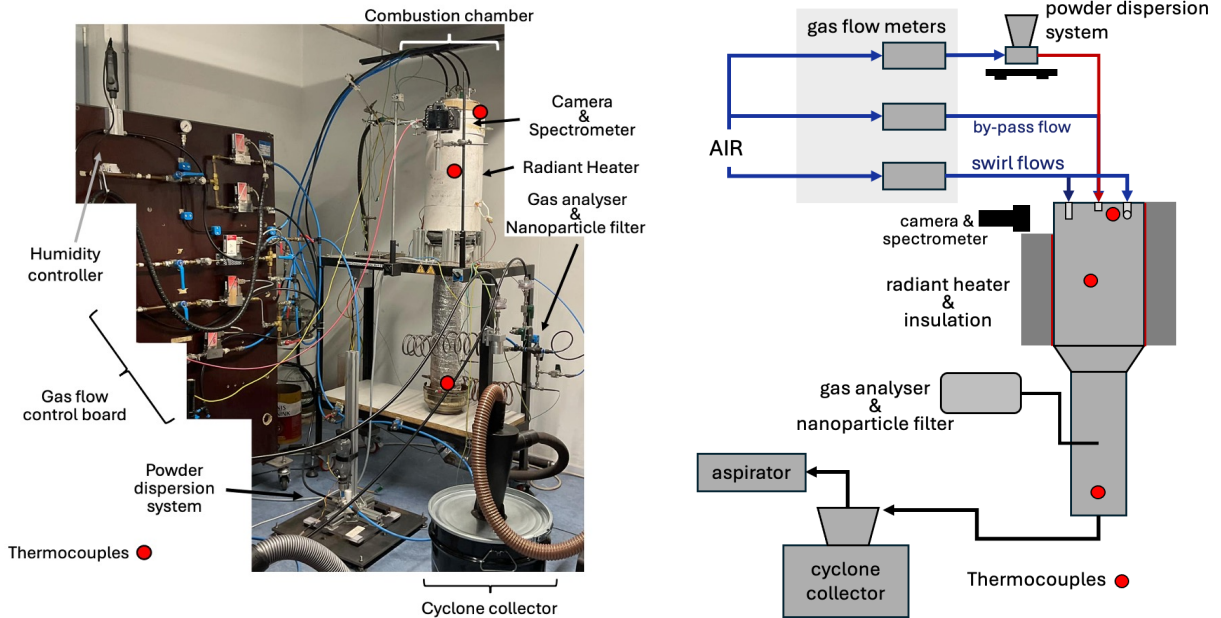


Figure 3.3: MC2 burner installed in TU/e labs, with flows and equipments schematic.

The powder is stored in a bottle, agitated by a small vibrator attached to it, and its mass is continuously measured to deduce the powder injection rate. The main flow is composed of a carrier flow, which extracts the powder from the bottle, and a bypass flow, adapted to obtain the desired quantity of air and powder concentration in the combustion chamber to have an air-fuel equivalence ratio slightly lower than 1 (rich conditions). The equivalence ratio was evaluated based on the conversion of iron (Fe) to magnetite (Fe₃O₄), without considering silicon content. Powder extraction relies solely on the carrier gas flow, leading to significant experimental uncertainties in both the powder flow rate and the resulting equivalence ratio, with a strong dependency on powder flowability.

Outside the combustion chamber, just below the injection, a missing piece of insulation allows the flame to be visualized using a StellarNet DWARF-Star NIR spectrometer,

coupled with a collimator and a camera. The spectrometer was calibrated using a certified tungsten ribbon lamp calibrated by the National Institute of Standards and Technology (NIST). The calibrated spectrometer measures light intensity across different wavelengths and estimates powder temperature by fitting the spectra to the Planck radiation function.

In the insulated and electrically heated section, the combustion chamber is made up of a Pyrex tube with a stainless steel tube inside to protect the Pyrex from splinters. The combustion chamber itself has a diameter of 13 cm and is 50 cm long.

Three K-type thermocouples are placed in the installation; the first two are placed inside the combustion chamber, one at the top and the other at the perfect center of the chamber. The centered thermocouple controls the radiant heaters by turning them ON or OFF if the temperature threshold (T_{RH}) is reached or not. The third thermocouple is placed in the exhaust, before the powder is sucked up. In the exhaust tube, a portable MRU Vario Plus gas analyser and a nanoparticle filter are placed. The gas analyser measures real-time concentrations of O_2 , NO_x , and CO, with a precision of 0.01 vol.% for O_2 and 1 ppmv for NO_x and CO. At the end of the exhaust tube, the powder and surrounding gas are drawn into a cyclone collector, enabling separation of the particles from the hot gas stream. The system comprises a Nilfisk cyclone separator coupled with a vacuum pump (Nilfisk VHW320L, 400 V, 1.5 kW). Additionally, microcyclone systems are employed to capture particles down to the nanoscale.

The combustion procedure is as follows:

- **Preheating:** A fraction of the nominal air flow is blown into the combustion chamber via the swirl intakes. The radiant heater surrounding the combustion chamber are turned on by setting the threshold temperature (T_{RH}). This allows preheating of the combustion chamber, which can take a few hours (1 to 3 h) depending on the target temperature.
- **Combustion:** When the desired temperature ($T_0 \leq T_{RH}$) is reached, the flows are set to their nominal value, previously evaluated to get the desired combustion conditions. In this way, the powder is injected into the chamber and the combustion occurs.
- **Cooling:** Once the powder stock is empty, the gas flows are set to their maximum for a few minutes to evacuate the residual powder in the carrier pipe and blow to the maximum in the cyclone collector. A small flow is kept after that for the cooling phase, which can take a few hours as well.
- **Powder collecting:** Finally, the powder is collected separately in the cyclone collector (-cycl) and on the wall of the chamber (-wall). The amount of powder adhering to the chamber walls is often comparable to that collected in the cyclone, though it varies with combustion conditions and initial powder quantity.

A total of 300 g of Fe-7Si powder was combusted in three separate tests, with approximately 100 g used per test, under different conditions detailed in Table 3.5. The first test was conducted under the same conditions as pure iron powder, that is, the same flows and preheating temperature of 810 °C. Under these conditions, the powder did not ignite as expected. To overcome this phenomenon, the injection temperature was increased to 930

°C for the second and third tests. During test 2, there was an uncontrolled change in the powder flow rate.

Table 3.5: MC2 burner main settings used for three Fe-7Si powder combustion tests

Parameters	test 1	test 2	test 3
[O ₂] ; [N ₂] - vol. %	21 ,79		
T_0 - °C	810	930	930
T_{RH} - °C	810	990	930
$\dot{V}_{swirl}$ - L _N /min	25.5		
$\dot{V}_{main}$ - L _N /min	20.5		
$\dot{V}_{tot}$ - L _N /min	46		
Swirl number	11		
powder rate - g/sec	0.71	0.66 → 0.45	0.68

These tests produced varying levels of oxidation, providing valuable insight into the combustion behavior of Fe-7Si powder, which is further analyzed in Section 4.1. Since test 2 showed powder flow rate instabilities, it was not further analyzed. For tests 1 and 3, the burned particles were examined by SEM and EDS in both cross-sectional and surface views. To simplify the understanding, the label used to differentiate the origin of particles/powder will be the following: a number corresponding to the test number (1 or 3), and the abbreviation -cycl or -wall depending on the collecting zone.

When surface view observations were performed, oxidized powder was placed on a sticking carbon tape. While to observe the cross-section of the powder, it was placed in a conductive embedding material (Polyfast, *Struers*) containing mostly iron, calcium, silicon, and nickel; then producing a praline with the Struers CitoPress-5 under a hot (180 °C) and pressurized (2.5 bar) environment. Then, polishing was performed to reveal the powder cross-section, following a non-formal procedure: initially with a 1200-grit silicon carbide (SiC) abrasive pad, followed by micron-sized diamond suspension (6 to 1 µm) in alcohol, and finally with chemical polishing using an oxide polishing suspension (OP-S Non-dry, *Struers*). Between each step, the samples were rinsed with ethanol or demineralized water and dried. At the end of the process, hand soap and hot water were used along with ultrasonic cleaning to remove any remaining residues.

Global analyses were also conducted on a few grams of burned powder, using X-ray diffraction (XRD) to identify the crystalline phases formed during combustion (more details about XRD analysis in Section 3.4), and granulometry to evaluate particle size distribution and morphology.

3.3 Thermogravimetric analysis

The elevated temperature required to ignite the Fe-7Si powder flame in the MC2 motivates a deeper investigation into its oxidation kinetics. To this end, isothermal TGAs of Fe-7Si powder oxidation in air were conducted. The Netzsch STA 449 Jupiter, equipped with a

silicon carbide furnace (max. 1600 °C) was used to perform thermogravimetric analysis at constant temperature, under constant air-flow (21/79 vol.% O₂/N₂). A test procedure is first composed of a blank test, during which the machine measures the mass variation due to gas flows and temperature variation with an empty crucible inside. The real test follows, with the powder charged in the same crucible used for the blank test, and the machine measures the mass variation. The increase in the mass of the sample is then deduced by subtracting both mass evolutions. The different phases of a test (blank and real), illustrated in Figure 3.4 for a 540 °C 3 h TGA, can be described as follows :

- **Neutral atmosphere:** The furnace is vacuumed and filled with argon three times, to ensure that any initial traces of oxygen are removed before increasing the temperature.
- **Heating:** The furnace is heated with an argon flow of 50 mL/min, to the desired temperature value with a heating rate of 50 °C/min.
- **Temperature stabilization:** Once the target temperature (T_{ox}) is reached, on average a temperature overshoot of approximately 20 °C is observed. Ten minutes of steady phase under argon allows the temperature and system to stabilize.
- **Oxidation:** Air is blown at the desired flow ($\dot{V}_{air}$) during the desired time, at the set temperature (T_{ox}). At the beginning and end of this phase, the air-flow is suddenly started or stopped.
- **Cooling :** Under argon, the temperature is decreased at a rate of 40 °C/min until room temperature is reached.

In addition to other flows, a protective 20 mL/min flow of argon is always blown into the furnace. During the test, air flow rates, temperature, and sample mass are recorded every 6 seconds, providing a balance between sufficient temporal resolution and manageable data volume.

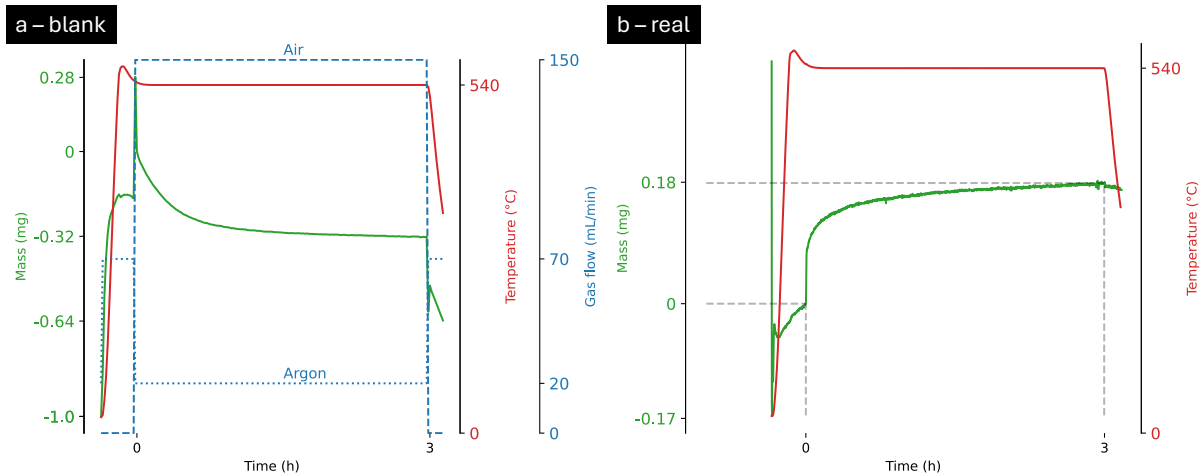


Figure 3.4: **Blank and real test curves for 540 °C 3 h TGA n°1.** Temperature (°C), gas flows (mL/min) and mass (mg) evolutions are presented, showing test phases.

The sudden introduction of air at a high flow rate creates a modification of mass measurement, forming a Dirac delta in the balance reading, which is particularly noticeable

in the blank test curves. The amplitude of this delta depends on various factors, but mainly on the fluid dynamics around the crucible due to gas changes. For this reason, in post-processing, the mass zero was set 6 seconds after the start of the oxidation phase, corresponding to one time step of measurement. The same curves are also included in the Appendix A.1 for all the tests referenced in Table 3.6.

Table 3.6: **Lists of thermogravimetric analysis.** Composition - powder composition; D - powder dimension; m_0 - initial powder mass; $\dot{V}_{\text{air}}$ - air flow; T_{ox} - oxidation temperature; t_f - isothermal duration

N°	Composition	D [μm]	m_0 [mg]	Crucible	$\dot{V}_{\text{air}}$ [mL/min]	T_{ox} [$^{\circ}\text{C}$]	t_f [h]
1	Fe-7Si	20-63	159.5	A	150	540	3
2	Fe-7Si	20-63	168.0	A	250	540	2
3	Fe-7Si	20-63	104.5	A	250	800	3
4	Fe	20-63	97.4	A	150	540	3
5	Fe	20-63	51.9	B	150	540	3
6	Fe-7Si	20-63	46.1	B	150	540	3
7	Fe-7Si	20	49.2	B	150	540	3
8	Fe-7Si	20	46.8	A	150	800	6
9	Fe-7Si	20	49.1	A	150	900	6
10	Fe-7Si	20	22.7	A	150	1000	6
11	Fe-7Si	20	30.4	A	150	1000	20
12	Fe-7Si	20	29.2	A	150	900	20
13	Fe-7Si	20	30.0	A	150	800	20
14	Fe-7Si	20	27.9	A	150	1100	6
15	Fe-7Si	20	31.7	A	150	1200	6
16	Fe-7Si	20	31.5	A	150	1100	20
17	Fe-7Si	20	36.1	A	150	1100	40 [min]

Crucibles, powder containers (PC), are made of alumina ceramics (Al_2O_3), and are therefore inert to oxidation. The most commonly used crucible A in this study is shown in Figure 3.5. It is porous to gas and the upper part of this crucible is used to contain the powder with a domed base. This shape allows the thermocouple to be close to the powder, yet separate from it. Three tests were also performed with the crucible B. This crucible gives direct contact to the powder with the gas flow, but the thermocouple is far from the powder.

Due to variations in initial powder mass, comparisons will be based on oxidation level rather than total mass increase. Oxidation level is defined as the ratio between the actual mass increase and the expected maximum mass increase due to oxidation, see Equation 3.1.

$$X = \frac{m(t) - m_0}{m_{\text{ox}} - m_0} \cdot 100 \quad [\%] \quad (3.1)$$

The term $m(t) - m_0$ is directly taken from the mass measurements during the real TGA test. However, m_{ox} is theoretically obtained from the maximum amount of oxygen that

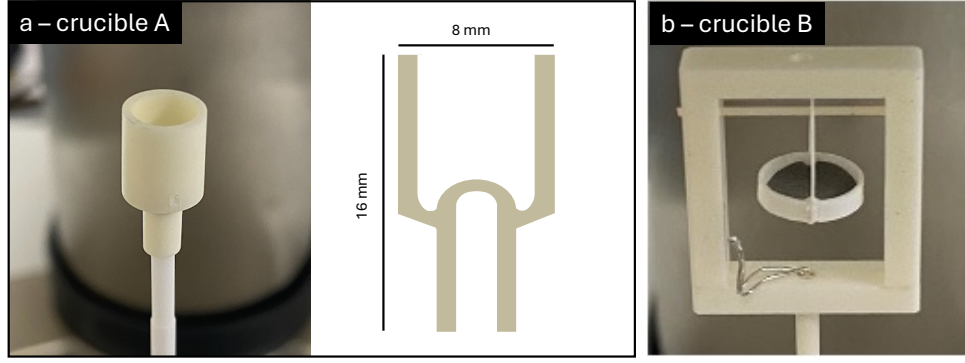


Figure 3.5: **Ceramic crucibles for TGA.** (a) High depth - 0.2 mL open. (b) low depth - 85 µL open

the initial matter could accept. In doing so, the silicon and iron content is supposed to be all silica (SiO_2) and hematite (Fe_2O_3), respectively, at the end. Mathematical definition of m_{ox} is then the following :

$$m_{\text{ox}} = M_{\text{SiO}_2} \cdot n_{\text{SiO}_2} + M_{\text{Fe}_2\text{O}_3} \cdot n_{\text{Fe}_2\text{O}_3} \quad (3.2)$$

$$= M_{\text{SiO}_2} \cdot n_{\text{Si},0} + M_{\text{Fe}_2\text{O}_3} \cdot \frac{n_{\text{Fe},0}}{2} \quad (3.3)$$

$$= \frac{M_{\text{SiO}_2}}{M_{\text{Si}}} \cdot m_0 \cdot 0.07 + \frac{M_{\text{Fe}_2\text{O}_3}}{2M_{\text{Fe}}} \cdot m_0 \cdot 0.93 \quad (3.4)$$

In this end, results comparisons will be possible. In the case of pure iron oxidation, silicon is removed from the expression, which becomes :

$$m_{\text{ox}}^{\text{Fe}} = \frac{M_{\text{Fe}_2\text{O}_3}}{M_{\text{Fe}}} \cdot m_0$$

The first seven tests, detailed in Table 3.6, were used to refine the experimental procedure by evaluating the influence of various parameters. Air flow rate, initial sample mass, powder grain size, sample holder geometry, and test duration were varied to identify a set of conditions that minimize the influence of these parameters, thereby ensuring a more robust and reproducible testing methodology.

Figure 3.6 shows the oxidation level for 4 tests performed at 540 °C with iron-silicon powder. Test 7 procures a higher oxidation level with lower initial powder mass, sample holder type B and Fe-7Si(20) powder. Lowering the powder dimension increases the reactive surface area per unit mass as particle diameter decreases, as previously observed for pure iron by Korshunov et al. [26] when comparing the oxidation of micron- and nano-sized particles.

It should be noted that care must be taken as the oxidation level is so small that experimental error can be the major cause of test differentiation. The high frequency signal is induced by the balance measurement error and the difference in environmental noise between the blanc and the real test. The machine is placed on rubber blocks, but the pumps, ventilation, and movements in the rooms induce noise on the signal. This noise will mostly disappear when the higher oxidation level is reached.

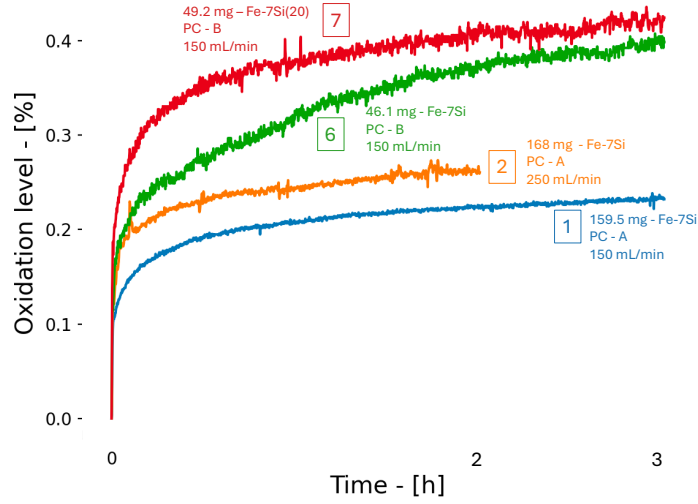


Figure 3.6: **Oxidation level comparison between 540°C TGA of Fe-7Si powder with varying parameters.** For each tests, the initial powder mass m_0 , the powder type, the powder container type, and the air flow rate $\dot{V}_{\text{air}}$ are specified. Initial powder mass and powder dimension reduction, as well as crucible B favor the oxidation.

The very low oxidation level observed, even during test 3 at 800 °C with $X \sim 1.67$ wt.%, motivates the utilization of pure iron powder to verify the correct operation of the installation and the choice of parameters. Two tests (4 and 5) were performed and the resulting oxidation curves are observable in Figure 3.7. Higher levels of oxidation were achieved during these tests, confirming the correct operation of the installation. The lower initial mass of powder and sample holder B seem to increase powder reactivity. However, Khun et al. [27] reported a similar oxidation level after one hour at 500 °C; although the temperatures differ slightly, this does not account for the discrepancy, and the lack of detailed experimental conditions in their report limits further comparison. Korshunov et al. [26] also reported an oxidation level of 33% after 1 hour. The powder used consisted of 95.8 wt.% iron, along with manganese, nickel, copper and other unspecified impurities that may influence the oxidation behavior. The particle size was centered around 45 μm in diameter. The primary factor that may have contributed to the rapid oxidation observed is the small initial mass of powder used, which ranged from only 5 to 15 mg. Observing this, initial powder mass seems to play a huge role in oxidation kinetics during the TGA test. But these variations could even come from experimental variations between installation and setup.

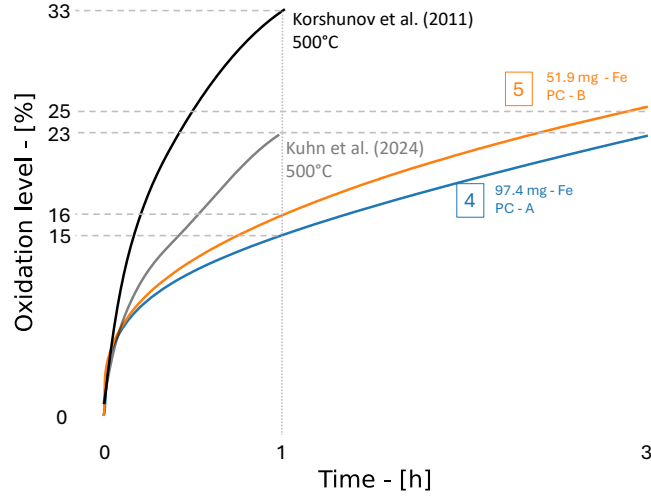


Figure 3.7: **Oxidation level comparison between 540 °C, TGA of Fe powder with varying parameters.** [4]: $m_0=97.4$ mg, PC A; [5]: $m_0=51.9$ mg, PC B. Decrease in powder mass increase the oxidation rate. Tests variation between the literature and the present set-up is non-negligible.

The further considered tests, from 8 to 17 in Table 3.6, were adjusted to longer oxidation durations, a minimum of 6 h, and up to 20 h to reach even higher oxidation levels. The first temperature value was 800 °C, and then increases with a step of 100 °C between tests to reach 1200 °C. The initial mass of the powder was also reduced to around 50 mg and then 30 mg to ensure as much isothermal conditions as possible, while providing good reactivity and enough oxidized powder for further analysis with SEM and EDS. Crucible type A was used because this amount of powder leads to an approximately 1 mm depth of powder, which does not obstruct the air accessibility to the particles. However, as the powder particles are superimposed, the surface area in contact with the air is reduced. As discussed, for a better interpretation of the kinetics, a powder with a mean diameter of 20 μm was used. As will be shown in Section 4.2, the 1100 °C test led to sudden steps of oxidation. To analyze the difference in composition before and after this fast oxidation, a 40 min test was performed.

After the TGA, oxidized powders were recovered from the crucible, when possible, to be analyzed with the SEM and EDX. At 540 °C and 800 °C, powder agglomeration was limited. When increasing the temperature, solid agglomerates required the use of a stainless steel scraper or tongs to break up the agglomerate and extract it from the crucible. For tests 16 and 17 at 1100 °C, agglomerate extraction was not possible, and the quantity of recovered particles was insufficient to allow for a representative analysis of these 20 h and 40 min tests.

3.4 High-temperature furnace and XRD

The limited amount of powder during TGAs did not permit analyzing it with XRD after its oxidation. Isothermal oxidation was then carried out using a basic high-temperature furnace, where ~ 1 g of Fe-7Si(20) powder was exposed for 4 to 20 h at temperatures ranging from 800 °C to 1200 °C. The powder was placed in a ceramic crucible to avoid

contamination. This approach produced a sufficient quantity of oxidized powder for analysis by XRD, which provides information on the crystalline phases formed during oxidation. X-rays are generated using a cobalt source; their interaction with the sample crystal structure causes diffraction, and the resulting peak positions correspond to characteristic signals of specific elements and phases.

The resulting diffraction pattern was analyzed using VESTA software, which identifies and quantifies the elements and phases present by matching known reference signals to those observed in the sample by applying the Rietveld refinement. The quantifications, initially provided in volumetric concentrations, were converted into weight concentrations using the theoretical densities (see Table 3.7) of the identified phases, while neglecting any variations in elemental composition induced by silicon presence in the iron or hematite structures, for example (further developed in Section 4.2).

Table 3.7: **Theoretical phases density** [28]

Phase	Fe	Si	FeO	Fe ₃ O ₄	Fe ₂ O ₃	Fe ₂ SiO ₄	SiO ₂
Density [g/cm ³]	7.87	2.33	5.70	5.17	5.26	4.39	2.65

3.5 Fe particle ignition model

The present Section describes the theoretical basis of the pure iron particle ignition model from Mi et al. [6] which was already approached in Chapter 2 and will be the foundation of the iron-silicon model developed in Section 5.4.

Three main assumptions form the basis of the model :

1. Densities are considered as constant and the effect of thermal expansion is neglected;
2. Phase change are not considered;
3. Curvature effect on the oxide layer growth is neglected.

By tuning the surrounding gas temperature, the purpose of the model is to find the thermal runaway temperature of the particle. It appears when the energy losses by the environment are lower than the heat released due to the iron oxidation reaction. Heat losses are governed by two phenomena: (i) convection due to the difference in temperature with the surrounding flow and (ii) radiation of the particle itself. For a question of ease, the flow around is considered to be motionless and so $Re = 0$. It is a very strong assumption made here, especially for the MC2 burner where there is a tornado flow at 25 °C that generates losses by convection.

The model is resumed in a balance of masses, forming the 3 ODEs of Equations 3.5 to 3.7, which represent the evolution of the mass during the oxidation process. The oxidation advancement leads to an iron oxide mass increase, while iron content decreases, pondered using stoichiometric mass ratios $\nu_{x/y}$. The variation of the different oxide masses is calculated knowing that the evolution of the oxide layer, Z_x follows a parabolic kinetic model determined by experience $\frac{dZ_i}{dt} = \frac{k_{p,i}}{Z_i}$, in which the parabolic growth rate (k_p) can be replaced by the definition of the Arrhenius law, $k_{p,i}(T) = k_{0,i} \exp\left(\frac{-T_{a,i}}{T_p}\right)$.

$$\frac{dm_{\text{Fe}}}{dt} = -\nu_{\text{Fe/FeO}} \frac{dm_{\text{FeO}}}{dt} - \nu_{\text{Fe/Fe}_3\text{O}_4} \frac{dm_{\text{Fe}_3\text{O}_4}}{dt} \quad (3.5)$$

$$\frac{dm_{\text{FeO}}}{dt} = \rho_{\text{FeO}} A_{\text{FeO}} \frac{dZ_{\text{FeO}}}{dt} = \frac{\rho_{\text{FeO}} A_{\text{FeO}} k_{0,\text{FeO}}}{Z_{\text{FeO}}} \exp\left(\frac{-T_{a,\text{FeO}}}{T_p}\right) \quad (3.6)$$

$$\frac{dm_{\text{Fe}_3\text{O}_4}}{dt} = \rho_{\text{Fe}_3\text{O}_4} A_p \frac{dZ_{\text{Fe}_3\text{O}_4}}{dt} = \frac{\rho_{\text{Fe}_3\text{O}_4} A_p k_{0,\text{Fe}_3\text{O}_4}}{Z_{\text{Fe}_3\text{O}_4}} \exp\left(\frac{-T_{a,\text{Fe}_3\text{O}_4}}{T_p}\right) \quad (3.7)$$

The final step to solve the ODE is to determine experimentally the kinetic coefficient k_0 and the temperature of activation $T_a = E_a/R$ for each oxide layer, where E_a is the energy of activation and R is the gas constant. The kinetics parameters are presented in Table 3.8.

Table 3.8: Global kinetics parameters for pure iron obtained from [6]

	k_0 [m^2/s]	T_a [K]
FeO	2.670×10^{-4}	20319
Fe ₃ O ₄	1.027×10^{-6}	21310

To find the thermal runaway, it is needed to follow the particle temperature (T_p) within constant gas temperature (T_g). To do that, energy releases due to oxidation (q_{FeO} and $q_{\text{Fe}_3\text{O}_4}$) are balanced with losses to the environment at a given time, see Equation 3.8. The third term of this equation corresponds to the energy gained by the incorporation of dioxygen; the negative sign is just related to the definition. The last term corresponds to the convection and radiation losses. The evaluated particle energy (H_p) is then compared to the theoretical internal energy of each component using a precomputed matrix of internal energies at various particle temperatures ranging from 300 K to 2000 K (see Equation 3.9). This allows for the determination of the particle temperature T_p at each time step of the simulation.

$$\frac{dH_p}{dt} = q_{\text{FeO}} \frac{dm_{\text{FeO}}}{dt} + q_{\text{Fe}_3\text{O}_4} \frac{dm_{\text{Fe}_3\text{O}_4}}{dt} - \frac{h_{\text{O}_2}(T_g)}{W_{\text{O}_2}} \frac{dm_{\text{O}_2}}{dt} - A_p \left[h_p(T_p - T_g) + \sigma \epsilon (T_p^4 - T_g^4) \right] \quad (3.8)$$

$$H_p = \sum_i^{N_s} \frac{m_i h_i(T_p)}{W_i} \quad (3.9)$$

Typical results obtained from the model can be seen in Figure 3.8, when the temperature of the thermal runaway is approached. The present simulation evaluates that the thermal runaway appears when T_g is equal to 820 °C. Below this gas temperature, T_p increases as oxidation releases enough energy to do so, but due to oxidation kinetics and temperature difference, the losses become bigger and prevent the further increase of the particle temperature. The result obtained differs slightly from the reference model [6]. As they obtained a value for the thermal runaway at 807 °C, the error is $\sim 1.6\%$. The difference between the models can come from the database used. For the internal energy, National Institute of Standards and Technology (NIST) is used, and also the Coolprop library is

used to compute parameters like the conduction coefficient. The temperature value of the thermal runaway changed also from a few kelvin with the amount of points used to solve the ODE.

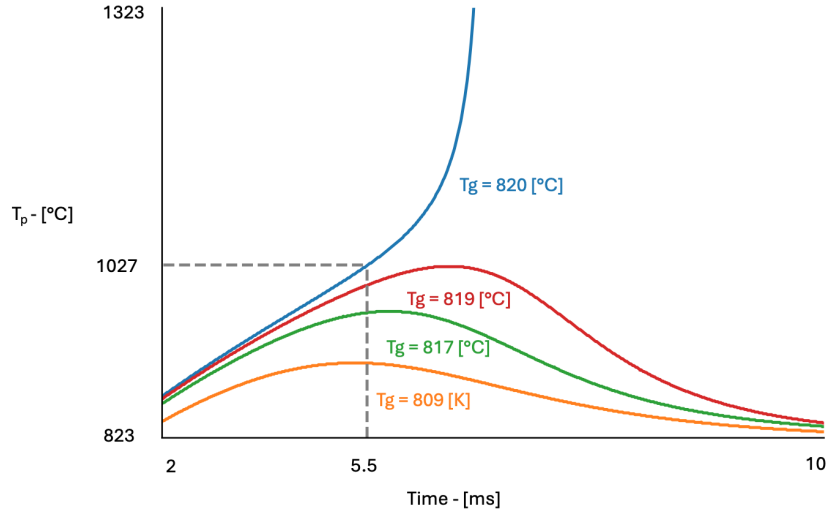


Figure 3.8: **Modelisation of the pure iron particle temperature evolution under different constant gas temperatures.** The thermal runaway for pure iron is obtained at a gas temperature (T_g) of 820 °C.

Chapter 4

Results

In the present Chapter, the results obtained for the two oxidation procedures of Fe-7Si powder are detailed: (i) multi-particle combustion in the metallic cyclonic combustor (MC2) (ii) isothermal oxidation with air using thermogravimetric analysis (TGA) and the high-temperature furnace. Both will be the basis to interpret the oxidation mechanisms and kinetics of iron-silicon powder to model the ignition temperature in Chapter 5.

4.1 Metallic cyclone combustor

This Section describes the results from the three tests performed with the MC2 at TU/Eindhoven. The analyses will start with the variation of the measured outputs (powder mass-flow rate, gas temperature, gas analysis, and spectrometer) with the combustion parameters. Next, the combustion products will be characterized to quantify the combustion and ignition efficiency of the Fe-7Si particles compared with Fe, and analyze the chemical, morphological, and microstructural evolution of the powders.

4.1.1 Combustion analysis

During the three combustion tests, two distinct flame configurations were observed. The first configuration occurred during test 1 and the second half of test 2 (see Table 3.5). The majority of the injected powder failed to ignite, and only localized ignition was observed, as illustrated in Figure 4.1 (A). In contrast, a stable and well-developed flame was observed at the beginning of test 2 and throughout the entirety of test 3, as shown in Figure 4.1 (B). This flame exhibited a characteristic tornado-like shape, induced by the swirl flow pattern in the burner. The swirling motion enhanced particle residence time, thereby promoting a higher degree of oxidation. It is important to note, however, that the flame was not self-sustaining, as the radiant heaters remained active during all tests to maintain combustion.

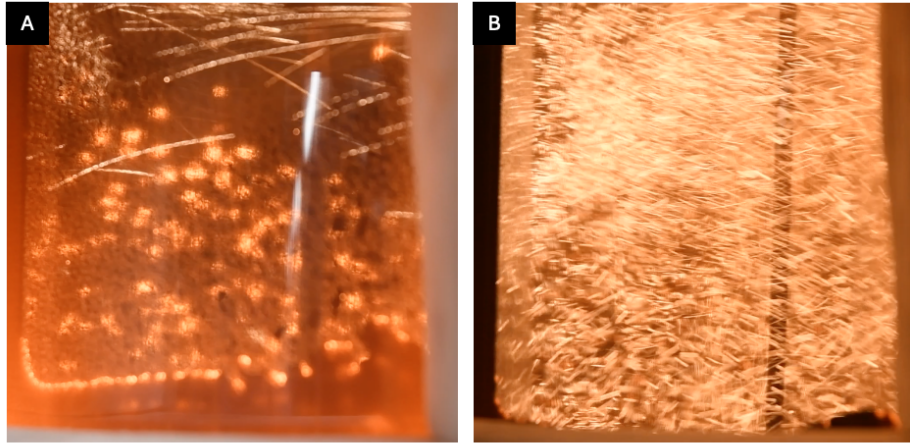


Figure 4.1: **Flame pictures during Fe-7Si combustion in MC2.** (A) Few ignited particles, obtained during test 1 and second half of test 2. (B) Established flame obtained at the beginning of test 2 and during test 3

As discussed in Chapter 2, similarly to homogeneous fuel combustion, richness and gas temperature are the two main conditions governing the formation of a stable heterogeneous metallic powder flame.

Richness

The air-to-powder mixture determines the availability of powder relative to oxygen during combustion. A rich mixture (high powder content) limits oxygen availability, leading to incomplete oxidation and insufficient heat generation. Conversely, a lean mixture (low powder content) increases the distance between particles, making heat transfer less efficient and potentially hindering self-sustained combustion.

Tests 1 and 3 exhibited relatively stable powder mass flow rates, as shown in Figure 4.2, with values of approximately 0.71 g/s and 0.68 g/s, respectively. These correspond to an air-to-fuel equivalence ratio (λ) of around 0.8, assuming complete oxidation to magnetite (Fe_3O_4).

In contrast, during Test 2, the initial conditions were similar with $\lambda \approx 0.8$, but the powder mass flow rate decreased to 0.45 g/s at around 62 seconds, leading to an increase in λ to approximately 1.2. The reason for this change is unknown, but it could come from the supply bottle in which some powder could be blocked. This reduction in the quantity of powder meant that the particles were more widely dispersed in the combustion chamber, which meant that the flame struggled to maintain itself with only a few particles that succeeded in igniting.

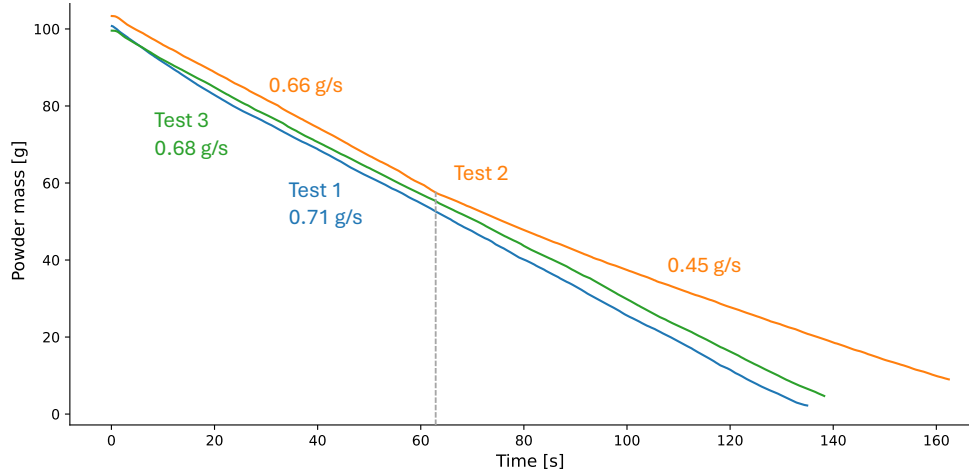


Figure 4.2: **Evolutions of the powder mass in the bottle** After 1 minute of combustion the mass flow rate of the test 2 decreases.

Gas temperature

Sufficient surrounding gas temperature is needed to ignite and burn particles, by lowering the convective losses due to the temperature difference between particles and gas. However, the temperature of the gas inside the combustion chamber is directly related to the combustion conditions, as heat is released from the powder oxidation, and radiant heaters are the other source of heat inside the combustion chamber.

Figure 4.3 presents gas temperature curves measured with the thermocouple at the center (T_{center}) and the top (T_{top}) of the combustion chamber. For both tests 1 and 2, radiant heaters were ON during the entire duration of the test, with threshold temperatures at 810 °C and 990 °C, respectively. For test 3, the temperature briefly dropped below the 930 °C threshold, activating the radiant heaters for about 20 seconds, before the heating was shut down approximately one minute after the start of the experiment.

The initial temperature difference between the top and the center thermocouples ($T_{\text{center}} - T_{\text{top}}$) was 130 °C, 120 °C, and 100 °C, for tests 1, 2, and 3, respectively. In all three tests, the initial airflow causes the temperatures to drop by approximately 10 °C within the first few seconds (~ 5 s). This is attributed to the cooling effect of the increase in incoming gas flows. Following this period, powder is assumed to begin entering the combustion chamber, enabling potential flame ignition.

Test 1 showed a significant decrease in both top and center temperatures (-50 °C in 30 sec). The thermal energy inside the burner appears insufficient to ignite a stable flame. The temperature difference between the center and top thermocouples is pronounced, indicating that the radiant heaters make a dominant contribution to keeping the temperature stable.

Test 2 demonstrated successful ignition: the gas temperature rose from 918 °C to 988 °C, accompanied by a reduction in the temperature gradient ($T_{\text{center}} - T_{\text{top}}$), suggesting improved thermal homogeneity due to the flame. After reaching a peak at 81 seconds, the temperature gradually decreased and stabilized around 950 °C for approximately 20 seconds, before decreasing again and reintroducing a higher temperature differential inside the chamber.

Test 3 initially mirrored the behavior observed in test 2, with a rapid temperature increase from ~ 920 °C to 970 °C and a corresponding decrease of $T_{\text{center}} - T_{\text{top}}$. Both

temperatures dropped at 30 s, as the center temperature reached 915 °C. However, a notable divergence occurred: while the center temperature stagnated around 920 °C, the top temperature rose again, peaking at 960 °C and surpassing T_{center} . After this peak, the overall temperature fell again until the end of the experiment, but remained higher at the top of the combustion chamber.

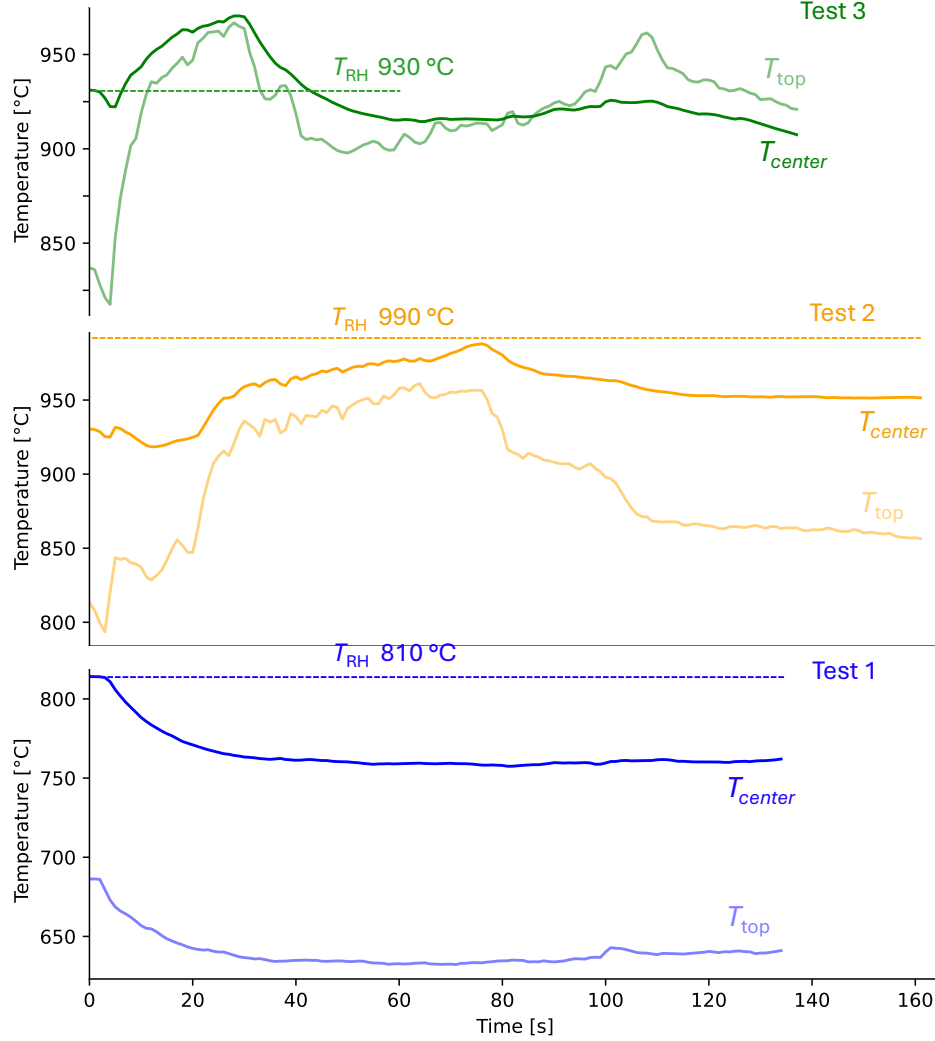


Figure 4.3: **Gas temperature evolution at the centre and top of the combustion chamber for tests 1 to 3.** Colored dashed lines represent the temperature thresholds (T_{RH}) for the different tests, controlling the radiant heater activation, based on center thermocouple measurement.

It is not possible to precisely determine the gas temperature throughout the entire burner. The central thermocouple is positioned 6.5 cm from the wall and 25 cm downstream from the injection inlets. A comparison between the central and top thermocouple measurements indicates that gas temperature homogeneity within the combustion chamber cannot be assumed. Radial temperature inhomogeneities are also expected, as the chamber walls are directly heated by the radiant heaters; they also contribute additional heat to the gas flow when active. Moreover, as the powder injection progresses, accumulation of particles on the thermocouples becomes more significant, potentially affecting the accuracy of their readings. It is then difficult to estimate the exact temperature faced by the

particles throughout their combustion path.

As shown in Figure 4.4, gas analyzer measurements revealed an oxygen concentration drop of only 0.1 vol.% during test 1, compared to around 2 vol.% in tests 2 and 3 (starting at 21 vol.%). The oxygen concentration continued to drop after the test end, which shows the slow response time of the gas analyser. NO_x emissions peaked at 5 ppm in tests 2 and 3, while none were detected in test 1. In contrast, CO emissions were higher in test 1 (20 ppm) than in tests 2 and 3 (5 ppm).

Spectrometer measurements showed an average particles temperature of 1493 ± 75 °C during test 2, while it was 1582 ± 70 °C during test 3. No measurements were taken during test 1, as no flame could be observed.

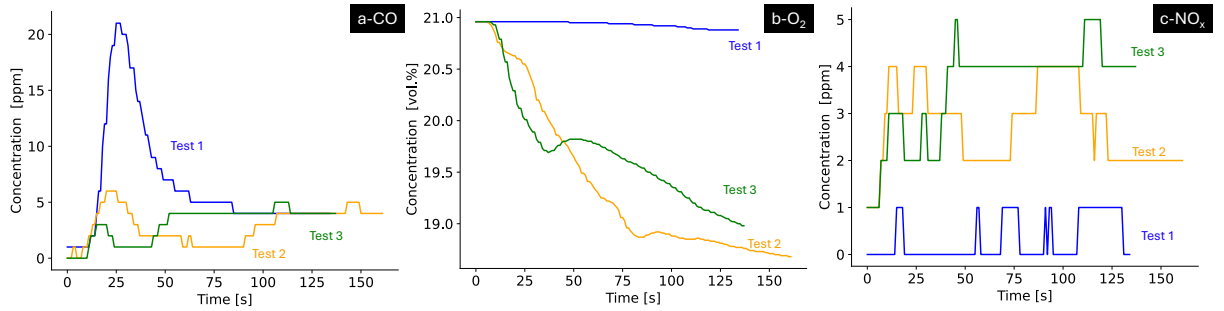


Figure 4.4: **Gas analyzer measurements of the exhaust gas:** (a) CO concentration in ppm, (b) O₂ concentration in vol.%, (c) NO_x concentration in ppm. The combustion of the powder produces small quantities of NO_x and CO. A decrease in O₂ concentration is observed during combustion, which confirms oxidation. The continued drop in O₂ after combustion events can be attributed to the response time (inertia) of the gas analyzer.

4.1.2 Powder analysis after combustion

The section present, microstructural analysis of combusted products from tests 1 and 3 because test 2 did not present stable conditions. As explained in Section 3.2, there are two zones where the powder was recovered: (i) in the cyclone collector (-cycl) and (ii) on the combustion chamber wall (-wall). The main difference is the residence time of the particles at high temperature in the combustion chamber.

Granulometric analysis

The size distributions of the burned powders were analyzed using granulometric analysis to be compared to the initial size distribution of the Fe-7Si powder. Agglomeration quantification will be a key factor when the cyclability of the Fe-7Si powder is discussed in Chapter 5. Before the measurement, the powder was sieved with a 140 µm filter to separate agglomerates that could damage the granulometer.

Since the 1-cycl powder did not present significant agglomeration, only the 1-wall powder was sieved for this analysis. As shown in Table 4.1, approximately 38.3 g of the ~100 g of powder injected during test 1 were recovered from the combustion chamber walls. However, the fraction of large particles in this sample was limited to 7.46 wt.%.

In contrast, during test 3, 85.5 g of powder accumulated on the chamber walls, while only 21.7 g reached the cyclone collector. The 3-cycl powder contained 1.94 wt.% of large

particles and showed minimal visible agglomeration. The highest degree of agglomeration was observed in the 3-wall powder, where 22.57 wt.% of the sample was separated prior to granulometric analysis.

Table 4.1: Table showing the percentage of agglomerates bigger than 140 μm removed before the granulometric analysis. The 3-wall shows a higher proportion of large agglomerates, while the others have only a small portion.

	m_{tot} [g]	< 140 μm [wt.%]	> 140 μm [wt.%]
1-wall	38.3	92.54	7.46
3-cycl	21.7	98.06	1.94
3-wall	85.5	77.43	22.57

The theoretical size increase resulting from the complete oxidation of Fe-7Si powder to hematite and silica was estimated based on the densities of the resulting phases (Table 3.7). This evaluation assumes perfect sphericity and a homogeneous composition of the particles. The theoretical oxidized particle size distribution is thus derived as a shifted version of the initial distribution, as presented in Figure 4.5, with a median of 40.9 μm compared to 38.7 μm initially.

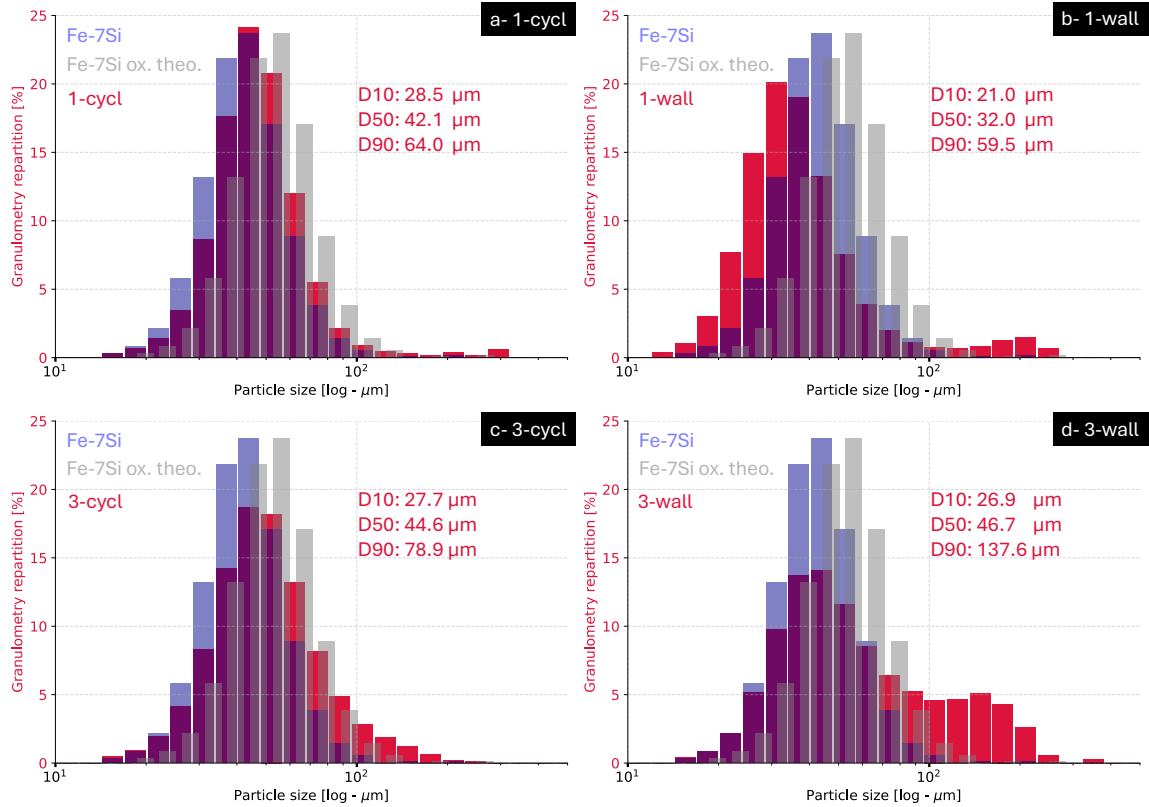


Figure 4.5: Particle size distribution comparison of burned particles in the MC2 for tests 1 and 3, with initial Fe-7Si powder and its theoretical size increase due to oxidation. (A) 1-wall: low change. (B) 3-wall: increase in particle size. (C) 3-cyl: increase in particle size.

In Figure 4.5 (a), the particle size distribution of the 1-cycl powder shows a slight increase in size, with only a limited shift in the distribution bars. Larger particles are

present, with a maximum diameter of 120 μm , but overall, the distribution remains framed between that of the initial and theoretical fully oxidized powders. Surprisingly, the 1-wall powder, after sieving, exhibits a size distribution shifted to the left, towards smaller diameters, even though the proportion of larger particles has increased, as shown in Figure 4.5 (b).

As expected, Figures 4.5 (c–d) show a global shift in the size distribution of the powder recovered from Test 3 compared to the initial powder. The 3-cycl powder distribution is broader and flatter than the theoretical oxidation curve, with an increased proportion of particles larger than 100 μm and a corresponding rise in the median diameter. The peak of the 3-cycl size distribution decreases while the tail extends, indicating a high level of particles agglomeration. Nevertheless, small particles are still present in the recovered fraction.

Moreover, the sphericity of the powder decreased after combustion, as evidenced by the declining median values and percentiles shown in Table 4.2. This indicates a progressive loss of particle roundness, particularly in powders recovered from the wall.

Table 4.2: **Percentiles (D10, D50, D90) of sphericity measurements for the initial and recovered powders**, illustrating the reduction in particle sphericity due to combustion and agglomeration effects.

Powder	D10	D50	D90
Fe-7Si	0.695	0.840	0.966
1-cycl	0.685	0.832	0.964
1-wall	0.678	0.827	0.962
3-cycl	0.661	0.813	0.960
3-wall	0.648	0.805	0.958

XRD analysis

XRD analyses of the burned powders, presented in Figure 4.6, highlight two key points: (i) the higher combustion efficiency during test 3, as shown by a lower ferritic phase (Fe) content; (ii) the powders collected from the chamber wall show a higher oxide content than those collected in the cyclone.

In 1-cycl powder, oxidation was minimal, with only a small peak corresponding to the main diffraction angle of magnetite (Fe_3O_4), leading to an estimated concentration of 0.2 wt.%.

The 1-wall powder presented more oxide peaks: wüstite (FeO), magnetite, hematite (Fe_2O_3), and fayalite (Fe_2SiO_4). However, its overall oxidation remains low, with 93.5 wt.% of ferritic phase and individual oxide phases ranging from 0.1 to 2.6 wt.%.

The same oxide phases as in the 1-wall powder were detected in both 3-cycl and 3-wall powders. Magnetite was the dominant oxide in 3-cycl and 3-wall powders, with concentrations of 22.5 wt.% and 27.1 wt.%, respectively. Wüstite is present in small quantities, with up to 2.1 wt.% in 3-cycl powder. Hematite becomes more significant in the 3-wall powder, reaching 12.3 wt.%. The ferritic phase content decreases to 70.5 wt.%

in 3-cycl powder and 57.8 wt.% in 3-wall powder, confirming a more efficient, but still incomplete, combustion during test 3.

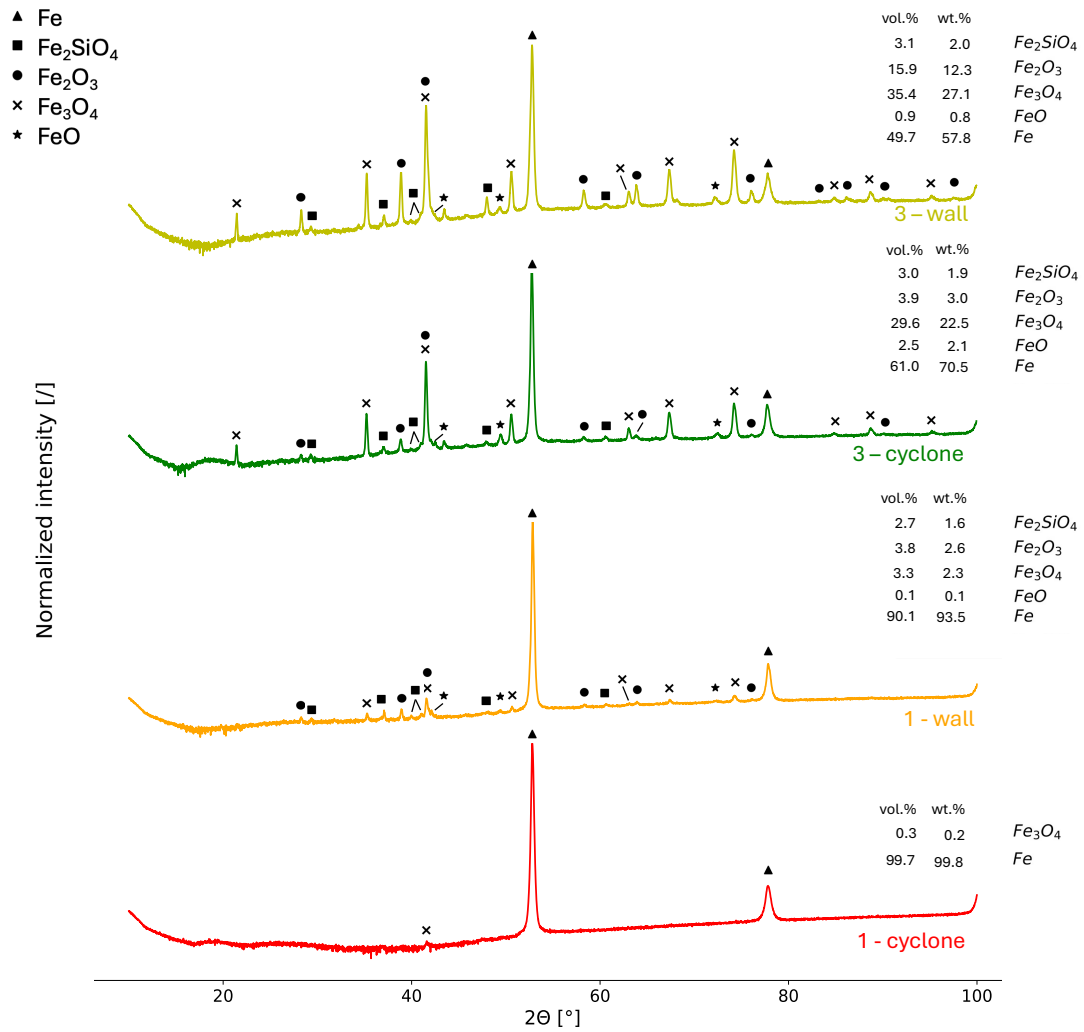


Figure 4.6: XRD spectrum and quantification of oxidized Fe-7Si powder using MC2 burner

Microstructure analysis

After the global results presented in the previous parts of this Section 4.1.2, the objective of the following analysis is to investigate the microstructure and composition of selected burned particles using scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS). First, Figure 4.7 shows a global view on particle surfaces collected from tests 1 and 3, reflecting the granulometry trends, with an increasing presence of agglomerates from Figure (a) to (d). The 1-cycl powder appears globally similar to the initial Fe-7Si powder, whereas the 1-wall powder reveals signs of particle agglomeration. In the 3-cycl sample, larger particles and holed ones are observed. These features are even more pronounced in the 3-wall powder, where a higher number of holed particles and agglomerates are visible. In both 1-wall and 3-wall samples, some agglomerates exhibit flat surfaces, likely resulting from interaction with the chamber walls.

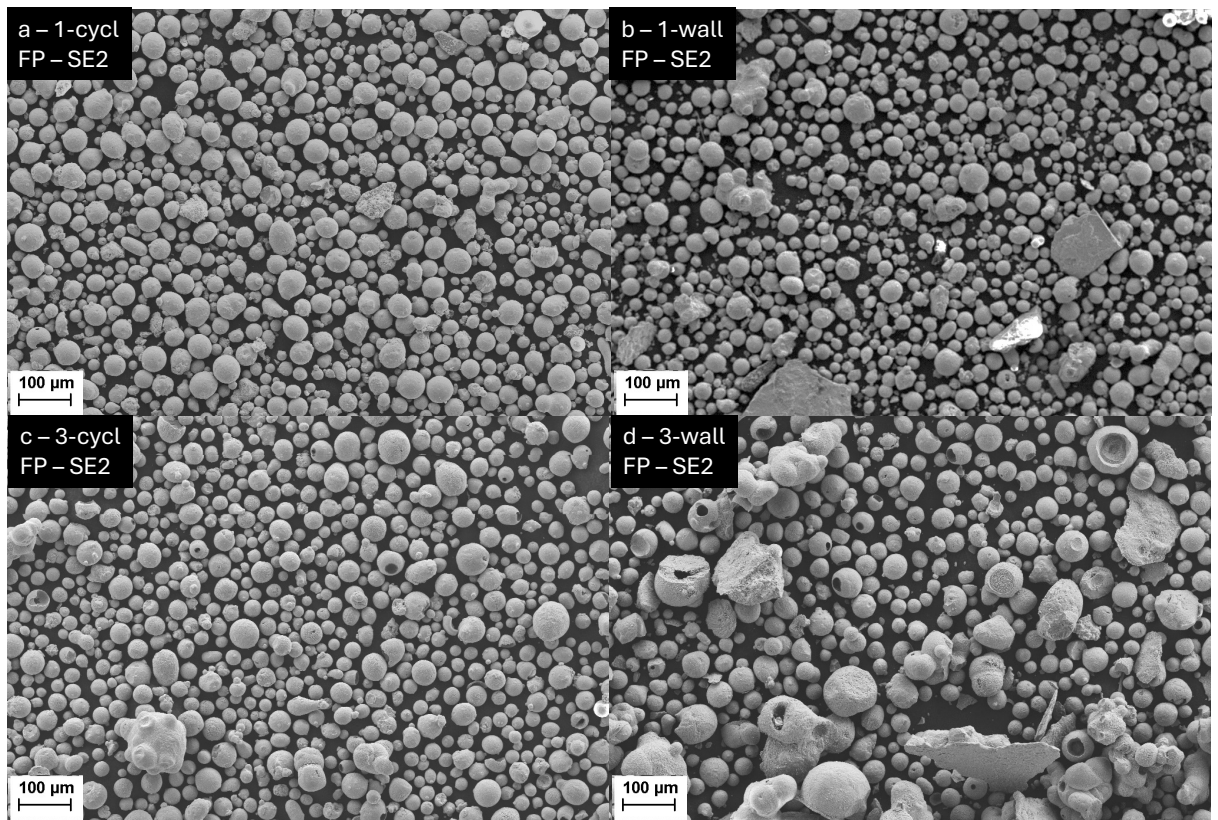


Figure 4.7: Global SEM images of the surface of Fe-7Si burned powder in MC2 during test 1 and 3, using SE2 detector. (a) 1-cycl particles shape is relatively similar to initial Fe-7Si powder. Agglomerate are highly present in (b-d). (c-d) Holed particles are more present.

1-cycl

As shown in Figure 4.8, rare holed particles are present, showing that some of them went to a liquid state during the combustion due to the dendritic structure observed on their surface. As circled in Figure 4.8 (b), some particles also present dark spots ($\sim 1\ \mu\text{m}$) on their surface. However, most of the particles look like the initial Fe-7Si powder.

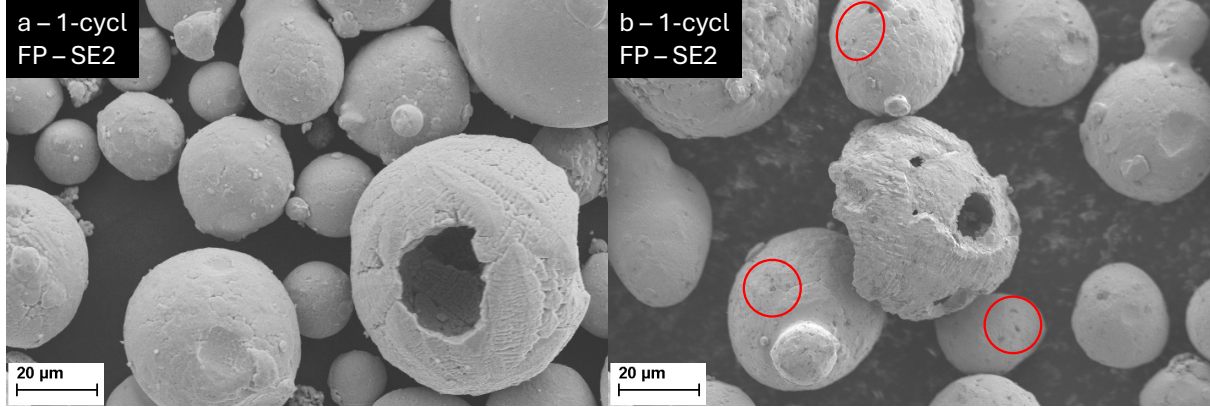


Figure 4.8: **SEM images with SE2 detector of 1-cycl powder.** 1-cycl powder is mostly similar to Fe-7Si, but: (a) holed particles showing dendritic structure, and (b) particles with small dark spots are present.

1-wall

Figure 4.9 (a) reveals that the agglomerates are composed of small particles ($\sim 25\ \mu\text{m}$), bound together by an oxide matrix, as indicated by the irregular surface morphology compared to the initial powder. Additionally, exploded particles exhibit cavities approximately $50\ \mu\text{m}$ in diameter, filled with numerous finer particles ($\sim 2\ \mu\text{m}$), suggesting disintegration during combustion.

In the BSE image of Figure 4.9 (b), dark spots are again visible on the particle surfaces. The strong contrast observed indicates significant compositional heterogeneity, which will be further discussed in the context of the 3-wall powder in Figure 4.13.

Figures 4.9 (c-d), showing the cross-section of a core-shell particle, demonstrate that the core did not undergo complete melting, as evidenced by the different layers and its non perfectly spherical shape. In contrast, the outer shell displays a dendritic microstructure, with eutectic phases in the interdendritic regions, indicating that it was molten during combustion.

Figure 4.9 (e) illustrates a different core-shell configuration for a particle of $\sim 25\ \mu\text{m}$ in diameter. The outer shell (3), with a thickness ranging from 2 to $5\ \mu\text{m}$, is primarily composed of iron oxide (containing only 0.7 wt.% Si), and exhibits a dendritic structure. The inner shell (2), composed of an Fe-Si mixed oxide, lacks visible signs of solidification such as dendrites, and its thickness varies between 0 and $5\ \mu\text{m}$. The non-oxidized core retains an irregular shape, confirming it remained in the solid state. However, it is enriched in silicon (11.4 wt.% Si) compared to the initial composition, suggesting that solid-state diffusion of silicon occurred during oxidation.

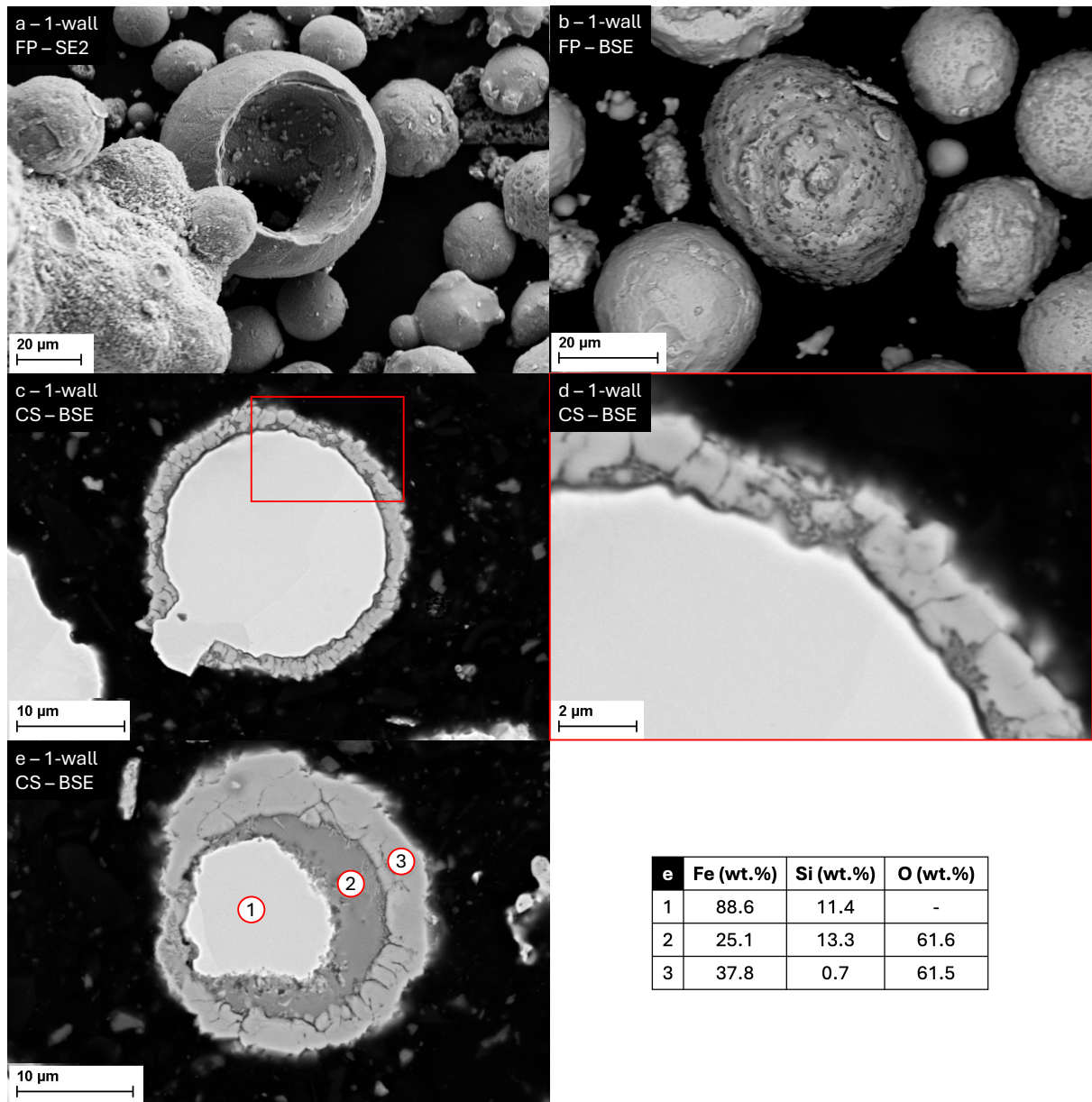


Figure 4.9: **SEM images of 1-wall powder.** Full particle (FP) images of holed particle and agglomerate using SE2 detector (a), and particle presenting dark spots on their surface using BSE detector (b). (c-e) Focus on two small particles ($\sim 25 \mu\text{m}$) cross section with BSE detector. (d) Particle layer showing dendritic and eutectic structures. (e) EDX quantification shows core and shells structure with varying Fe-Si-O concentrations.

3-cycl

Figure 4.10 (a) presents a strong contrast between particles in the BSE image, likely distinguishing fully combusted particles from unreacted ones. Similar observations are presented in figure 4.11 (a), with a cross-sectional image of the same powder, which also shows that most particles are either fully burnt or not oxidized at all. This observation further supports the low combustion efficiency of the experiment, as previously indicated by the XRD analysis.

Focus on an oxidized particle in Figure 4.10 (b) presents that its surface is uniformly and densely covered with microcrystalline oxide particles, typically $\sim 1\ \mu\text{m}$ in size. The morphology is angular, indicating the formation of crystalline oxides, which could be the product of solid iron oxide growth on the surface after solidification.

The smaller particle ($\sim 30\ \mu\text{m}$) presented in Figures 4.10 (c-d) has a lower amount of crystalline oxide on its surface. However, a dendritic surface structure is observed, likely composed of iron oxide, with a dark interdendritic phase that may correspond to Si-rich oxide. Additionally, a speckled pattern is present, which could indicate an eutectic microstructure. However, this interpretation requires confirmation through complementary characterization techniques with higher spatial resolution, such as transmission electron microscopy (TEM). A hole of $\sim 3\ \mu\text{m}$ is also present on this particle surface, showing that micron-explosions were also present.

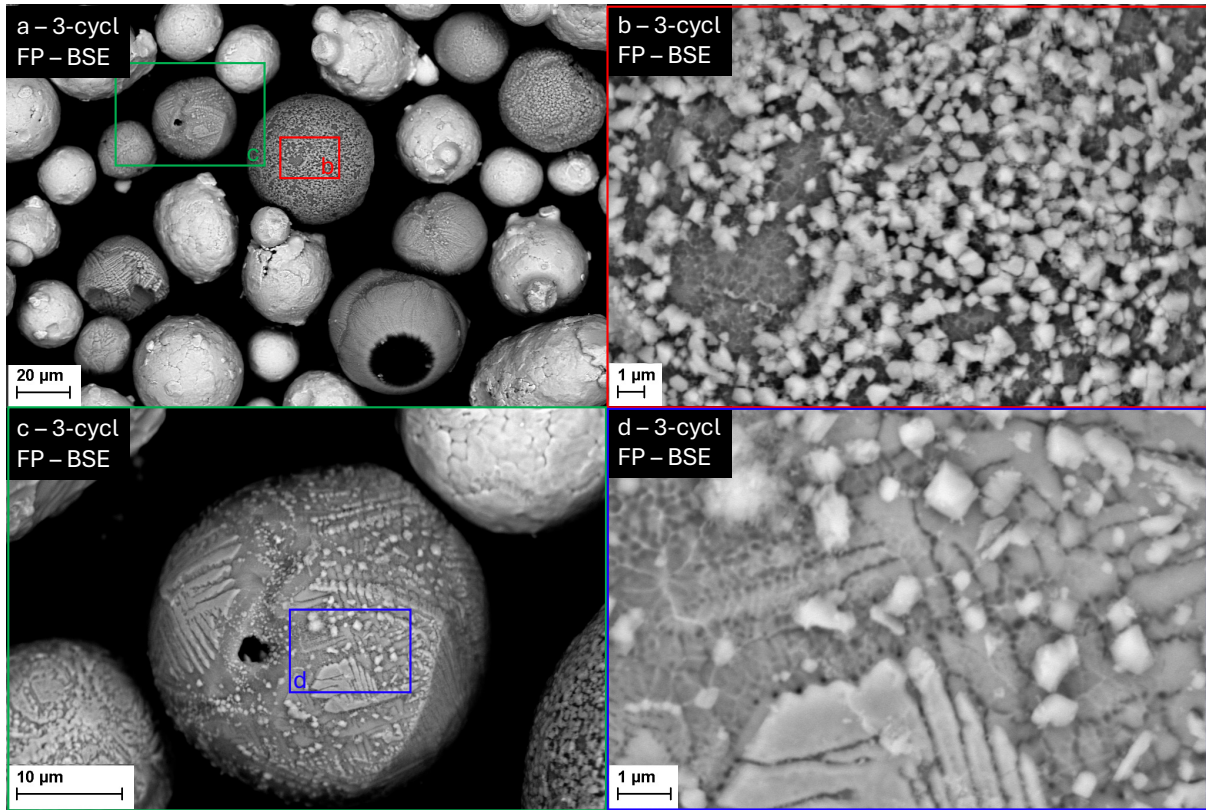


Figure 4.10: SEM images using the BSE detector of full 3-cycl particles. (a) Overview revealing strong contrast between oxidized and unoxidized particles. (b) Surface detail of a $50\ \mu\text{m}$ particle exhibiting bright crystalline oxide and a darker phase, likely indicative of compositional heterogeneity. (c-d) Dendritic surface structures and small cavities, suggesting melting and micro-explosions during combustion.

Figure 4.11 further illustrates the significant heterogeneity in particle combustion, as evidenced by the diversity in oxidation states among the analyzed particles with BSE contrasts.

Representing the majority of fully oxidized particles, Figure 4.11 (b) presents the internal microstructure of a particle $\sim 40\text{ }\mu\text{m}$ in diameter, which may correspond to the particle shown in Figure 4.10 (c). The internal morphology is characterized by a well-defined dendritic network. The interdendritic regions, appearing darker in BSE imaging, are likely richer in silicon and exhibit numerous cavities, suggesting localized volatilization during combustion.

Cross-sections of partially oxidized particles offer valuable insights into the underlying combustion mechanisms. The particle presented in Figure 4.11 (c) exhibits a well-defined core-shell structure. The core appears to have remained in the solid state throughout combustion, while the surrounding shell shows a dense dendritic microstructure with pronounced and extended interdendritic voids. This morphology strongly suggests that the shell underwent a liquid-phase transformation during combustion, followed by rapid solidification.

In contrast, the particle in Figure 4.11 (d) is totally spherical, suggesting it was entirely molten at some stage during combustion. The presence of small cavities within both the particle core and the surrounding layers supports this hypothesis. Its structure appears to consist of (i) a partially unoxidized core and (ii) three concentric oxidized layers with varying compositions. A compositional gradient is visible across the interfaces between the layers, indicating diffusion processes likely occurred during a post-solidification oxidation phase. The outermost layer is presumed to be iron-rich, followed by a darker intermediate layer probably enriched in silicon oxides. The dominant inner layer likely results from a combination of both phases.

Finally, the particle shown in Figures 4.11 (e–f) exhibits asymmetric oxidation, with one side more significantly affected. The core appears to retain a uniform composition, similar to previous observations, except at the oxide-metal interface where compositional gradients are likely. Unlike prior cases, the shell does not display a dendritic morphology; instead, a well-defined eutectic structure is present. Crystalline oxide phases are again observed on the particle surface.

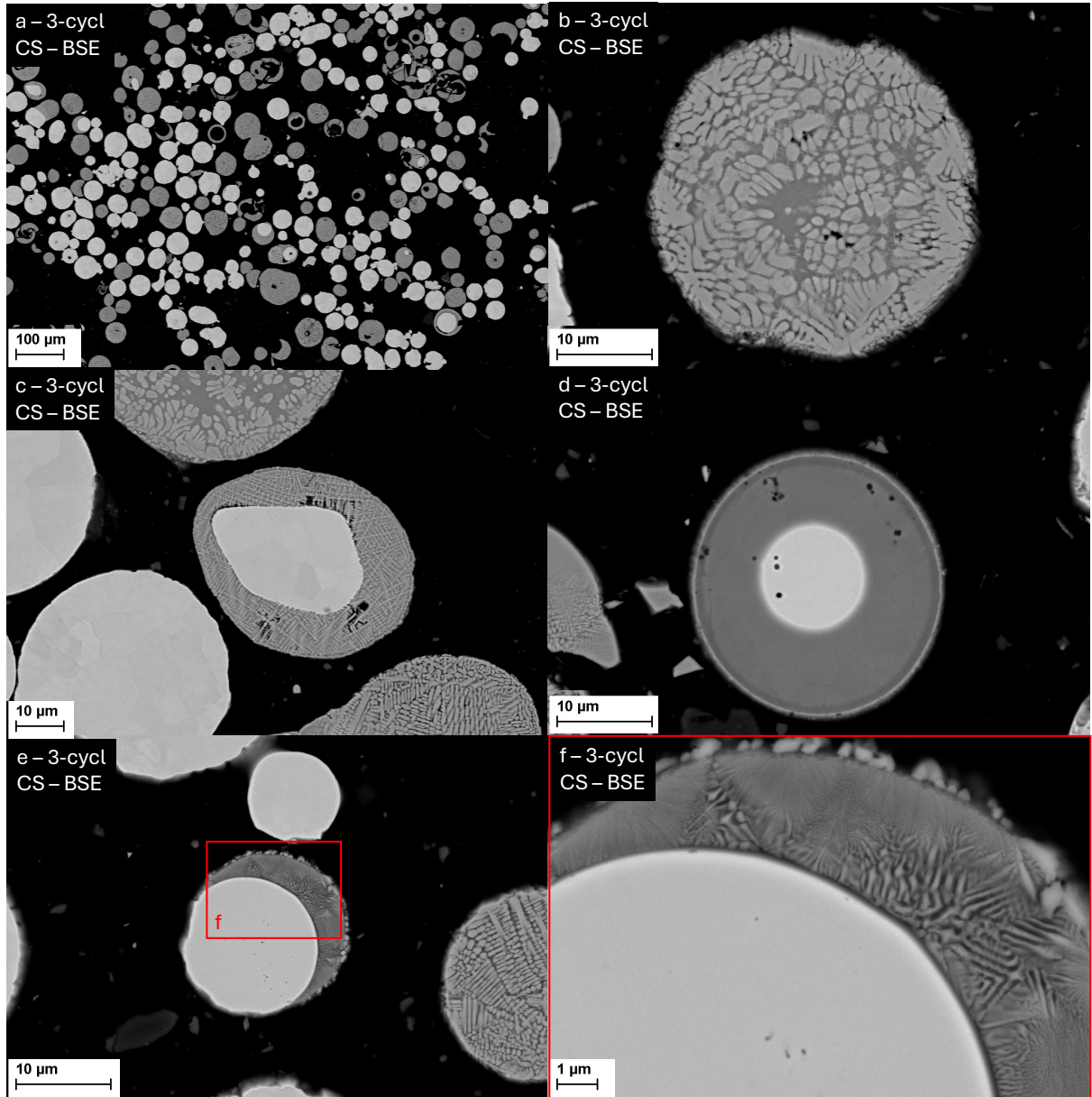


Figure 4.11: **SEM images using the BSE detector of 3-cycl particle cross-sections.** (a) Overview showing contrast between burned and unoxidized particles. (b) Fully oxidized particle exhibiting a dendritic microstructure and porous regions. (c) Core-shell particle showing dendritic features in the shell and a non-spherical, remained solid core. (d) Nearly spherical particle with multiple oxidation layers. (e-f) Partially oxidized particle displaying a eutectic structure, along with fine crystalline oxides on the outer shell surface.

3-wall

Figure 4.12 presents representative examples of the most frequently observed particle types in the 3-wall powder, excluding completely unoxidized particles and large agglomerates.

In Figure 4.12 (a), three distinct particle morphologies with signs of oxidation are illustrated. Particle (A) exhibits a dendritic structure with two opposing solidification fronts, suggesting bi-directional solidification or the possible fusion of two molten particles. Surface porosity is observed at the interface of these fronts. Particle (B) displays a clear sign of micro-explosion, with a cavity approximately 25 μm in diameter. Particle (C) shows a dotted surface featuring dark spots (2), which EDX analysis in Figure 4.12 (c) identifies as a Si-rich oxide phase (~ 20.0 wt.% Si). The clearer surface regions (1) on the same particle remain unoxidized and exhibit a lower silicon content (~ 4.1 wt.% Si) than the original Fe-7Si powder.

Additionally, Figure 4.12 (b) shows a particle with a porous surface, potentially formed through solid-state oxidation of iron. Numerous small particles (3–10 μm) are observed on and around its surface, likely originating from the micro-explosions of other particles within the batch.

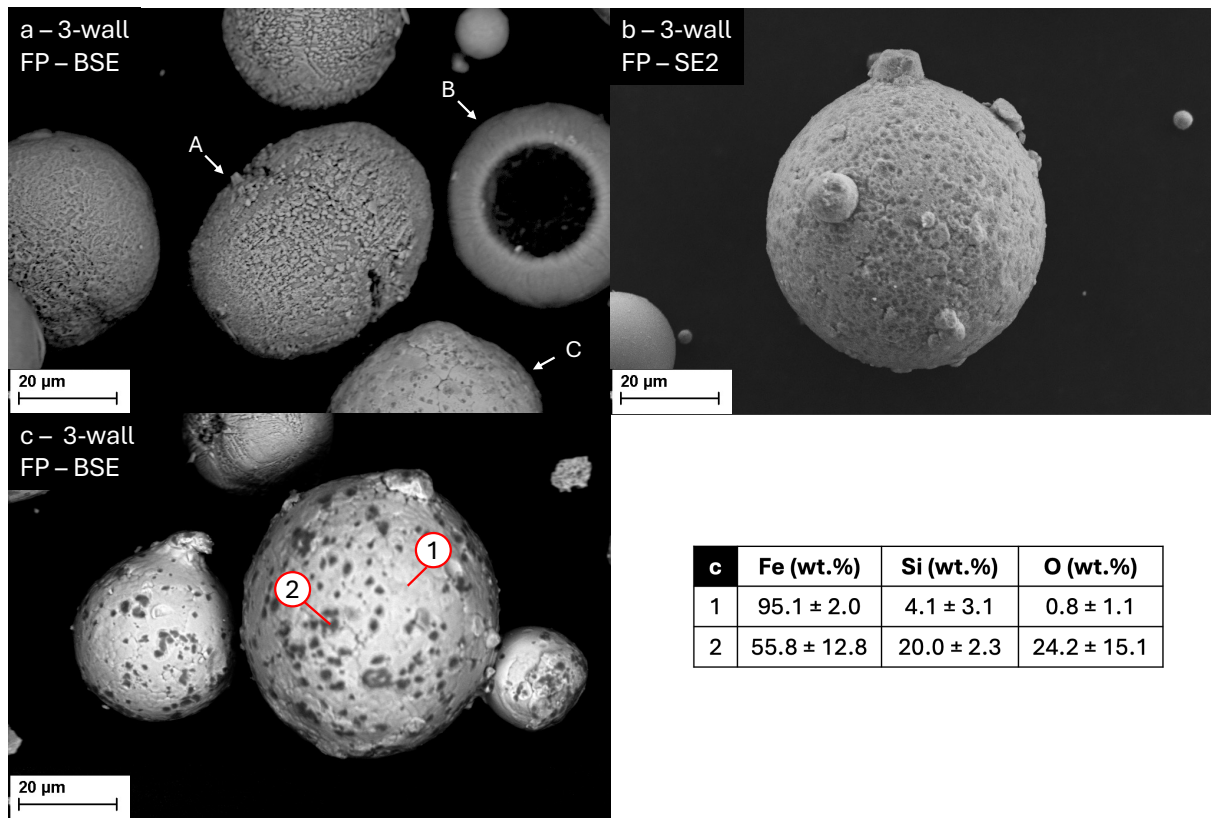


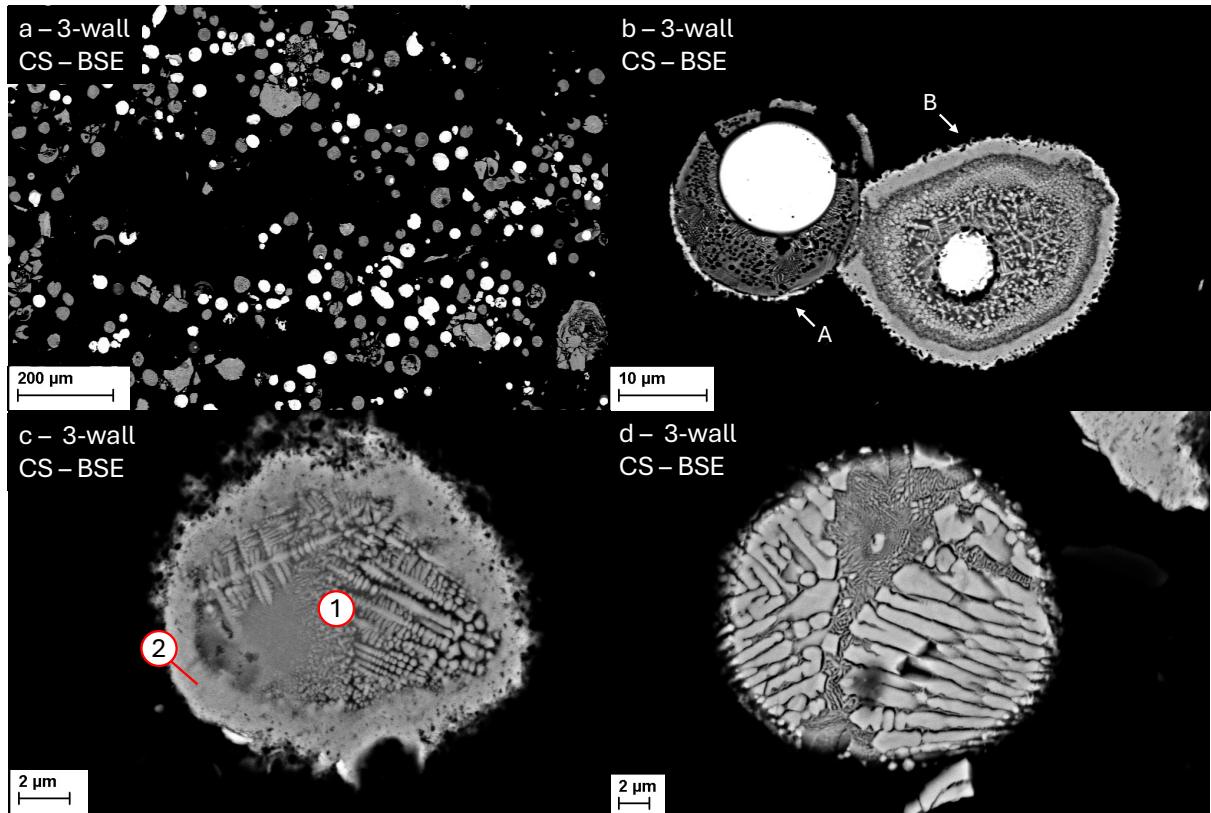
Figure 4.12: **SEM images of complete 3-wall particles using the BSE detector.** (a) Three distinct particle types are observed: (A) two solidification fronts originating from opposite directions, with holes at the joint; (B) micro-explosion; (C) dotted surface with dark Si-rich oxide. (b) Porous particle imaged using the SE2 detector, with several smaller particles (~ 10 μm) adhered to its surface. (c) EDX analysis indicates that the dark dots features (2) correspond to silicon-rich oxides emerging on the non-oxidized surface (1).

As anticipated based on the XRD results, Figure 4.13 (a) reveals a high proportion of oxidized particles, which appear darker under the BSE detector. Fragmented or disintegrated particles are also observed, highlighting the brittleness of the oxide shell.

Despite this, core-shell structures are still present, as illustrated in Figure 4.13 (b). Particle (A) demonstrates that the oxide shell is significantly more fragile than the core, with visible cracking or detachment. The overall darker contrast of the shell suggests a high silicon content, indicating that both fragility and chemical composition may be correlated. The core of particle (A) appears spherical, suggesting that it was fully molten during combustion, and contains numerous submicron-sized pores. A surrounding iron-rich oxide shell appears to have formed during cooling and oxidation. In contrast, particle (B) has a smaller, porous core. A well-developed dendritic network envelops the core, becoming progressively denser towards the particle surface, with diminishing interdendritic regions area. This gradient in morphology likely reflects solidification dynamics. The outermost layer presents a porous texture, characteristic of iron-rich oxides formed during solid-state oxidation.

The assumption of an iron-rich oxide layer is supported by EDX quantification performed on the particle shown in Figure 4.13 (c), which indicates a low silicon content of approximately 1.5 wt.%. The porous morphology of this layer further suggests that oxidation occurred in the solid state. This particle likely exhibits Fe-rich dendrites interspersed with Si-rich interdendritic regions. However, due to the submicron scale of the dendrites ($<1\text{ }\mu\text{m}$), EDX quantification could only be conducted on a global scale. The analysis revealed a high oxygen content (59.4 wt.%) and a silicon concentration of approximately 6 wt.%, which is consistent with the presence of mixed oxides. Despite the limitations in resolution, the presence of a dendritic microstructure confirms that the particle underwent complete melting prior to solidification.

Finally, Figure 4.13 (d) highlights a distinctive dendritic morphology with a central eutectic region in a $\sim 20\text{ }\mu\text{m}$ particle. Two solidification fronts are clearly identifiable, converging toward the eutectic zone at the center of the particle. No evidence of solid-state oxidation is observed on this particle, suggesting that complete oxidation of the particle was attempted in the liquid state.



c	Fe (wt.%)	Si (wt.%)	O (wt.%)
1	34.6 ± 0.6	6.0 ± 0.6	59.4 ± 0.4
2	36.2 ± 0.8	1.5 ± 0.2	62.2 ± 1.1

Figure 4.13: SEM images of 3-wall particle cross-sections acquired with the BSE detector. (a) Overview showing contrast between burned and unoxidized particles. (b) Partially burned particles sticking together, with a dendritic structure in the inner shell and a more porous outer layer. (c) Fully oxidized particle presenting a dendritic microstructure, with a central region suggesting the presence of an eutectic phase. (d) Fully oxidized particle featuring internal dendrites (Si content is ~6 wt.% in average) and a porous outer layer composed of Fe-rich oxide.

4.2 Isothermal oxidation

4.2.1 Thermogravimetric analysis

In this Section, focus is placed on the isothermal thermogravimetric analysis (TGA) of Fe-7Si(20) powder oxidation, covering tests 7 to 17 as detailed in Table 3.6, where the temperature was varied from 540 °C to 1200 °C. Figure 4.14 shows the evolution of the oxidation level using different time scales to highlight both the initial and overall oxidation behavior. Numerical values of the oxidation level at specific time points are provided in Appendix A.2 for further reference.

Oxidation was very slow at 540 °C with an oxidation level of only 0.42 % reached after 3 h, as described in Section 3.3. In accordance with the Arrhenius law, which states that reaction rates increase exponentially with temperature, the level of oxidation was expected to rise as temperature increased.

An increase in oxidation was observed across all tests, except at 900 °C, where systematically lower oxidation kinetics were measured compared to 800 °C. However, at 800 °C, oxidation kinetics appeared to saturate after approximately 6 hours, while at 900 °C, oxidation continued to progress steadily even after 20 hours. Oxidation levels of 2.4 % and 3.26 % were reached after 6 and 20 h, respectively, at 800 °C. In contrast, tests at 900 °C resulted in approximately 1.4 % oxidation after 6 hours and 2.56 % after 20 h.

When comparisons could be made under identical conditions, a decrease in initial powder mass generally led to an increase in oxidation kinetics. However, at 800 °C, this trend was not observed; the reduction in initial mass had little effect on reactivity and even slightly decreased it, as shown in Figure 4.14.

At 1000 °C, 3.2 % oxidation was reached in less than 30 seconds, while the final oxidation levels were 5.75 % and 7.97 % after 6 and 20 h, respectively. The difference in oxidation level after 6 h between the two tests was only 0.06 %.

At 1100 °C, both the 6 h (test 14) and 20 h (test 16) TGA tests showed a sharp step in the oxidation curve at 40 and 59 min (~30 s duration), respectively, with a noticeable increase in oxidation: +3.5 % for 27.9 mg of initial powder (from 15.5 % to 19 %) and +2.5 % for 31.5 mg (from 21 % to 23.5 %). These steps are circled on the respective curves. The 40 min test did not show such a step in the oxidation curve.

The test at 1200 °C reached 98 % oxidation after 6 h of testing, but 50 % and 80 % of oxidation were already reached after 3 and 10 min, respectively.

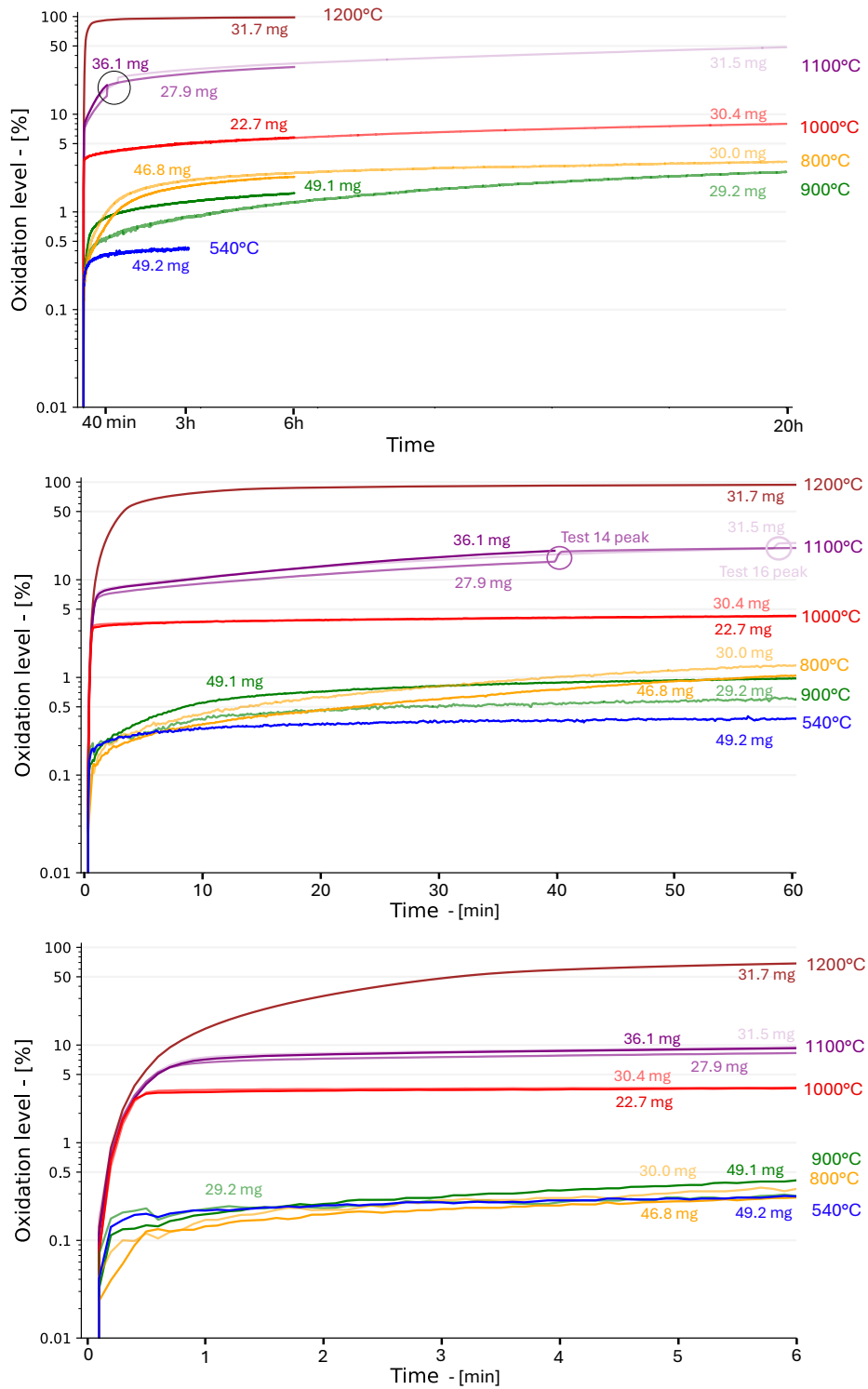


Figure 4.14: **Oxidation level as a function of time for different time scale**, for tests 7 to 17 (see Table 3.6). Oxidation temperature and initial mass are indicated. The oxidation level generally increased with temperature, except for the tests conducted at 800 °C, which exhibited a higher final oxidation level than the 900 °C tests over the same duration. Notably, the 1100 °C tests displayed distinct oxidation peaks at 40 and 59 minutes, as highlighted in the graphs. A rapid oxidation phase was observed at the beginning of each test.

Due to a temperature overshoot during the TGA heating phase and an insufficient stabilization period, each test started at a temperature slightly above the target value. The temperature shift decreased with the increase of oxidation temperature: from +6 °C at 540 °C to +0.1 °C at 1200 °C.

Despite the low powder mass used and controlled furnace temperature, temperature variations occurred due to the exothermic nature of the oxidation reaction (see Figure 4.15), with heat release increasing with initial powder mass. At 540 °C, the flow temperature gradually decreases and stabilizes within 10 minutes, but as the target temperature increases, curve variations appear, forming increasing temperature peaks: the peak is minimal at 800 °C, remains below 0.2 °C at 900 °C, reaches ~3.6 °C at 1000 °C, ~4.5 °C at 1100 °C, and ~6.4 °C at 1200 °C. For the tests between 1000 °C and 1200 °C, the target temperature is approached from below after the initial peak and stabilizes within 10 minutes.

The steps observed in the oxidation level curves for the 1100 °C TGA, occurring at 40 and 59 min, are also visible on the temperature curves as small peaks in Figure 4.15 (g-h).

As discussed further in Section 5.3, it is likely that there are larger local temperature variations at the particle scale that were not measured by the thermocouple, and therefore that the reactions were not truly isothermal.

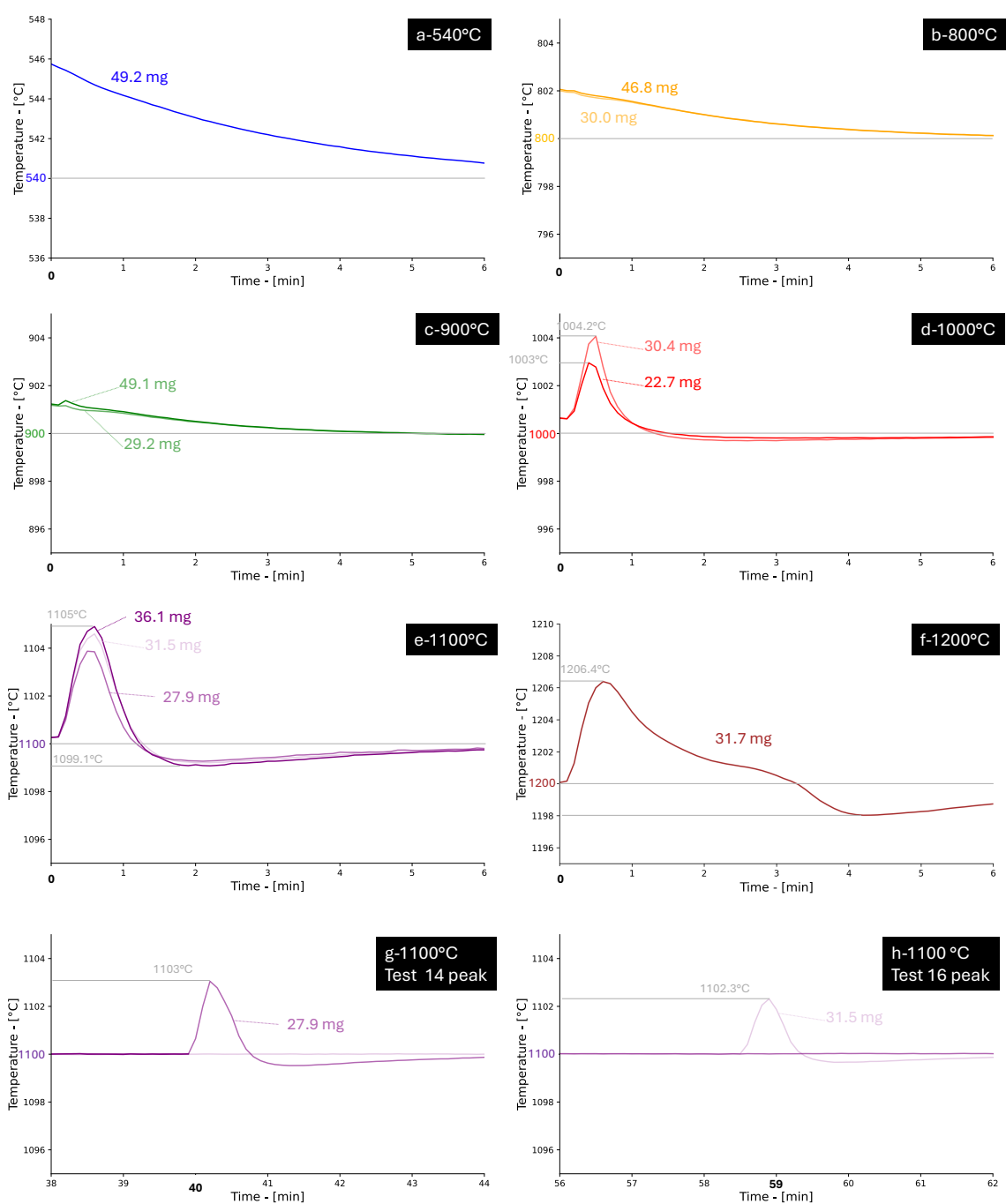


Figure 4.15: Focus on temperature evolution during TGA for tests 7 to 17 (see Table 3.6). Initial powder mass and precise temperatures are indicated. Additional curves are presented for 1100 °C tests when oxidation steps were observed in Figure 4.14. Temperature stabilization at the beginning of the tests was not perfect, and the rapid oxidation of the powder led to slight temperature increases. These increases were more pronounced with higher oxidation rates and greater initial powder masses.

4.2.2 Post-thermogravimetry: samples analysis

Figure 4.16 presents BSE images of full particles recovered after TGA. Initial particles are presented as a reference. After 3 hours at 540 °C, the particles look unchanged from the initial state. BSE did not reveal any contrast. The particles retained their spherical shape and no agglomeration was observed. As the oxidation temperature increases, changes in particle morphology occur: 800 °C - contrast on the particles surface; 900 °C - high beads concentration on particles surface; 1000 °C - apparition of sintering between particles; 1100 °C - indistinguishable individual particles due to oxide covering. These observations led to dedicated analyses depending on oxidation temperature developed in the next Figures.

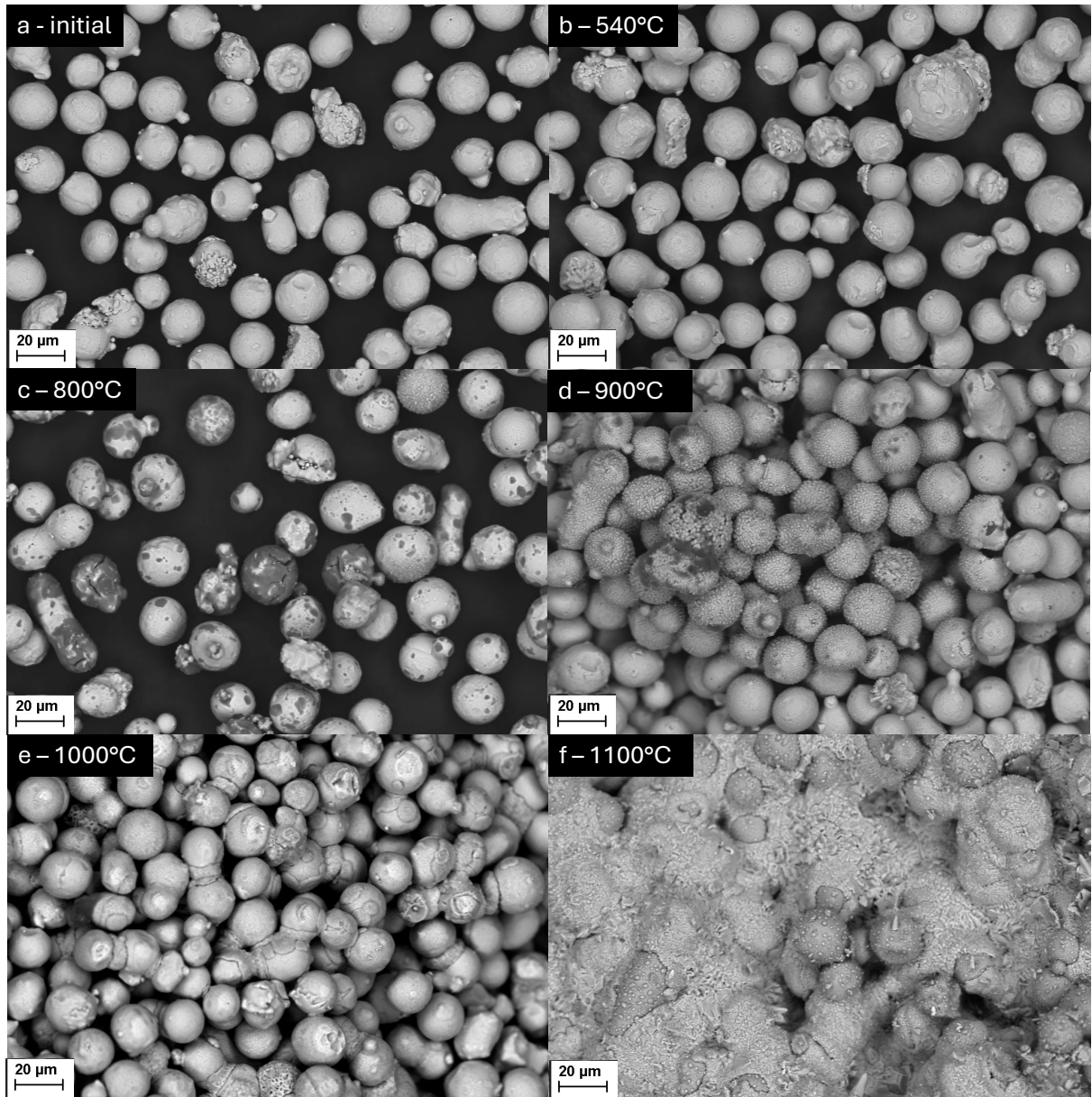


Figure 4.16: BSE images of Fe-7Si(20) particles after isothermal oxidation. (a) initial powder. (b) after 3h at 540 °C. (c-f) after 6h at indicated temperatures (800-1100 °C).

800 °C

As mentioned, BSE contrast appears at 800 °C, with the apparition of a darker phase at the surface of the particles. Traces of oxidation are present in this form on most of the particles, with variable coverage. This phase is identified as a silicon-rich oxide in Figure 4.17. Variation in depth of this oxide (from 0 to 5 μm), and a high depletion of silicon from the core are present on these particles. Corrosion pits are observed with the favored penetration of the oxide on specific spots of the particle surface, see Figures 4.17 (a-b). These spots generally correspond to the formation of a crack, only present in the dark oxide phase. Figure 4.17 (d) also shows high-density layers around dark zones on the particle surface.

SE2 image reveals bead formation on the particle surface, with bead sizes varying between particles, always below 1 μm , and sometimes too small to be detected in BSE images. The composition of these beads indicates the formation of Fe-rich oxides. Silicon is also detected, but this may result from interaction with the surrounding Si-rich oxide, given the small bead size, below the spatial resolution of EDS (as detailed in Section 3).

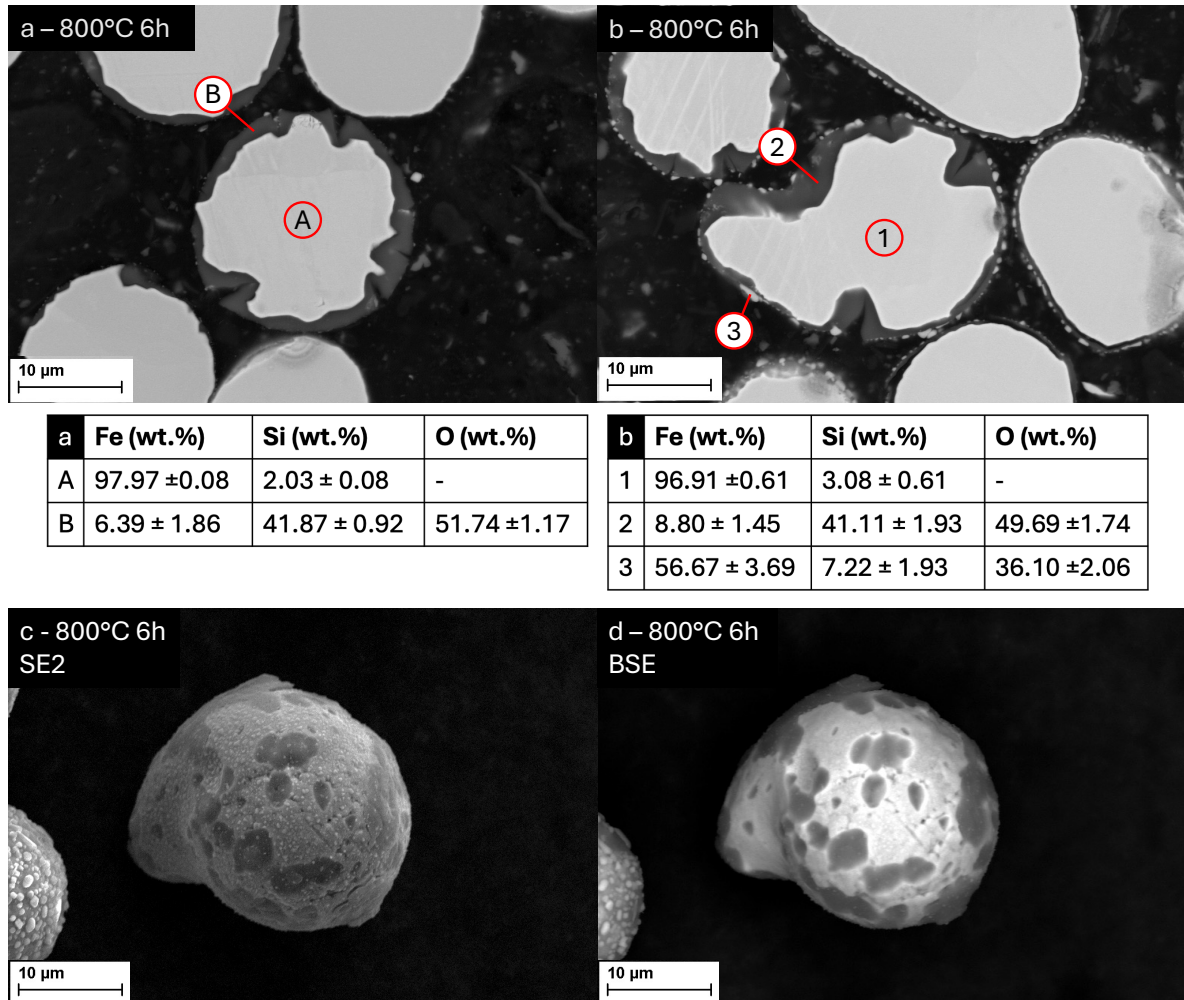


Figure 4.17: **Fe-7Si(20) particles after 6 h at 800 °C.** (a-b) Cross-section with EDS quantification showing silicon depletion from the particle core (A and 1), and dark Si-rich oxide layer (B and 2). (b) presents Fe-rich oxide beads on the surface (3). (c) SE2 image showing small beads on the particle surface (d) BSE image showing surface contrast

The line-scan (a) presented in Figure 4.18 shows a concentration gradient at the interface between the layer and the core. Within the dark oxide layer (B-C), the iron content decreases as the distance to the unoxidised core increases, while the silicon and oxygen contents increase. Line-scan (b) on two agglomerated particles in Figure 4.18 shows that total silicon depletion from the core at 800 °C is not a generality, since silicon content in the core is 6.0 ± 0.33 wt%. In this case, the gradient of concentration still exists, even if the dark phase layer is thinner (< 2 μm). Beads formation on the surface is nonetheless present (thickness < 1 μm). The grey, fully oxidized and porous particle containing chromium, vanadium, and nickel, which are not normally present in the initial powder, is considered as an impurity.

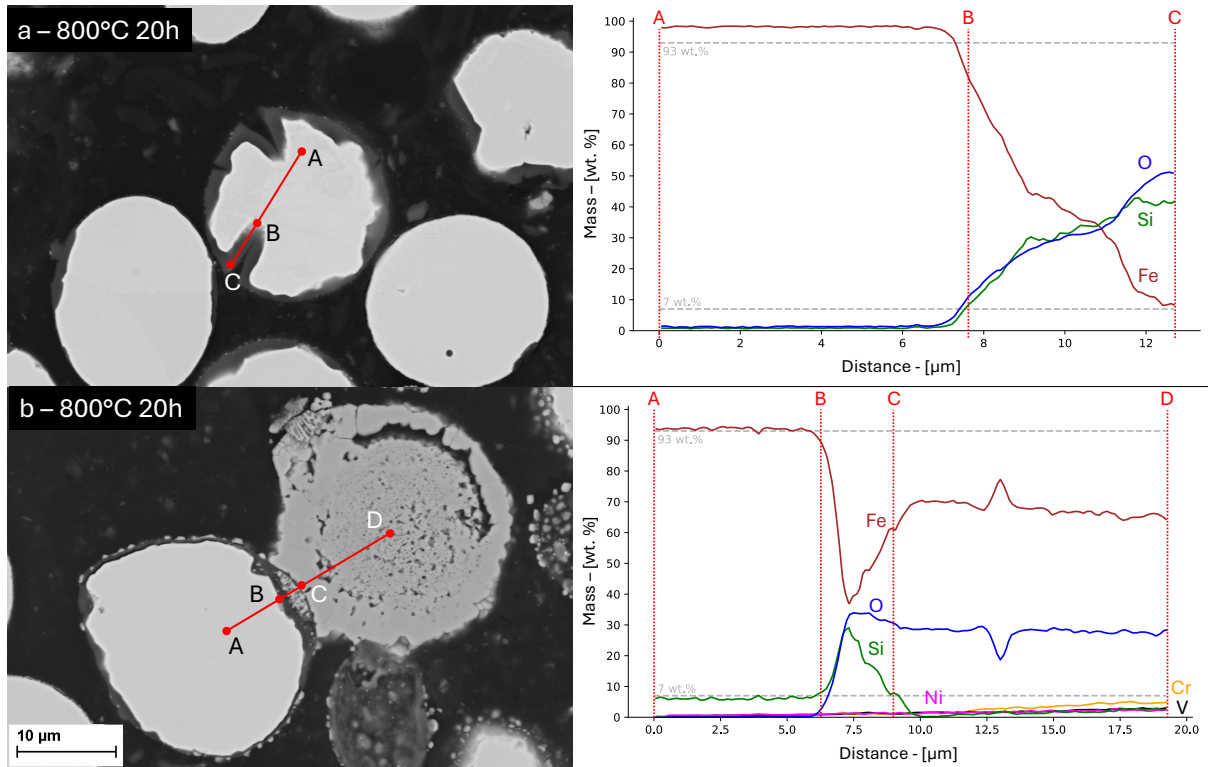


Figure 4.18: **Fe-7Si(20) particles cross-section after 20 h at 800 °C and EDS line-scan.** (a) Silicon depletion from the core with homogeneous composition; gradient of concentration around interface (a.B); iron concentration decrease when approaching particle surface. (b) Joined particles. (b.A) Small silicon depletion from the core; thin silicon oxide layer, and beads on the surface. (b.D) Fully oxidized porous particle containing chromium, nickel and vanadium. (b.B-C) Junction with high silicon content.

900 °C

At 900 °C and beyond, agglomeration becomes mechanically stable due to sintering, unlike at lower temperatures where agglomerates remain fragile and break during handling. Most of the particles present beads on their surface at this temperature. Figure 4.19 shows that beading coverage and thickness increase with time ($\sim 1 \mu\text{m}$ after 20 h) . The silicon oxide layer is always present, but its thickness is reduced ($< 0.5 \mu\text{m}$) compared to the 800 °C test. However, Si-rich oxide layer and Fe-Si rich oxide beads are homogeneously present over the surface. Beads form a more continuous layer without increasing the silicon layer thickness from 6 h to 20 h at 900 °C. The silicon depletion in the unoxidised core is no longer dominant at this temperature and beyond.

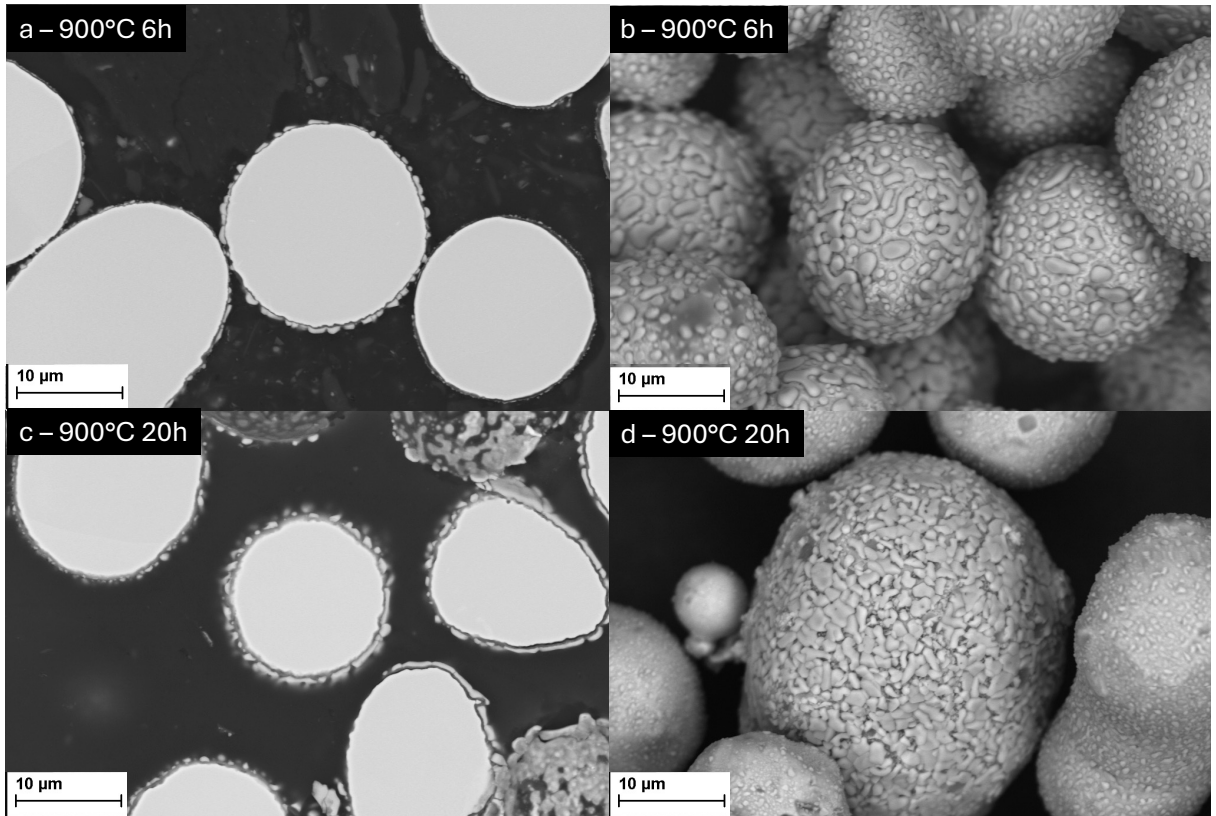


Figure 4.19: **BSE images of Fe-7Si(20) after 900 °C oxidation.** (a-b) 6h. (c-d) 20h. Beads formation on the particle surface, with thin dark oxide layer around the unoxidised core

1000 °C

When the temperature is increased to 1000 °C, the agglomeration is stronger and necks in the range of 2-6 μm thickness and 14-20 μm diameter are observed, as illustrated in Figure 4.20 after 6 h. The oxide layers have mostly migrated to the particle intersections to form these sintering necks. The cross-section of these necks reveals a microstructure composed of: (i) a dark Si-rich oxide layer surrounding the particles, (ii) bright Fe-rich oxide dendrites occupying most of the neck area, and (iii) Si-rich oxide or eutectic phases in the interdendritic regions—either indistinct due to insufficient spatial resolution after 6 hours, or clearly resolved as a eutectic microstructure after 20 hours. The formation of dendritic and eutectic microstructures suggests the formation of a liquid phase, only at the particle intersections. After 20 h, the dendritic and eutectic microstructures are no longer restricted to the necks but also form a shell around the particles with up to 5 μm thickness.

When comparing the sintering necks composition in Figure 4.21, oxygen concentration is high in both cases (~ 32 wt.%), but silicon content increases with time in all oxide phases, going on average from 0.81 to 8.2 wt.% in the dendrites, and from 14.01 up to 16.6 wt.% in the interdendritic phase after 6 h and 20 h, respectively. The two phases composing the eutectic are not quantifiable ($\ll 1$ μm), but the BSE contrast suggests a dispersing phase composed of a Fe-rich oxide and a dispersed phase composed of Si-rich oxide.

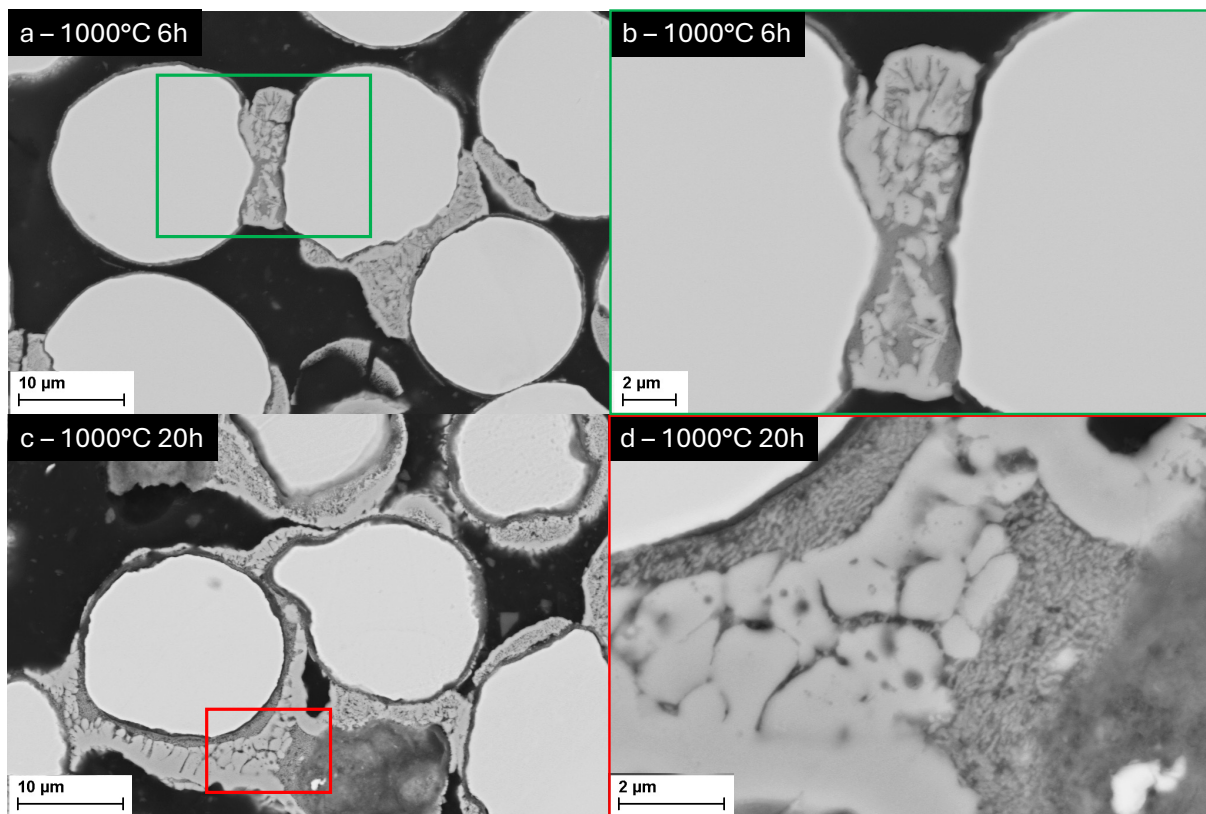


Figure 4.20: BSE images of Fe-7Si(20) powder junction after 6 h and 20 h of oxidation at 1000 °C. Dendritic and inter-dendritic eutectic microstructure formation after (a-b) 6 h and (c-d) 20 h, shows that the oxide went to liquid state.

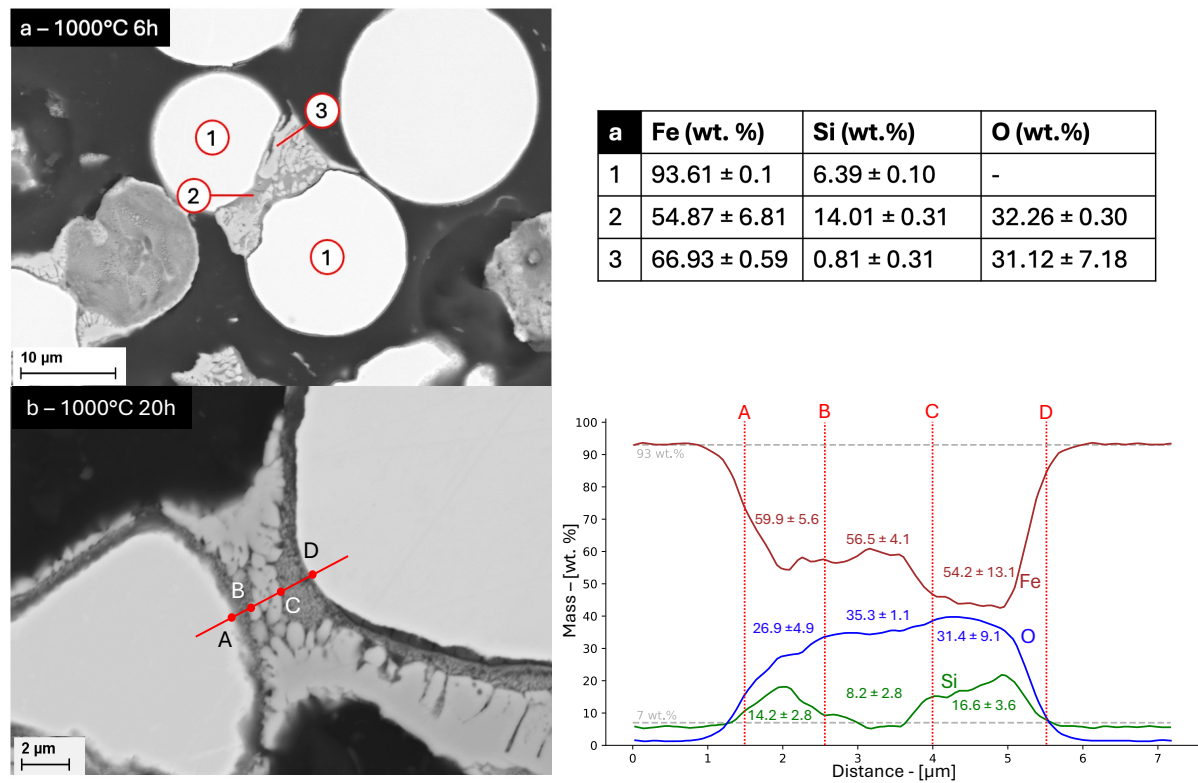


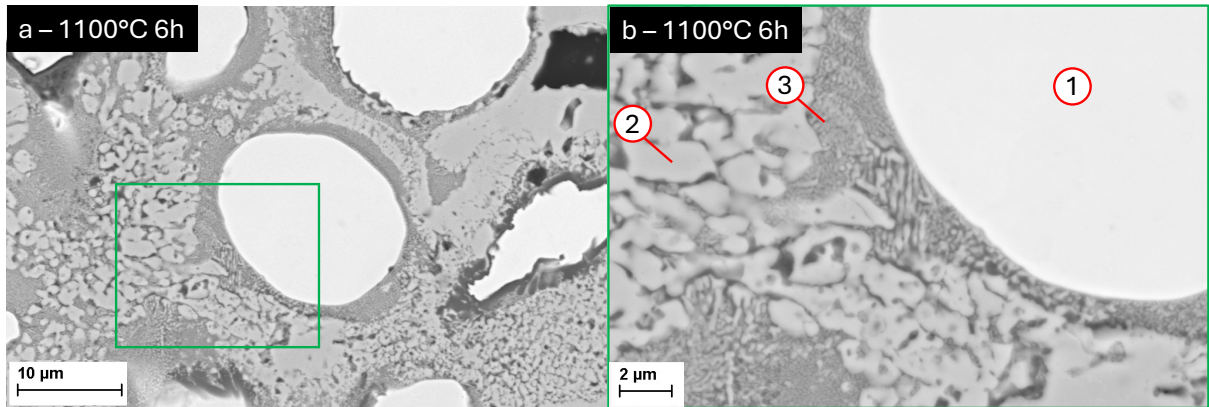
Figure 4.21: EDS quantification of Fe-7Si(20) powder junction after 6h and 20h of oxidation at 1000 °C. Silicon depletion from the unoxidized core remains limited. The dendritic and interdendritic structures exhibit compositional variations with test duration.

1100 °C

Figure 4.22 presents a cross-section of particles after 1100 °C treatment, revealing a morphology similar to that observed at 1000 °C, with more present eutectic structures surrounding the unoxidised cores, followed by dendritic regions. The dendrites are composed exclusively of iron oxide, with no detectable traces of silicon. The eutectic composition appears similar to that at 1000 °C, but its thickness has increased to over 4 μm. The silicon oxide layer that previously surrounded the core is no longer visible.

Spherical particles surrounded by a dark oxide are observable at the agglomerate surface. Beads are forming on these particles, with varying sizes (0 to 2 μm diameter). These particles are covered with oxide, which presents a more angular and crystalline aspect.

No significant differences in oxide structure were observed in the powders recovered from the TGA at 1100 °C for 40 min and 20 h, likely due to difficulties in sample recovery, as detailed in Section 3.3.



a-b	Fe (wt.%)	Si (wt.%)	O (wt.%)
1	93.43 ± 0.26	6.57 ± 0.26	-
2	79.19 ± 0.17	0.09 ± 0.10	20.72 ± 0.17
3	55.74 ± 1.57	17.17 ± 1.96	27.08 ± 0.70

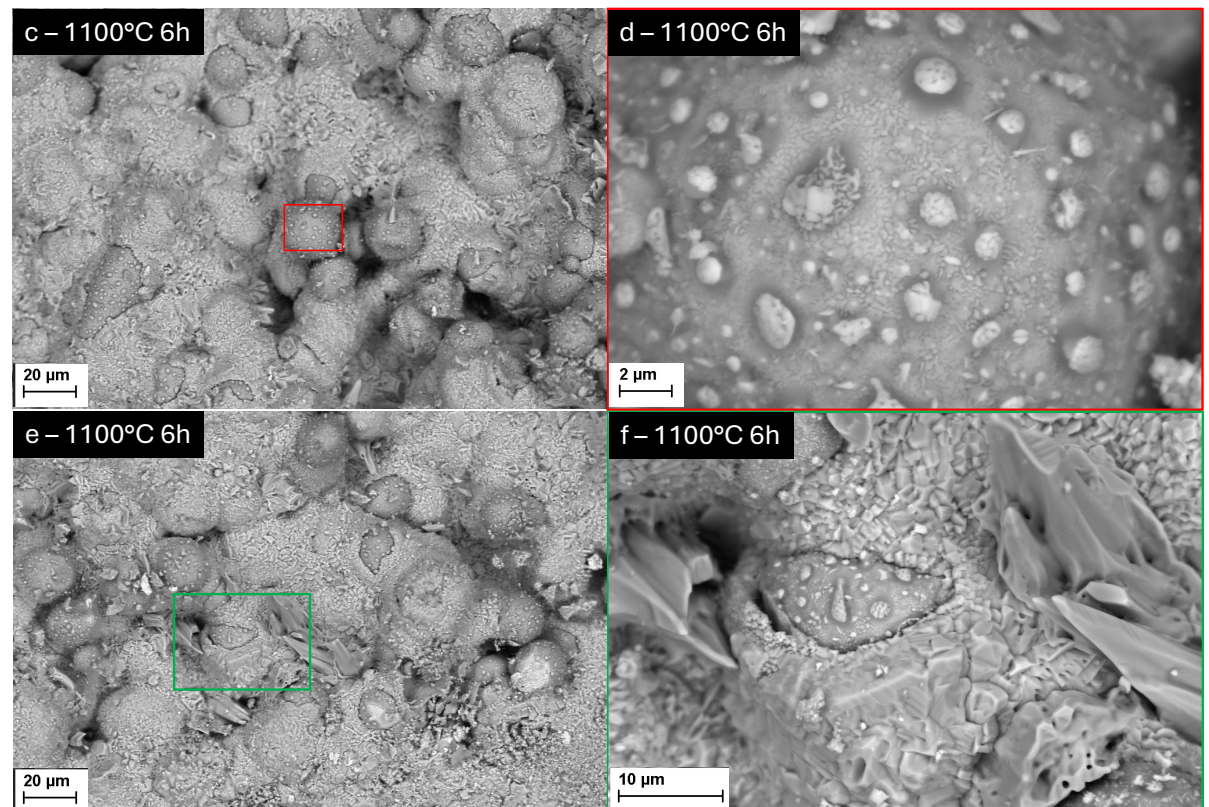


Figure 4.22: BSE images of Fe-7Si(20) powder after 6 h at 1100 °C. (a-b) Cross-section showing oxidation structure with EDS quantification. (c-f) Particle agglomeration surface

1200 °C

At 1200 °C, individual particles are no longer visible in dense agglomerates, as shown in Figure 4.23. Dendritic zones are dispersed within the agglomerates, with Fe-rich oxide dendrites surrounded by Si-rich oxide in the interdendritic regions. However, the agglomerates are predominantly composed of iron oxide. Aluminium was detected in both phases at non-negligible levels, probably caused by the alumina crucible contamination.

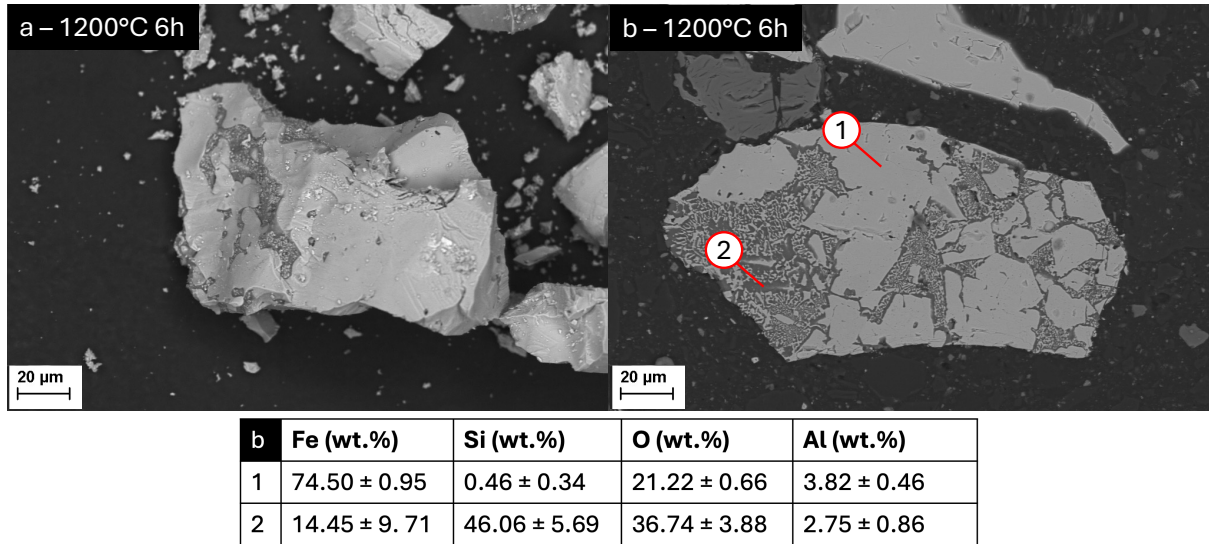


Figure 4.23: BSE image of Fe-7Si(20) powder after 6h at 1200 °C. (a) Surface of an agglomerate (b) Cross-section and EDS quantification.

4.2.3 High-temperature furnace: XRD analysis

Finally, the high-temperature furnace was used to produce a larger amount of oxidized powder to characterize the phase distribution after isothermal oxidation. The results show that the oxidation was favored at 1100 °C and above, as presented in Figure 4.24 showing XRD analysis results.

From 800 °C to 1000 °C, oxidation was low, and the only oxide phase that emerged from these tests was hematite. At 800 °C, the hematite amount is low, but increases slowly with time, to reach 1.5 wt.% after 20 h. Hematite content reached 3.9 wt.% after 20 h at 900 °C, but a lower amount was measured after 1000 °C tests with 3.2 wt.%.

At higher oxidation temperatures, specifically 1100 °C and 1200 °C, only three oxide phases are identified: quartz silica (SiO_2), magnetite (Fe_3O_4), and hematite (Fe_2O_3). Non-authenticated (N/A) peaks are increasing in intensity with the oxidation. These peaks probably come from a structure that cannot be identified in the Fe-Si-O phase diagram.

Increasing the oxidation duration at 1100 °C from 6 to 20 hours results in: (i) a reduction in quartz content from 1.5 wt.% to 0.7 wt.%, (ii) an increase in hematite and magnetite content from 80.2 wt.% to 87.4 wt.% and 0.5 wt.% to 1.3 wt.%, respectively, and (iii) a higher overall oxidation level, as inferred from the decrease in remaining metallic iron concentration.

At 1200 °C, the residual iron content drops to 2.4 wt.%, while magnetite and quartz reach 9.0 wt.% and 1.8 wt.%, respectively. Hematite remains the dominant phase, with a concentration of 86.8 wt.%.

With the present results, no silicon content was detected, except in the quartz silica structure. This is due to the silicon dilution into pure iron, and the replacement of iron ions by silicon ions in the oxidised structure. However, iron ions of hematite (Fe^{3+} the most present) are larger than silicon ions (Si^{4+}), with 65 pm and 40 pm respectively; inducing a slight modification to the lattice structure, and so, a shift of the signal measured with XRD occurred. This can be seen by the broadening of the base of the peak identified for hematite for $2\theta \in [68, 74, 77]^\circ$ for the 1200 °C sample, as illustrated in Figure 4.25.

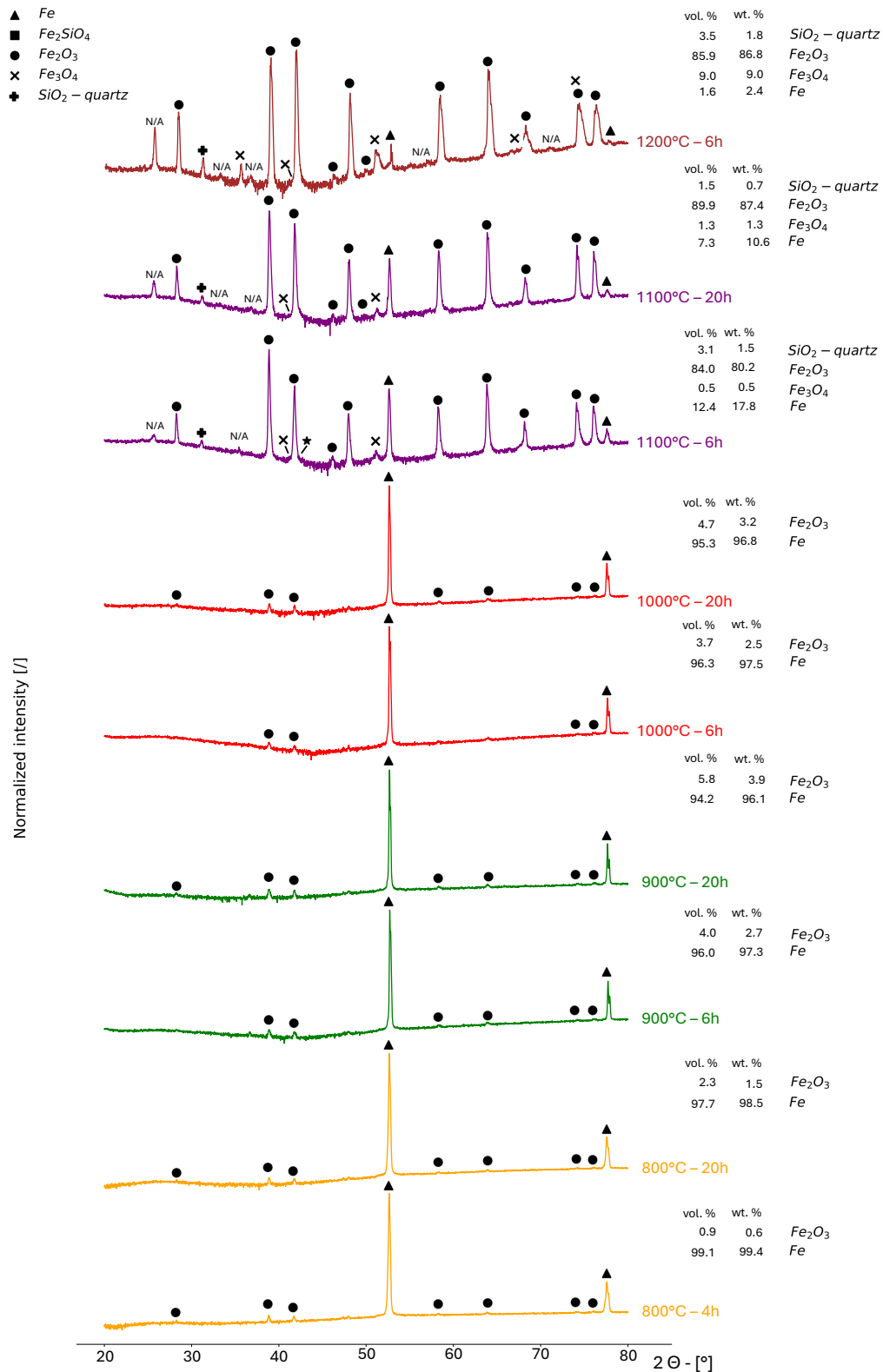


Figure 4.24: XRD spectrum and quantification of oxidized Fe-7Si(20) powder using high-temperature furnace

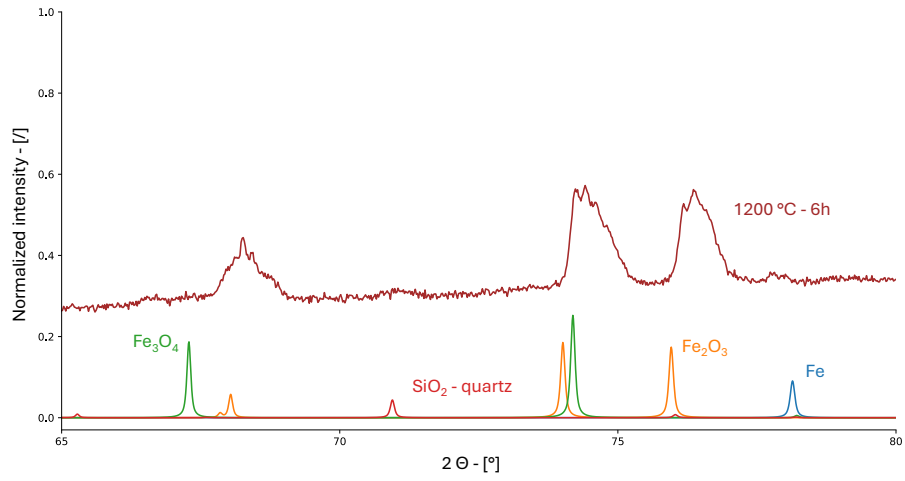


Figure 4.25: XRD spectrum of oxidized Fe-7Si(20) powder using high-temperature furnace at 1200 °C for 6h. Focus on broad peaks due to iron ions replacement by silicon ions into hematite, shifting the XRD signal.

Chapter 5

Discussion

This Chapter begins by outlining the key properties of the initial Fe-7Si powder, along with the limitations encountered during its characterization. Subsequently, the combustion behavior of Fe-7Si multi-particles is examined through analysis of the MC2 experimental results. An oxidation mechanism is then proposed based on isothermal oxidation experiments and powder characterization, while also addressing the limitations and uncertainties of the experimental approach. Finally, the development of the Fe-7Si ignition model is detailed, followed by a discussion of its results.

5.1 General context

From a broader perspective, the 7 wt.% silicon in the powder could improve cycle efficiency by (i) increasing the energy density (see Figure 1.1), and (ii) lowering the refining cost of iron powder. However, as introduced in Chapter 2, silicon in iron influences the oxidation mechanisms and is often used to form a passivation layer between the environment and the unoxidized metal. In the Section 3.1, X-ray Photoelectron Spectroscopy confirmed the presence of a Si-rich oxide layer around the particle, with an undetermined thickness ranging from 10 nm to 1 μm . This passivation layer decreases the powder reactivity due to lower initial oxygen proximity with unoxidized metal.

Inductively Coupled Plasma (ICP) spectroscopy detected small amounts (< 0.1 wt.%) of chromium, manganese, nickel, copper, and cobalt. However, these elements were not identified in the composition of the oxidized particles using scanning electron microscopy (SEM) equipped with a dispersive X-ray spectrometer (EDS). Their direct influence on the oxidation process cannot be assessed in this discussion and is considered negligible.

Furthermore, although SEM and EDS analyses provide valuable insights into oxidation behavior at the particle scale, they only offer a limited and localized view of the powder transformation during combustion. Given that approximately one billion particles are present in just 30 mg of powder, based on an average diameter of 20 μm , the few cross-sections analyzed represent only an extremely small fraction of the total sample. Furthermore, the initial state of each individual particle remains fundamentally inaccessible: neither their oxidation level nor their exact composition prior to combustion can be determined retrospectively. EDX measurements on several Fe-7Si particles revealed silicon content variations of ± 0.47 wt.% around a mean of 6.89 wt.%, already differing from the value obtained by ICP, illustrating the intrinsic heterogeneity of the powder. These

uncertainties complicate any definitive correlation between initial composition and final oxidation state, and must be carefully considered when interpreting the results.

5.2 Multi-particle combustion

5.2.1 MC2

The MC2 presented many advantages, as it allows burning batches of several hundred grams in relatively stable and well-defined conditions. The design is simple, but it can create issues, such as a random decrease in the powder mass flow rate due to the dispersion system, as observed during test 2.

For the swirl flow, it increases the residence time of particles in the combustion chamber and the flame homogeneity, but it also projects particles onto the walls. During the combustion, the accumulation and the collision between particles in the liquid state produce a non-negligible amount of agglomerates. Agglomerates often need to be crushed for the reduction part, adding a new powder treatment in the cycle.

During the tests, it was difficult to determine if the combustion was established due to the change in conditions: (i) test 3 showed large temperature variation ($T_{\text{center}} = 926.5 \pm 17.9$ °C), (ii) test 2 the powder mass flow rate dropped to 0.45 g/s after 62 sec. Also, for a batch of 100 g, it is possible that the quantity was not enough to have well-established conditions. Making more tests and increasing the initial powder mass could give valuable stabilization conditions, even if it would increase the effect of powder accumulation in the combustion chamber.

5.2.2 Fe-7Si combustion

The presence of silicon impurities slows down the oxidation. Combustion is affected because the temperature must be increased to ignite the powder.

Test 1 illustrated that the combustion with iron-silicon powder requires a higher initial temperature, as evidenced by an unstable flame with the same conditions of combustion as for pure iron, (see Table 3.5). As soon as the powder was injected, the temperature evolution showed a significant decrease. This result can be explained by the oxidation of the particles, which was too slow to generate enough heat, and the cooling by the swirl flow at 25 °C was too high to be compensated only by the radial heaters.

The gas emission analysis during test 1 showed a higher concentration of CO than in the other tests. As the Fe-7Si powder contains only 0.01 wt.% of carbon, the formation of CO was likely due to impurities present in the burner. The impurities may have been introduced during the cleaning phase through the use of plastic tools or by contamination from previous tests. The absence of NO_x formation can be attributed to the temperature stayed below 1400 °C, which is insufficient to initiate the oxidation of atmospheric nitrogen.

The granulometric analysis illustrated that for the 1-cycl powder, the particle size did not increase significantly and stayed remained close to that of the initial powder due to the small formation of oxide. The 90th percentile of diameter (D90) is 64 µm instead of 57.9 µm for the initial powder. For the 1-wall powder, the entire size distribution shifted toward smaller diameters, which may be explained by one or more of the following factors: (i) the

projection of particles on the wall deformed either deformed or broke them, reducing their mean area diameter, (ii) most of the ignited particles were small, their liquefaction favoring their explosion and accumulation on the wall, (iii) residual presence of particles from the previous test. The chart also shows the appearance of large particles, resulting from the formation of agglomerates on the wall. The quantity of agglomerates is represented by the tail of the chart (8.9 % > 63 μm) and the 2.8 g that was filtered before the granulometric analysis. The distribution of the 1-cycl powder had also a tail but it is very small, so there are only a few agglomerates.

Regarding the composition, XRD analyses illustrated that for test 1 the amount of ferritic structure remained dominant with 99.8 wt.% and 93.5 wt.% for the 1-cycl and 1-wall powders, respectively. This indicates that most particles did not oxidize. In the 1-wall powder, the oxide formation is expected to be due to the increase of exposure time at high temperature in the combustion chamber, but still the amount stays low with 6.5 wt.% in total.

The observable flame during test 3 was more stable, resulting from the preheating temperature increase to 930 °C. The temperature evolution curve presents an increase of T_{center} to 970 °C and then decreased before stagnating at 920 °C.

The temperatures evolution from 100 sec to the end of test 3 showed that T_{top} surpassed T_{center} , before reaching 960 °C. Although the influence of the radiant heaters cannot be clearly determined, the temperature rose at the top (T_{top}), also observed at ignition, may indicate the establishment of a self-sustaining flame, by suggesting good flame propagation.

From spectrometer measurements, the temperature of the particles rose at least up to 1493 °C. The temperature threshold of the NO_x formation is reached.

The size distribution of the 3-cycl particles was shifted to the right ($D_{90} = 78.9 \mu\text{m}$) due to the increase in the particles size caused by their oxidation. For 3-wall, the behaviour is similar ($D_{90} = 137.6 \mu\text{m}$). The distribution curve is flatter, and the tail is more pronounced due to the large amount of agglomerates. The number of agglomerates likely increased because more particles entered the liquid state and merged upon contact with the wall. The filtered fraction is approximately 22.57%, and D_{50} is 46.7 μm , indicating that more than half of the particles are larger than those in the initial powder.

For the composition, the main oxide formed in the burner is magnetite Fe_3O_4 , with 22.5 wt.% and 27.1 wt.%, for 3-cycl and for 3-wall. This result shows that either oxygen supply or residence time was insufficient for iron to be fully oxidized to hematite. The presence of ferritic structure remained quite high, 70.5 wt.% and 57.8 wt.%, for 3-cycl and 3-wall, respectively. This amount showed that more than half of the fuel did not react. The efficiency of the combustion was low. Increasing the duration of the combustion or the temperature could increase the efficiency. For 3-wall, the presence of 12.3 wt.% of hematite illustrates that a non-negligible quantity of powder has reached full oxidation. From the cyclone collection, the amount does not surpass 3 wt.%. The presence of Fe_2SiO_4 (2 wt.%) for 3-cycl and 3-wall is probably due to the solid-state oxidation.

Microstructure analysis

For the microstructure analysis, the global picture from the two tests showed that the powder recovered from the wall presents more abnormal particles, such as agglomerated or flat particles, due to the impact with the wall and the bigger residence time. The

defaults as exploded particles come from the increase of internal pressure due to the high temperature [16].

For test 1, the BSE images from cross-section analysis showed that the particles have different layers resulting from the solid-state oxidation. There are some clues of the solidification process with the eutectic structure, but only at the outer shell as also seen in TGA results at 1000 °C. The oxidation of the particles was too slow to generate enough heat and surpass the losses by convection. The particles did not ignite and the temperature of the burner stayed low.

For test 3, the powder recovered from the cyclone showed particles with a shell that went through a liquid state, while the core remained solid. The shell had a dendritic morphology and there was the presence of eutectic structures. A cause of these results could be that the particles temperature was enough, above 1137 °C according to thermodynamics, to liquefy part of the oxide layer. The shell became liquid but the particles did not stay enough time in the combustion chamber to oxidise more before being recovered by the cyclone and to finish their oxidation. For 3-wall, fully liquid particles are present as the dendritic structure covers the entire cross-section. These dendrites appeared during the solidifying process. When the particles became liquid, all the oxide layers mixed and formed a mixture following the formula $\text{Fe}_x\text{Si}_y\text{O}_z$. Once the particles solidified, there were different undetermined phases that have different solidification temperatures. The dendrites will be formed due to the solidification of these different phases; one phase solidified while the others remained liquid. The dendrites grow from the edge of the particles toward the center, following the cooling gradient. The formation of these phenomena could create segregation of some elements, explaining the depletion of silicon at the particle edges, where only 1.5 wt.% remains.

To complete this study, it would be interesting to make new tests on the burner to determine the ignition temperature of the powder. The tests could start at 930 °C and decrease the temperature step by step to see the minimal temperature required to ignite the powder and have a stable flame. Also, during the tests, the radial heaters need to be shut down to have a self-sustainable flame.

5.3 Oxidation mechanism of Fe-7Si powder

As already shown in the Section 3.3 by comparing the oxidation kinetics of pure Fe powder with Fe-7Si powder at 540 °C, the presence of silicon in iron powder significantly slows down its solid-state oxidation kinetics. No visible changes in the particles oxidized at 540 °C for 3 h were observed with the SEM. A rough estimate suggests that the oxidation of $X = \sim 0.4$ % of the 20 μm particles should result in an oxide thickness of about 12 nm. More advanced XPS analyses of both the initial and oxidized powders at this temperature could assess changes in surface oxide thickness and composition.

At 800°C, silicon depletion from the particle core forms the dark, Si-rich oxide layer around the particle. This Si-rich oxide has a composition close to silica (SiO_2), in which iron ions are diluted. This iron dilution was measured with EDS between 0.9 wt.% and 11.1 wt.% in the dark layers. This reaction follows the predicted thermodynamics, represented

by the Fe-7Si arrow in the ternary phase diagram given in Figure 5.1 (a) at 800 °C. Fayalite (Fe_2SiO_4) formation was then expected once the silicon has been fully consumed into quartz.

In the same Figure, the location of the EDS measurements shows that silica in the form of quartz is forming at the layer, while increasing, as expected, the iron concentration in the core. Fe-rich oxide formed beads on the surface before the full oxidation of silicon content in the core, which does not follow the path expected by the thermodynamics. The composition of the beads is close to hematite and fayalite, but based on XRD measurements, the structure is expected to be hematite with a substitution of iron ions (Fe^{3+}) by silicon ions (Si^{4+}). The deviation from the thermodynamic predictions could be explained by a kinetic effect, i.e. the limitation of silicon ion diffusion in the core favoring iron ions to react to the surface.

At 900 °C, the silica layer was thinner than at 800 °C, and Fe-rich oxide beads formation was favored. However, thermodynamics as represented by the ternary phase diagram of Figure 5.1 (b), predicted first the formation of silica in the form of tridymite at this temperature, and then the formation of fayalite and iron oxides. This suggests that kinetic effects were even more pronounced at 900 °C than at 800 °C, likely due to the elevated temperature, differences in silica structure slowing down silicon oxidation, or a combination of both. The oxidation process is presumably governed by iron diffusion, which becomes more favorable with increasing temperature, as predicted by the Arrhenius law, even if the same should be applied to silicon ions. Nevertheless, thermogravimetric analysis (TGA) revealed a lower overall oxidation level at 900 °C compared to 800 °C. This counterintuitive result may be attributed to variations in ion diffusion behavior at higher temperatures, possibly affecting the formation and growth of oxide layer phases.

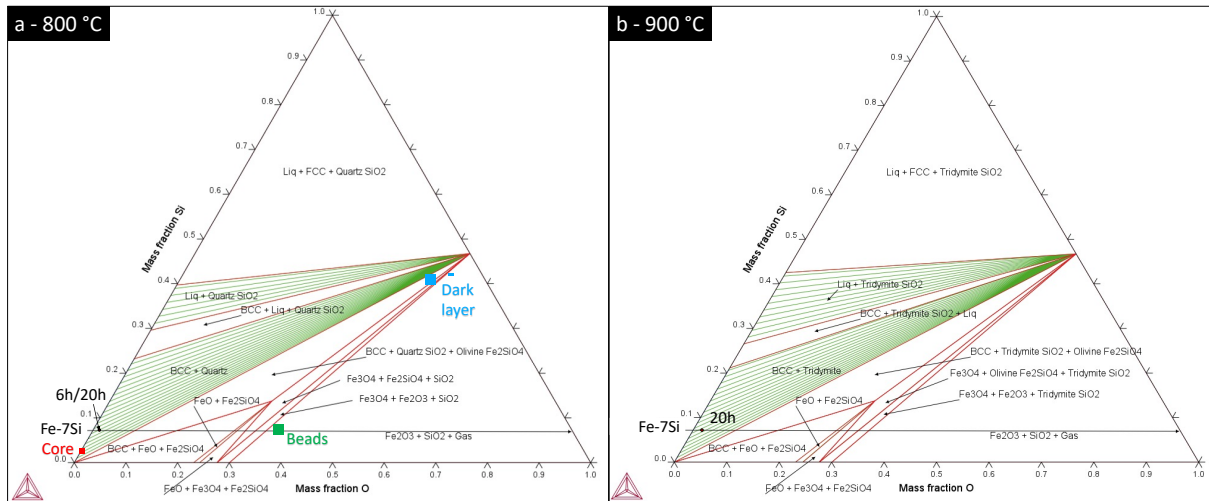
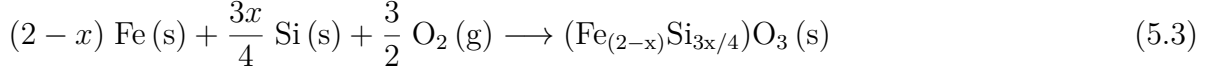
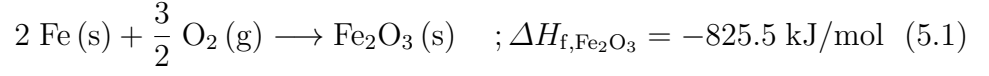


Figure 5.1: Ternary phase diagram of Fe-Si-O at 800 °C and 900 °C Horizontal line Fe7Si represent the expected global oxidation path following the thermodynamic, dots on this line represent the global oxidation state based on TGA measurements. Coloured rectangles represent EDS measurements from Figure 4.17 at 800 °C, and their dimensions represent the measurement variations. As a reminder, oxygen quantification is not precise when using EDS, positions of rectangles on the phase diagram is then approximative but give a good insight of composition tendencies.

At 800 °C and 900 °C, most of the material likely remained in the solid state. Oxidation

under these conditions can therefore be interpreted through the following solid-state Reactions:



$$\Delta H_{f,(\text{Fe}_{(2-x)}\text{Si}_{3x/4})\text{O}_3 \text{ (s)}}^{\circ} \approx \frac{2 - x}{2} \Delta h_{\text{Fe}_2\text{O}_3} + \frac{3x}{4} \Delta h_{\text{SiO}_2}$$

Reaction 5.3 represents the formation of the hematite structure in which x iron ions are substituted by silicon ions. The heat released expression is an approximation based on silica and hematite formation. At 800 °C, Reaction 5.2 was likely predominant during the initial stage of oxidation, particularly within the first hour, and/or until the silicon content in the non-oxidized cores decreased to approximately 2–3 wt.%. Beyond this point, the formation of Fe-rich oxide beads—resulting from Reactions 5.1 and 5.3—may have taken over, though with a limited overall contribution. At 900 °C, the oxidation appears to be primarily driven by Reactions 5.1 and 5.3, as evidenced by the more substantial formation of Fe-rich oxide beads. These reactions likely occurred simultaneously with, or slightly ahead of, a limited formation of silica through Reaction 5.2.

At 1000 °C and 1100 °C, the fast oxidation during the first minute is suspected to be due to the apparition of a liquid state, generating, at the same time, the peak in temperature measured by the thermocouple. The presence of a liquid phase is inferred from SEM images analysis, which revealed oxidized dendritic and eutectic structures. However, the metallic cores appear to have remained solid, as indicated by their non-spherical shapes. According to the ternary Fe-Si-O phase diagram (Figure 5.2), liquid phase formation is expected to begin around 1137 °C, suggesting that local temperatures exceeded this value and that isothermal conditions were not fully maintained. The observation of solid, unoxidized cores containing around 6.5 wt.% silicon (equivalent to 12.1 at.%) indicates that local temperatures likely remained below ~1400 °C. This temperature estimation is based on the intersection between the core composition and the solidus line on the binary Fe-Si phase diagram (Figure 5.3).

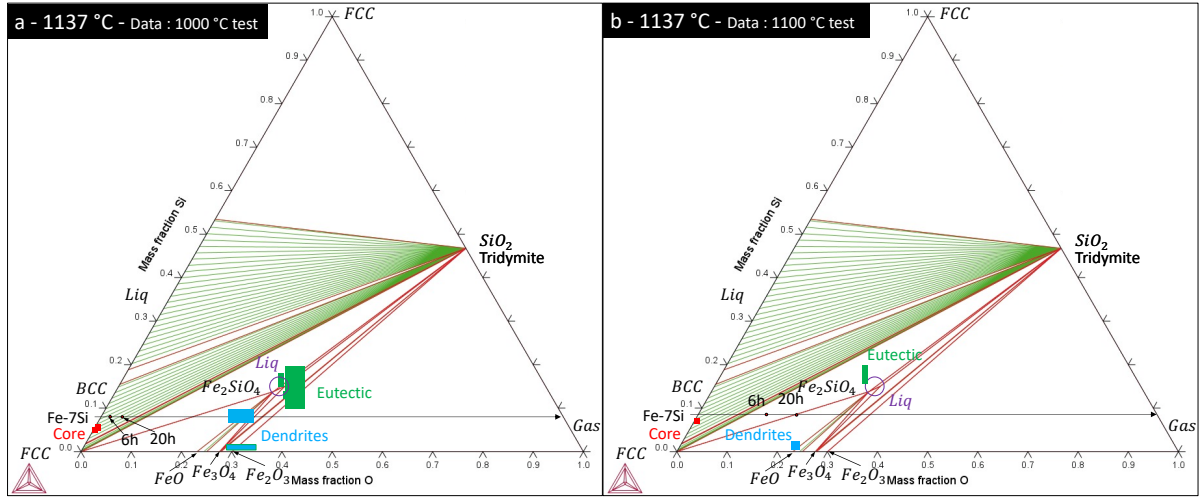


Figure 5.2: Ternary phase diagram of Fe-Si-O at 1137 °C, with EDS quantification on oxidized powder at 1000 °C and 1100 °C. Horizontal line Fe7Si represent the expected global oxidation path following thermodynamic, dots on this line represent the global oxidation state based on TGA measurement. Coloured rectangles represent EDS measurement, and their dimensions represent the measurement variations. The values for 1000 °C are taken from Figure 4.21 and for 1100 °C on Figure 4.22.

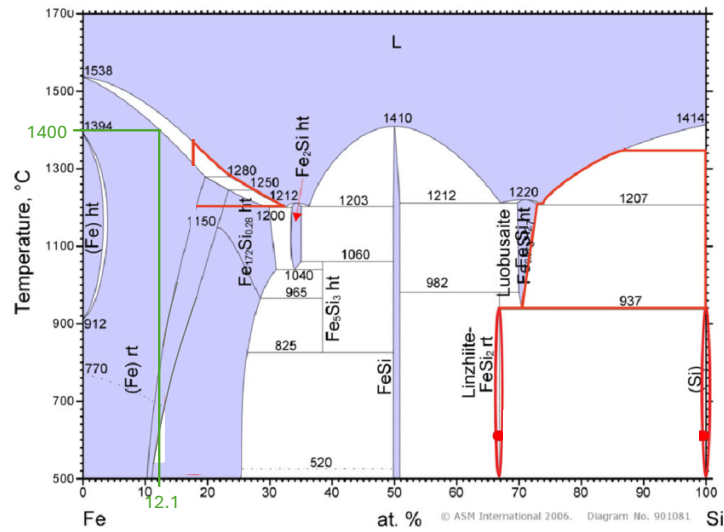
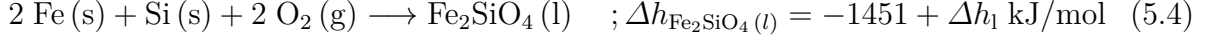


Figure 5.3: Binary phase diagram Fe-Si [29]. Highlight of the fusion temperature of Fe-Si mixture with 12.1 at% Si, i.e. 6.5 wt.% Si.

At 1000 °C, the presence of a silica layer indicates that Reaction 5.2 likely initiated the oxidation mechanism at this temperature.

Liquid fayalite ($\text{Fe}_2\text{SiO}_4(l)$) formation occurred during the first minute of the TGAs at 1000 °C (20 h) and 1100 °C (6 h and 20 h), see Reaction 5.4, and produced an eutectic structure (silica–hematite) upon solidification, as identified by XRD and EDS quantifications. The formation of fayalite and Fe-rich oxides was thermodynamically predicted for the 1100 °C, 20 h test, as the overall oxidation state lies within the corresponding triphasic stability region. However, contrary to expectations, tests at 1000 °C and 1100

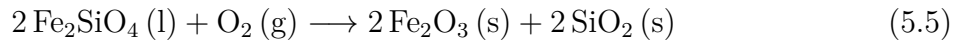
°C revealed that silicon was not predominantly consumed to form silica. This suggests that the oxidation process did not follow the thermodynamic path, likely due to kinetic domination associated with temperature rise.



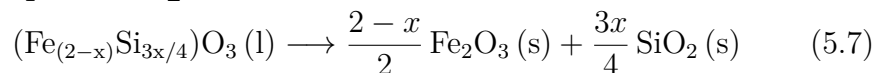
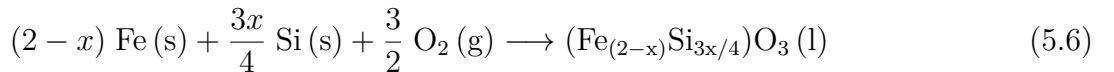
However, the local temperature is assumed to stabilize around the target temperature, as the oxidation rate decreases after approximately one minute during TGA. The solidification of fayalite ($T_{\text{liq}} = 1137 \text{ }^\circ\text{C}$) can then lead to the decomposition into silica and Fe-rich oxides. The dominant Fe-rich oxide phase is expected to be hematite following the XRD measurements. However, the intuition would suggest that magnetite is more likely to be formed at these temperatures, since hematite is less stable and requires a larger amount of oxygen. As the oxygen quantification with EDS is not precise, valuable conclusions on this potential phase variation cannot be done in the present work, but could be performed using electron backscatter diffraction (EBSD) analysis. However, to support the hematite formation hypothesis during TGAs, the following can be explained:

- Abba et al. [20] identified an hematite layer formation during oxidizing Fe-Si mixture at the same temperatures.;
- Major phase variations was not observed with BSE during the analysis of powder cross section, suggesting the formation of a unique predominant phase.;
- XRD measurements reveal a high proportion of hematite (at least 97.8 wt.% of the oxides) and a low presence of magnetite (up to 1.4 wt.%), suggesting that hematite formed primarily during the oxidation phase. Since the cooling phase after furnace oxidation was not conducted under an inert atmosphere, oxidation likely continued slightly during cooling. However, it is unlikely that such a large proportion of hematite formed exclusively during the short cooling phase, even though some additional oxidation may have occurred.

The eutectic solidification reaction of the present fayalite is then expressed as :



Furthermore, the initial silicon content was not sufficient to produce only fayalite, implying that a more Fe-rich liquid oxide, as described by Reaction 5.3, was also likely formed. The silicon concentration, however, appears sufficient to lower the melting point of hematite, as evidenced by the dendritic structures of similar composition forming the majority of the sintering necks observed across all TGA tests at 1000 °C and 1100 °C. In addition to fayalite formation, Reaction 5.6 involving liquid pseudo-hematite is therefore incorporated into the proposed oxidation mechanism at these temperatures, likely playing a dominant role in the reaction mechanism. Its solidification likely resulted in a dendritic structure composed of silica and hematite, as suggested by the contrast observed in the BSE images. Note that, regardless of the value of x , this solidification process does not require any additional oxygen, see Reaction 5.7 which completes the present reaction mechanism at 1000 °C and 1100 °C.



Finally, at 1100 °C, the observed temperature and oxidation level peaks around 50 min were linked to a possible migration of the oxide from the particle surface, increasing oxygen access to previously unoxidized nuclei and inducing fast oxidation. Both 1000 °C and 1100 °C tests showed significant sintering, resulting in oxide formation primarily at particle contact points. The sintering at high temperature for a long time induces strong mechanical forces, even if atmospheric pressure is applied. These forces could be the result of the oxide migration during the 1100 °C tests. As the amount of powder recovered for test 17 (see Table 3.6) was not enough to be rigorously analysed with the SEM and EDS, a conclusion on the powder state before the oxidation step is then not possible. Other powder extraction procedures, or crucibles could be used allowing to recover a sufficient amount of oxidized powder to be further analysed.

At 1200°C, all phases liquefied in the first few minutes of oxidation, leading to the high level of oxidation (80 %) in a few minutes, and temperature instabilities. The local temperature was most likely over 1400°C during this test. The presence of aluminium in the oxidized agglomerate also suggests a reaction of the powder with the alumina crucible, even if aluminium concentration is low. Figure 5.4 with the value from Figure 4.23 shows the increase of the liquid phase area with the temperature on the ternary phase diagram. Once again, the difference between locally measured composition with EDS and the thermodynamic prediction can be explained by the uncertainties on the oxygen EDS measurement. Fe-rich dendrites and Si-rich interdendritic regions are most likely to be fully composed of hematite and silica, respectively, regarding the 98 % of oxidation level measured. Both phases likely resulted from the solidification of liquid fayalite and/or hematite-silicon mixtures during the cooling phase, either when the mixture's solidification temperature fell below 1200 °C or when the oxidation rate decreased, releasing less heat. The oxidation mechanism can then be approximated by Reactions 5.4 and 5.6, as discussed in the context of the 1000 °C and 1100 °C tests. However, the final magnetite content reached 9 wt.% measured with XRD, meaning that hypotheses set to justify the leading hematite formation are less valid at this temperature.

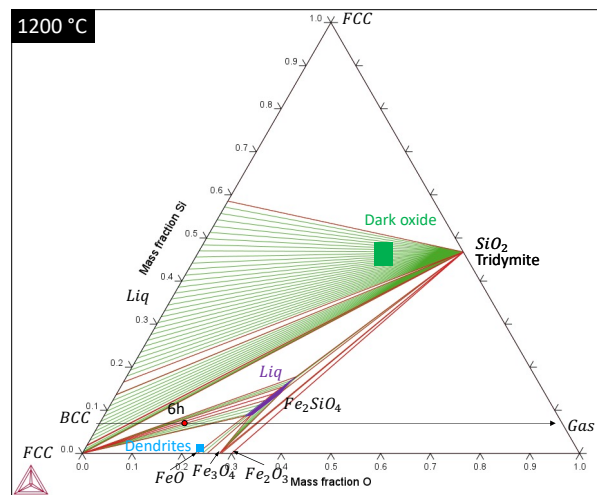


Figure 5.4: Ternary phase diagram of Fe-Si-O at 1200 °C

In the high-temperature furnace, oxidation tests conducted between 800 °C and 1000 °C did not result in the formation of silica phases such as quartz or tridymite. Instead, only

hematite-like structures were observed, with silicon ions incorporated in iron ion regions. Differentiation between quartz and tridymite at these temperatures was then impossible. At higher temperatures (1100 °C and 1200 °C), formation of quartz was detected using XRD, while the ternary phase diagrams predicted tridymite formation.

The oxidation observed in the high-temperature furnace is not fully consistent with the results from the TGA. Specifically, the 900 °C furnace tests showed greater oxidation than both the 800 °C and 1000 °C tests, which contrasts with the TGA trend. However, the oxygen concentration after oxidation at 900 °C is similar in both setups, around ~1 wt.%. In contrast, the oxygen content after the 800 °C and 1000 °C furnace tests is 1 to 2 wt.% lower than that observed in the corresponding TGA tests.

At 1100°C, oxidation of the powder was higher in the furnace than during the TGA, with twice the oxygen concentration at the end. However, as during TGA at 1200 °C, furnace test at the same temperature led to almost full oxidation of the powder.

This suggests that the furnace conditions differed from those of the TGA, potentially due to differences in initial powder mass, heat losses, or variations in air quality or flow conditions. Additionally, the cooling phase in the TGA was carried out under an inert atmosphere, whereas cooling after furnace oxidation occurred under ambient air conditions, possibly allowing further oxidation.

To enhance the quality of the experimental results and refine the procedure, the following improvements are proposed for the TGA:

- Decrease again the initial powder mass to 5 or 15 mg and replicate tests at the same condition to ensure consistency.
- Increase the number of test temperatures to improve the resolution and accuracy of observed changes in oxidation behavior.
- Dilute the Fe-7Si powder with an inert material to reduce particle proximity. This approach may help minimize interparticle interactions and local temperature rises. While ceramic powders could be suitable, issues such as powder recoverability and potential reactions with alumina—observed during TGA tests—may become significant at high temperatures.
- Consider alternative crucible designs that allow for greater spacing between particles while maintaining a sufficient powder quantity for post-test analysis.
- Couple differential scanning calorimetry (DSC) with TGA to measure heat flow during the oxidation.

5.4 Fe-7Si particle ignition model

In this Section, the ignition temperature of Fe-7Si is modeled by extending the model proposed for pure iron introduced in Section 3.5, on the basis of reaction kinetics.

To implement silicon in the model, a change of the ODE system and new assumptions are needed. The strategy here for the model is to start with a simple case. The goal

is to serve as a basis for further models of higher accuracy, by gradually refining the assumptions made.

The first hypothesis is to consider one kinetic and not several interconnected mechanisms. This is because the TGA results do not give the evolution of each oxide layer but only the total evolution of all the layers combined. To know the precise evolution of each phase, in-situ XRD is required. The second hypothesis is that the only layer formed during the oxidation is iron oxide. The silicon oxide layer will be considered as if it had been created instantly and composed only of silica. It is a strong hypothesis but it is justified by the fact that the silica layer is always created at the beginning of the process. The energy release due to the silicon oxidation does not ignite the particle, and the rest of the oxidation is limited by the diffusion of iron ions through the silica layer. In fact, once the silica layer is formed, the only growing layer remaining is the iron oxide layer. With this assumption, the formation of the silica layer can be made during the initial conditions and the ODE system can be simplified, see Equation 5.8. A last hypothesis is that the iron oxide formed is only wüstite, that contradicts the results that show that only hematite is formed. This hypothesis is made because, unlike oxidation using the TGA or the furnace, which lasts several hours, the ignition is evaluated to happen after a few milliseconds, which do not give the time to iron to oxidise into hematite before reaching the liquid state.

$$\frac{dm_{\text{Fe}}}{dt} = -\nu_{\text{Fe/FeO}} \frac{dm_{\text{FeO}}}{dt} \quad (5.8)$$

$$\frac{dm_{\text{FeO}}}{dt} = \frac{\rho_{\text{FeO}} A_p k_{0,\text{glob}}}{Z_{\text{glob}}} \exp\left(\frac{-T_{a,\text{glob}}}{T_p}\right) \quad (5.9)$$

After the adaptation of the ODE system, the next step is to compute the global kinetic coefficient $k_{0,\text{glob}}$ and the energy of activation $T_{a,\text{glob}}$ from TGA results, which are represented by the evolution of the oxide level α , computed with Equation 3.2, in function of time, see Figure 5.5. As explained before, the mechanism of oxidation is very different between all the tests, so some assumptions must be taken to compute the kinetic parameters. First, at 800 °C, the oxidation was faster than during the 900 °C tests. This behavior is probably due to the formation of quartz and gives values that are totally out of range of the kinetics from the other results. For 1000 °C and 1100 °C, the SEM images show that a liquid phase appears. An assumption made is that a huge increase of oxidation due to this liquid phase appears at the beginning of the curves. The rest of the curve is considered to be only iron diffusion as at 900 °C. In order to model only the solid diffusion, the first part of the curves has been cut, represented by the huge vertical increase at the beginning, to keep only the last part. After the data treatment, the next step is to express the data in a linear shape by using a model following this form $g(\alpha) = kt$. α is always the level of oxide and k is the global kinetic coefficient. To find k , one must express the data as a line where k is the slope. From [30], the model of 3D diffusion is taken, see Equation 5.10. From all the diffusion models (1D, 2D, 3D), it gives the fewest errors when applying a linear regression, see Appendix B.1.

$$g(\alpha) = (1 - (1 - \alpha)^{1/3})^2 \quad (5.10)$$

In Figure 5.6, $g(\alpha)$, is fitted linearly, $g(\alpha) = kt$. The quality of the regressions is checked by the R^2 coefficient which is always bigger than 0.95 for all the curves.

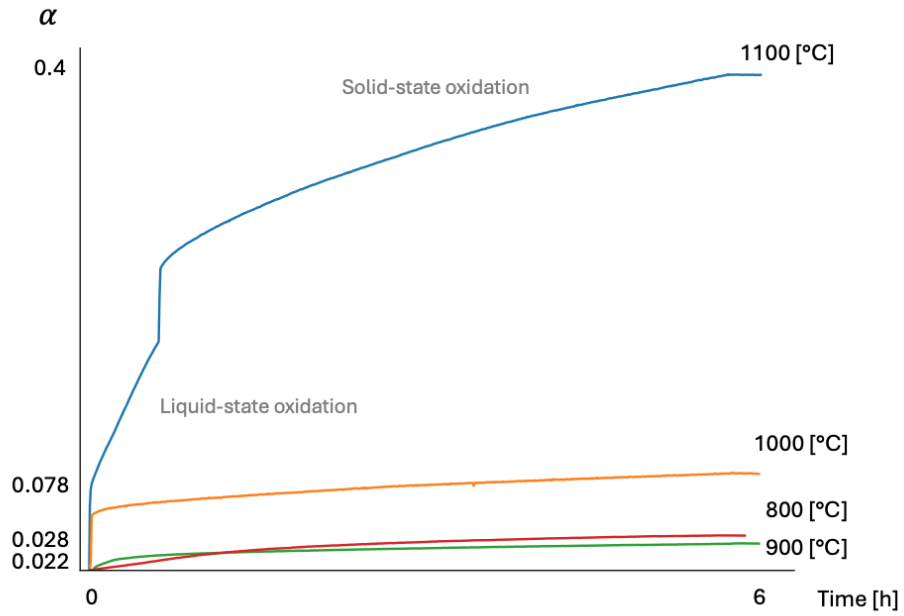


Figure 5.5: **TGA results showing the evolution of the level of oxidation α in function of time.** The hypothesis taken to distinguish solid and liquid oxidation is highlighted by the beginning of curve at 1100 °C. The behavior do not follow the other curves.

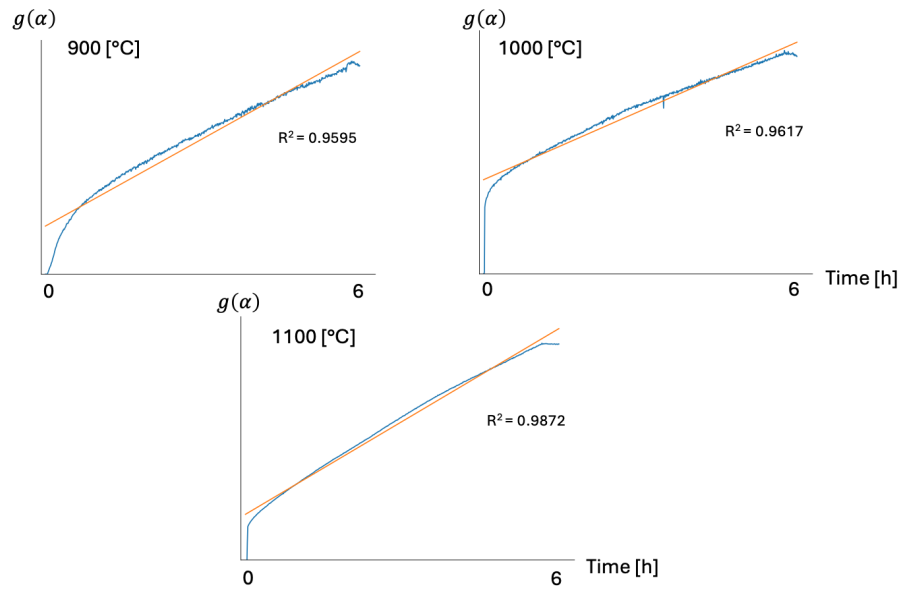


Figure 5.6: **Linear regression application on modelled experimental curves for 900 - 1000 - 1100 °C,** to find the slope that gives the kinetic coefficient. Also, the quality of the curves is check by the R^2 coefficient, which is higher than 0.95 for each curve

5.4.1 Derivation of the oxidation kinetics

In Figure 5.7. The red dots represent the three different TGA tests following the Arrhenius law. With a simple linear regression, the slope gives $T_{a, \text{glob}}$ and the intercept gives $k_{0, \text{glob}}$.

The number of tests is quite few for the reasons explained before. To have a better estimation of the line, a good improvement would be to increase the amount of tests in this range to see if the new data follow the same curve or if a separation of kinetic mechanisms must be applied with the increase of temperature. It should be noted that the temperature of the tests is considered constant here, but an increase of the local temperature is observed, see Section 4.2. To take into account this rise of temperature, the kinetic parameters can be computed with the new temperature guessed with the thermodynamics and the ternary phase diagram, and then do an uncertainty analysis.

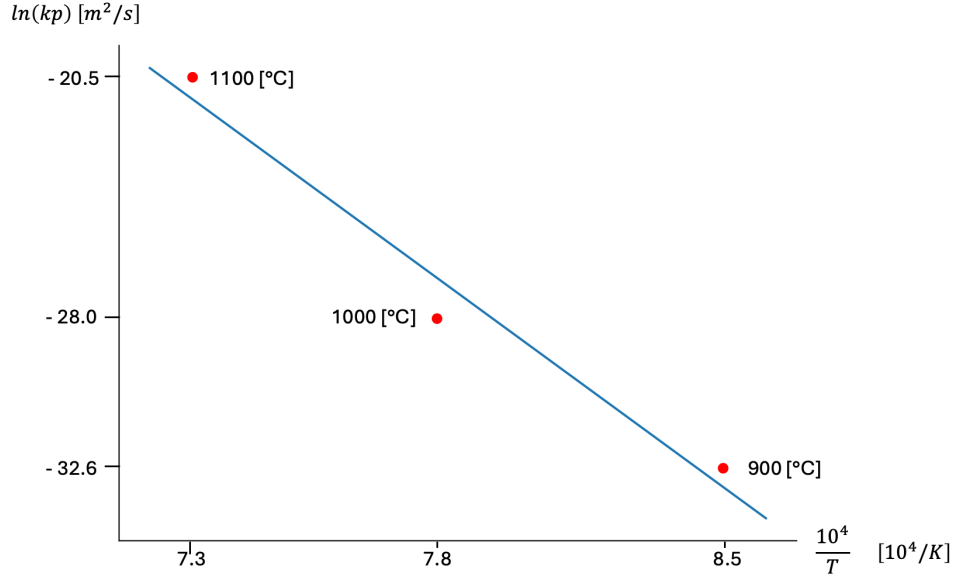


Figure 5.7: **Arrhenius fit based on the kinetics mechanisms from TGA** : Red dots are the kinetics mechanisms obtained with TGA after applied a 3D diffusion model. The blue line is a linear regression, where the slope gives $T_{a, \text{glob}}$ and the intercept $k_{0, \text{glob}}$ based on the Arrhenius law, $k_{p,i}(T) = k_0 \exp\left(\frac{-T_a}{T_p}\right)$, where $T_a = \frac{E_a}{R}$.

Table 5.1: **Global calibrated parameters** obtained from TGA experimental data

	k_0 [m^2/s]	E_a/R [K]
Global	$\exp(49.2)$	96589

The energy of activation is nearly 5 times bigger than the one obtained for pure iron, see Tab 3.8. As a comparison, SAE 304 stainless steel parameter values are $k_0 = \exp(30.15)$ and $T_a = 56445$ K, [31]. It is difficult to compare kinetics, but these values show that the orders of magnitude are not totally different.

5.4.2 Thermal Runaway

The main objective of the model is to predict the apparition of the thermal runaway that marks the ignition temperature of the particle. In Figure 5.8, the model predicts the ignition temperature of the particle at 947 °C if the oxide formed is only wüstite.

The thermal runaway can be identified by the huge increase in particle temperature obtained because the heat released exceeds the losses. The other curves also show an increase in temperature but then decrease due to the loss by convection and radiation. The phenomena is very fast, about 4 ms. To compare with pure iron, the model predicts a temperature ignition of pure iron at about 810 °C. To go further, the thermal runaway has been computed if the iron only oxidizes into hematite (Fe_2O_3) to be consistent with TGA results. The kinetic parameters are similar, $k_0 = \exp(46.2)$ and $E_a/R = 94566$ K. The model computed the thermal runaway at 965 °C.

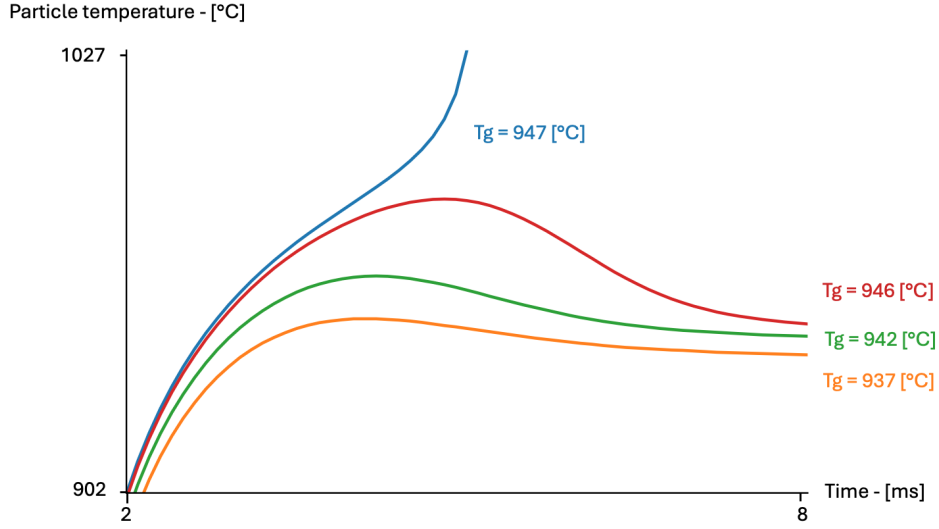


Figure 5.8: **Modelisation of the Fe-7Si particle temperature evolution under different constant gas temperatures.** Thermal runaway appears at a temperature of the gas (T_p) of 947 °C after 4 ms. Below this temperature the losses are too big to ignite as shown by the others curves

5.4.3 Results analysis

The present Section discusses the results from the model and the possible improvements.

First, the kinetics mechanism obtained shows that the presence of silicon increases the energy of activation E_a/R from ≈ 20000 K for pure iron to 96589 K for iron with silicon content. This increase illustrates that the energetic barrier that the iron-silicon needs to surpass to oxidize is nearly 5 times higher than the one for pure iron. At the same temperature, particles of Fe-7Si will react slower than pure iron because fewer molecules will overcome the potential barrier to oxidize. The value of the activation energy suggests that the ignition temperature will be higher for iron-silicon. The initial energy required to ignite the particle would be higher. In line with the kinetics, the model gives a value for the ignition temperature at 947 °C, which is higher than for pure iron (809 °C). The particle is considered to ignite when the thermal runaway is reached. To be aligned with TGA results, the ignition temperature was computed if the iron oxidizes only into Fe_2O_3 . The energies of activation are nearly the same: 96589 K for FeO and 94566 K for Fe_2O_3 . The temperature of ignition was predicted to be 965 °C, that is only 18 °C above, that does not represent a big change.

The model presents limitations that can be shown by the strong hypotheses that will be specified:

- The particle is assumed to be perfectly spherical.
- Oxidation of silicon is instantaneous.
- The kinetic mechanism is governed only by 3D diffusion of Fe.
- No phase change
- Heat exchange only by radiation and convection.
- No flow around, $Re = 0$.

To improve the model, the goal is to remove as many assumptions as possible. A first improvement can be to model the evolution of the silicon oxide layer. To do that, a DRX experiment is needed to determine the thickness of the layers and thus compute the kinetics parameter for each layer's evolution. Then, it is possible to simulate the increase of the silicon oxide layer and iron oxide layer simultaneously, as is done for FeO and Fe_3O_4 in the case of pure iron, see Eq. 3.5.

Next, the kinetic parameters computed are not precise. To obtain a better value, the data from TGA needs to be refined. Increasing the number of experiments near 900 °C could allow enhancing the accuracy of the linear regression by adding data and having better values for kinetic parameters for solid-state oxidation. Also, one needs to make sure to stay within ranges of temperatures where particles do not change phase, to avoid having to suppress part of the level of oxide curves. About the kinetic mechanism, it evolves with the particle temperature. Currently, it is only the 3D diffusion of iron, but at a temperature threshold, the limiting mechanism becomes the diffusion of oxygen. In the model, it is possible to change the limiting mechanism in function of the temperature of the particle, but the threshold needs to be determined experimentally.

For the heat exchange, it depends on the setup. The model can be adapted to fit with the case studied. For example, in the MC2 burner, the swirl should be taken into account, which will increase the convection losses.

Chapter 6

Conclusion

During this work, the combustion of the Fe-7Si powder has been studied. First, the powder has been tested inside the MC2 burner, in three different batches of 100 g, at a temperature of 810 °C and two times at 930 °C. For each test, analysis of the flame, the temperature evolution and the emission gases has been made. After the combustion, the powders have been analysed by SEM, EDS and XRD. Also, granulometric analysis has been performed. Following these tests, TGA has been made to see the evolution of the oxidation of the powder isothermally at different temperatures. The tests have been made at temperatures of 540 °C, 800 °C, 900 °C, 1000 °C, 1100 °C and 1200 °C, with a time duration of 6 h or 20 h. Charts with the level of oxidation in function of time are obtained. SEM, EDS and XRD have also been performed. Based on the data obtained from TGA experiments, a model of combustion of one-single particle has been made to find the temperature of ignition of Fe-7Si.

All the results show that the presence of silicon slows down the solid-state oxidation and one needs a higher temperature to ignite the particles, and so the combustion process is impacted.

- The tests made with the MC2 burner show that, in order to have a combustion and a stable flame, the temperature of the gases need to be increased at least to 930°C.
- TGA results illustrate that at 900 °C and below the oxidation process is slow due to the silica layer that blocks the diffusion. It results in a low oxide level which does not exceed 5 %.
- At 1000 °C and above, microstructure analysis show that unexpected liquid phases appeared. It results in an oxidation level which is around 9% for 1000°C and 98 % for 1200 °C.
- Based on TGA the activation energy (E_a/R) of the oxidation process computed is 96589 K. The reaction needs more energy to occur and so the temperature of ignition is logically higher than for pure iron particle.
- With the kinetics parameters extracted from the TGAs at 900°C, 1000 °C and 1100 °C, the model evaluation estimated a temperature of ignition at 947 °C, for one-single particle combustion.

The study presents limitations concerning the burner. At the end, despite the manifest slowdown of the oxidation due to the presence of silicon, the powder has been successfully burnt at a temperature of the gas of 930 °C inside the MC2. The increase of the gas temperature, compared to pure iron conditions, has the inconvenience of increasing the agglomeration and micro-explosion effects. More tests at different temperatures should be necessary to determine the precise ignition temperature of the Fe-7Si powder in the MC2.

During TGA, local temperature rises were observed, introducing uncertainties in the analysis of the results. Nevertheless, the characterization of the oxidized powders enabled the development of a preliminary understanding of the oxidation mechanism in powders containing a significant amount of silicon. Hematite formation appears to dominate the oxidation process, as it is consistently present in both dendritic and eutectic structures. The hematite structure also seems to incorporate silicon ions, likely substituting iron ions within the hematite lattice. However, these conclusions remain qualitative and hypothetical. Further confirmation would require more advanced analyses, such as TEM and EBSD, to precisely determine the structural and chemical nature of the observed phases. Improvements concerning the TGA experiment were also given to enhance the temperature and powder stability. For example, it would be beneficial to perform more tests at different temperatures to be more accurate in changes in oxidation behavior, or to incorporate an inert powder to limit local rise in temperature.

The model showed an increase in the evaluated ignition temperature compared to pure iron, which was expected regarding the different experiments. However, to improve the quality of the prediction, it would be interesting to remove step by step the various assumptions made. A first improvement would be to refine the experimentally obtained values by increasing the number of TGA experiments on Fe-7Si oxidation. A second would be to adapt the model more closely to the experimental setup, in order to better account for heat transfer mechanisms.

This work represents only a first step in the characterization of the silicon influence on iron powder combustion. Nonetheless, the limitations and challenges associated with using this powder composition as an energy carrier have already been identified, despite the clear economic appeal of employing an impure powder such as the one studied here.

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This Master Thesis concludes five years at EPL, more precisely in the Energy Engineering and Mechanical Engineering fields. These years of hard work have made us grow intellectually and personally in a rich academic environment. The icing on the cake of these years was this Master Thesis, which made us dive into the world of material sciences. Of course, this work would not have been possible without the invaluable advice and support of Professor Francesco Contino, whom we would like to thank. A very big thank you to the research team who helped us, who kept us going, who gave us so much of their time to complete this work. We would like to express our sincere gratitude to Zakarie Bruyr, Laurine Choisez, and Lilian Ahmad. We would also like to thank Willie Prashida for welcoming us to the TU/e, for the time he gave us, and for allowing us to use his experimental setup. Many thanks also to the team of technicians who taught us and helped us to use all the different machines. A big thank you to our families, friends, and especially our girlfriends, who have supported us, helped us to move forward throughout these years.

AI use

AI tools, such as ChatGPT, were used during the writing of this report to enhance sentence structure and grammar. Additionally, small portions of code were generated to assist in the extraction of raw data from experimental results. The use of AI was conducted with a critical approach, and all outputs were carefully reviewed and validated.

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Appendix A

Experiment

A.1 TGA: Raw data

Legend

- D : powder dimension
- m_0 : initial powder mass
- Sample holder : Figure 3.5
- $\dot{V}_{air}$: air flow
- T_{ox} : oxidation temperature
- t_f : isothermal duration

Test 1

N°	Composition	D [μm]	m_0 [mg]	Sample holder	$\dot{V}_{air}$ [mL/min]	T_{ox} [°C]	t_f [h]
1	Fe-7Si	20-63	159.5	A	150	540	3

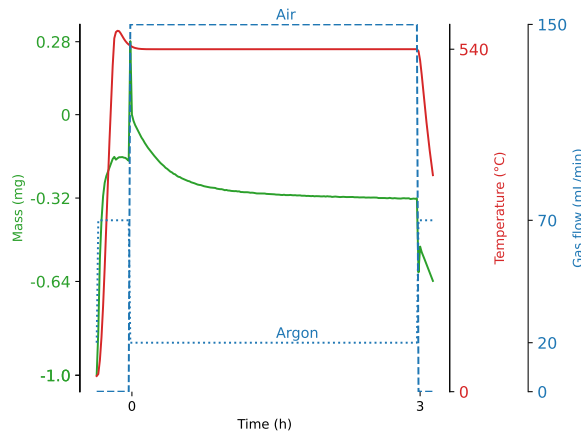


Figure A.1: Blank test 1

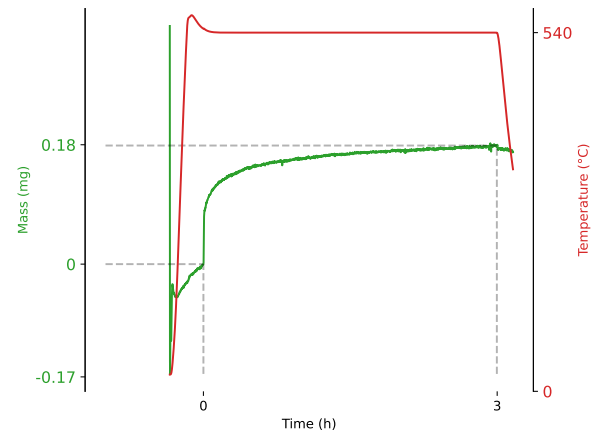


Figure A.2: Corrected test 1

Test 2

N°	Composition	D [μm]	m_0 [mg]	Sample holder	$\dot{V}_{air}$ [mL/min]	T_{ox} [°C]	t_f [h]
2	Fe-7Si	20-63	168.0	A	250	540	2

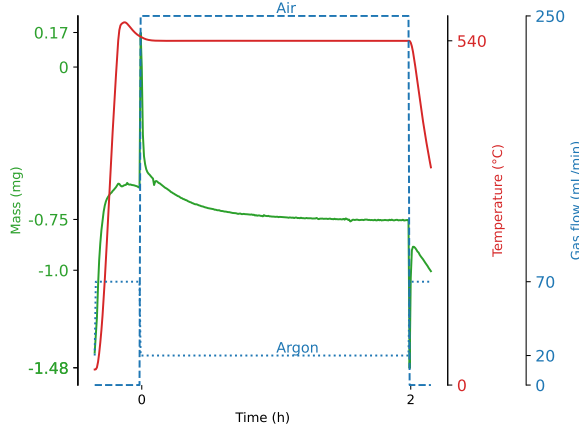


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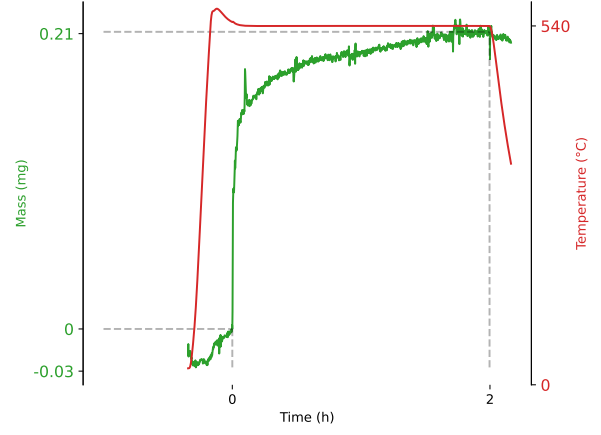


Figure A.4: Corrected test 2

Test 3

N°	Composition	D [μm]	m_0 [mg]	Sample holder	$\dot{V}_{air}$ [mL/min]	T_{ox} [°C]	t_f [h]
3	Fe-7Si	20-63	104.5	A	250	800	3

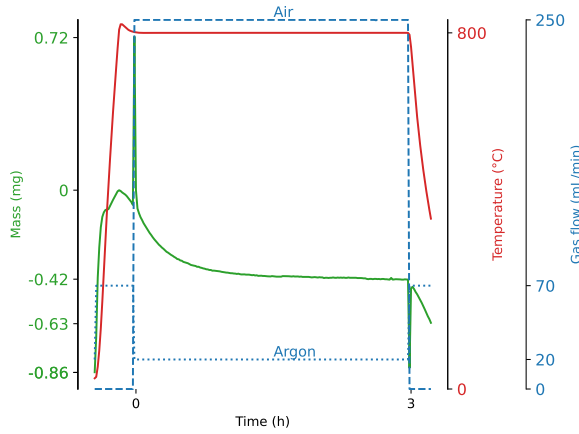


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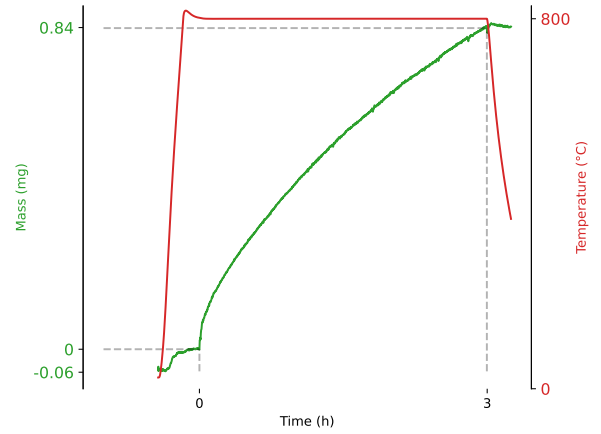


Figure A.6: Corrected test 3

Test 4

N°	Composition	D [μm]	m_0 [mg]	Sample holder	$\dot{V}_{air}$ [mL/min]	T_{ox} [°C]	t_f [h]
4	Fe	20-63	97.4	A	150	540	3

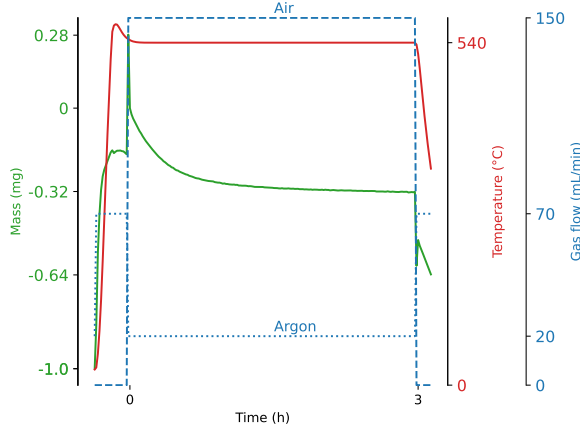


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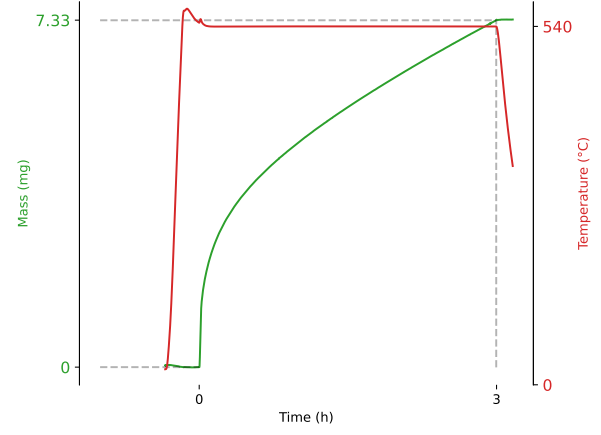


Figure A.8: Corrected test 4

Test 5

N°	Composition	D [μm]	m_0 [mg]	Sample holder	$\dot{V}_{air}$ [mL/min]	T_{ox} [°C]	t_f [h]
5	Fe	20-63	51.9	B	150	540	3

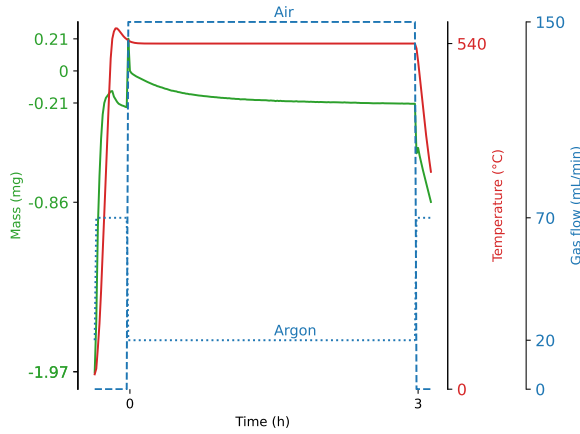


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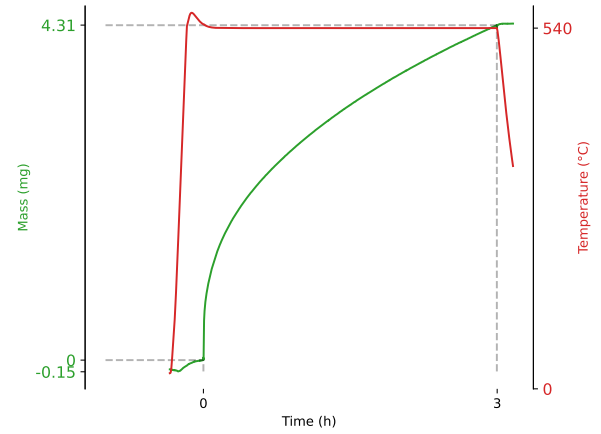


Figure A.10: Corrected test 5

Test 6

N°	Composition	D [μm]	m_0 [mg]	Sample holder	$\dot{V}_{air}$ [mL/min]	T_{ox} [°C]	t_f [h]
6	Fe-7Si	20-63	46.1	B	150	540	3

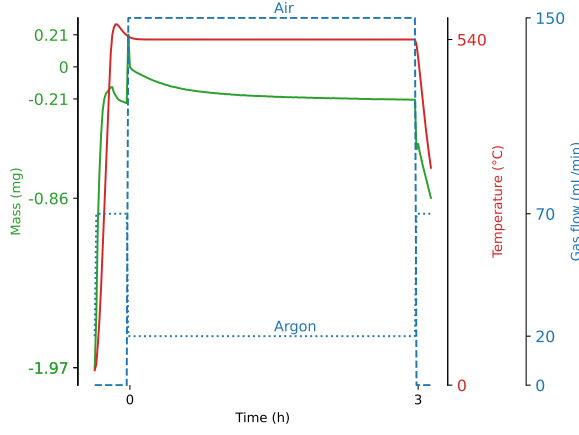


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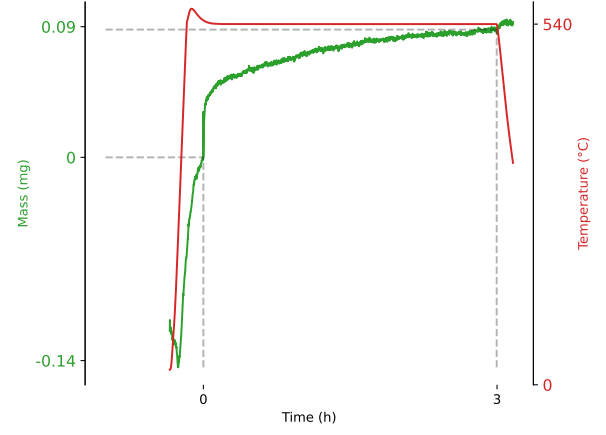


Figure A.12: Corrected test 6

Test 7

N°	Composition	D [μm]	m_0 [mg]	Sample holder	$\dot{V}_{air}$ [mL/min]	T_{ox} [°C]	t_f [h]
7	Fe-7Si	20	49.2	B	150	540	3

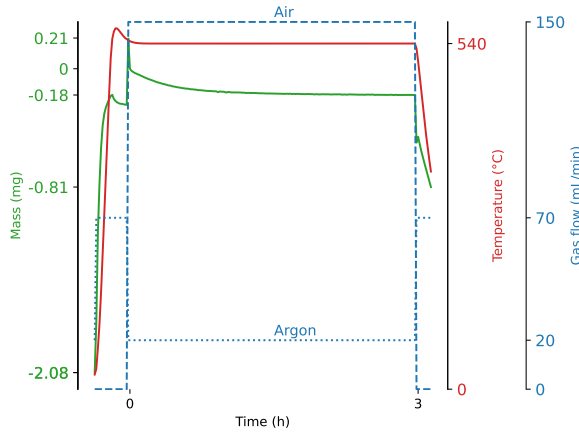


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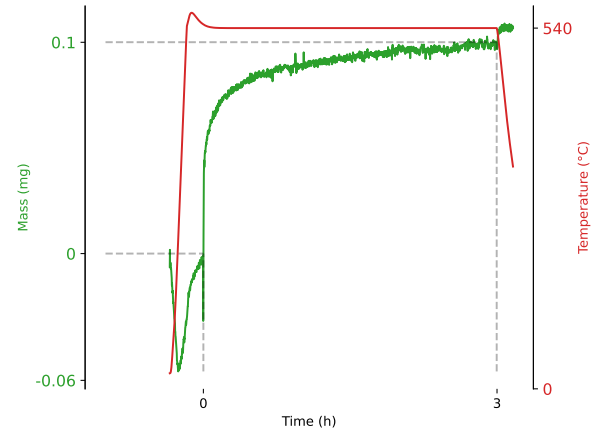


Figure A.14: Corrected test 7

Test 8

N°	Composition	D [μm]	m_0 [mg]	Sample holder	$\dot{V}_{air}$ [mL/min]	T_{ox} [°C]	t_f [h]
8	Fe-7Si	20	46.8	A	150	800	6

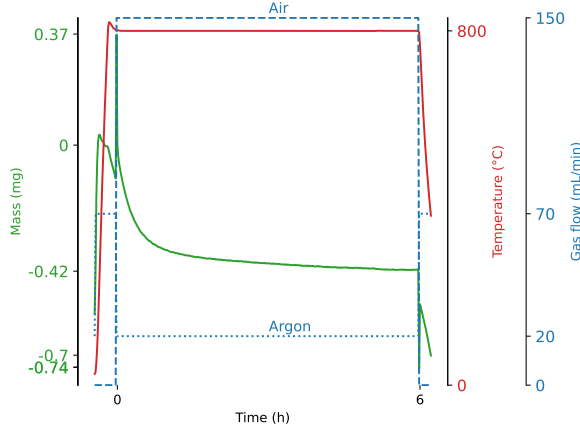


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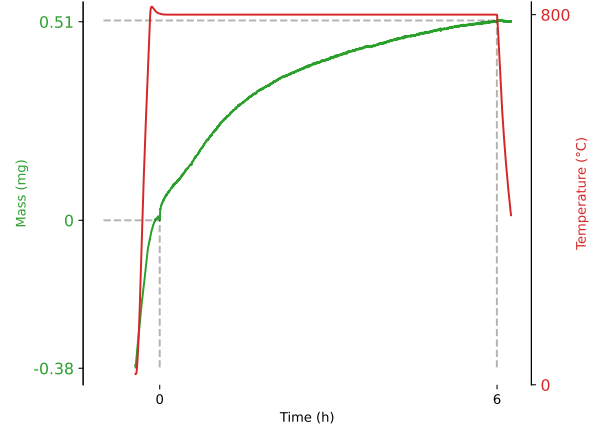


Figure A.16: Corrected test 8

Test 9

N°	Composition	D [μm]	m_0 [mg]	Sample holder	$\dot{V}_{air}$ [mL/min]	T_{ox} [°C]	t_f [h]
9	Fe-7Si	20	49.1	A	150	900	6

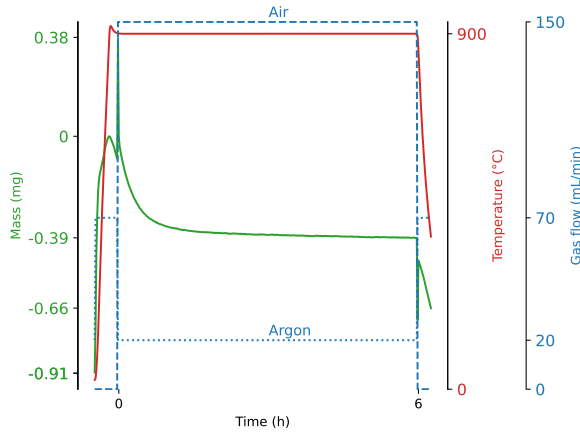


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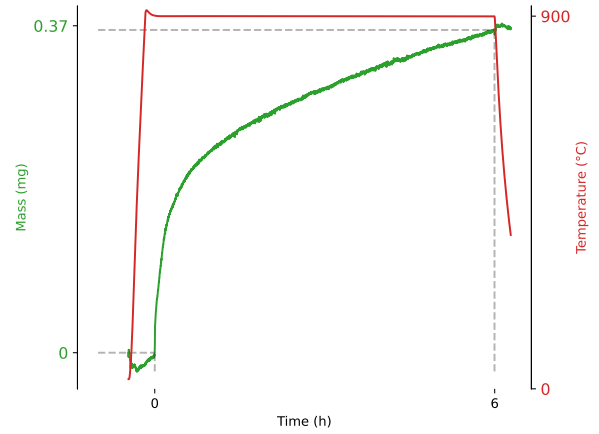


Figure A.18: Corrected test 9

Test 10

N°	Composition	D [μm]	m_0 [mg]	Sample holder	$\dot{V}_{air}$ [mL/min]	T_{ox} [°C]	t_f [h]
10	Fe-7Si	20	22.7	A	150	1000	6

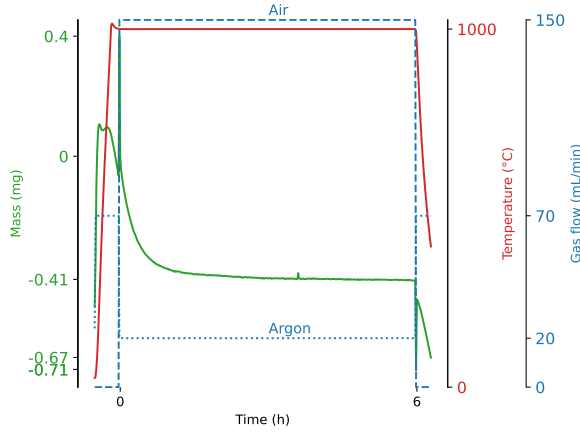


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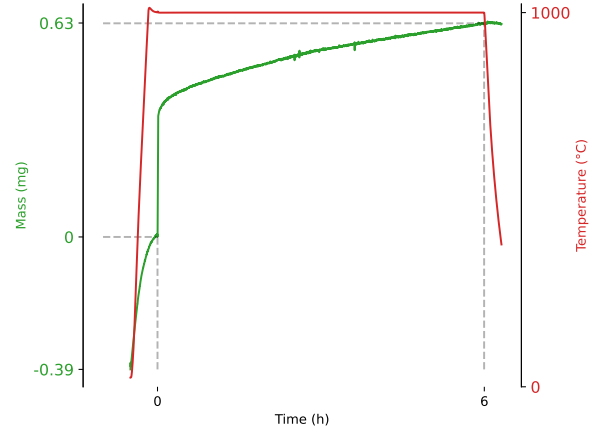


Figure A.20: Corrected test 10

Test 11

N°	Composition	D [μm]	m_0 [mg]	Sample holder	$\dot{V}_{air}$ [mL/min]	T_{ox} [°C]	t_f [h]
11	Fe-7Si	20	30.4	A	150	1000	20

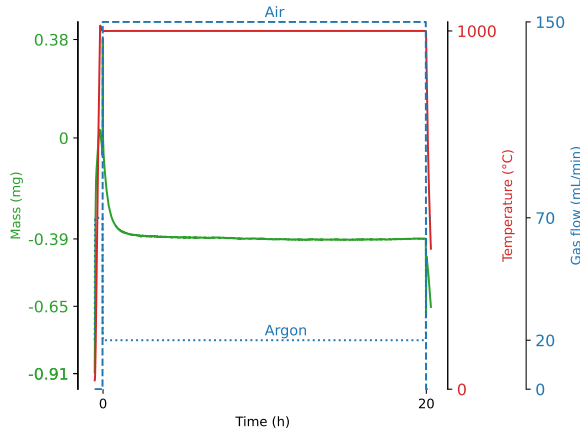


Figure A.21: Blank test 11

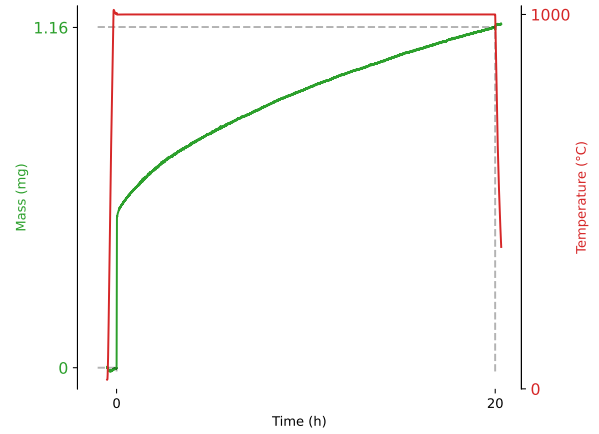


Figure A.22: Corrected test 11

Test 12

N°	Composition	D [μm]	m_0 [mg]	Sample holder	$\dot{V}_{air}$ [mL/min]	T_{ox} [°C]	t_f [h]
12	Fe-7Si	20	29.2	A	150	900	20

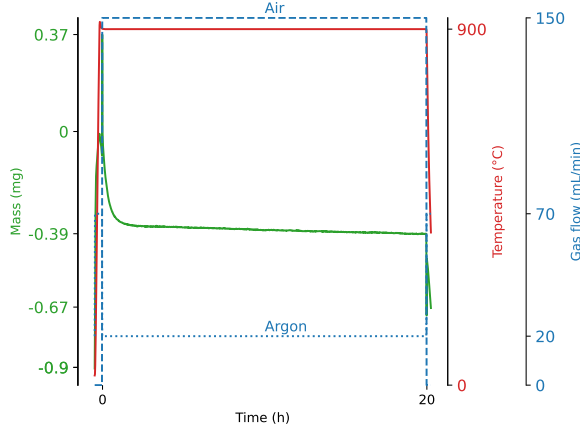


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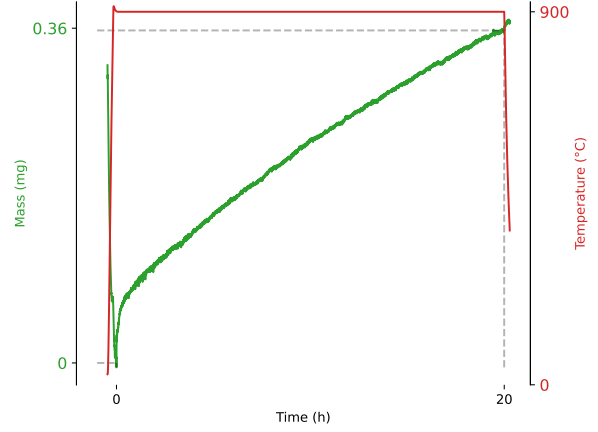


Figure A.24: Corrected test 12

Test 13

N°	Composition	D [μm]	m_0 [mg]	Sample holder	$\dot{V}_{air}$ [mL/min]	T_{ox} [°C]	t_f [h]
13	Fe-7Si	20	30.0	A	150	800	20

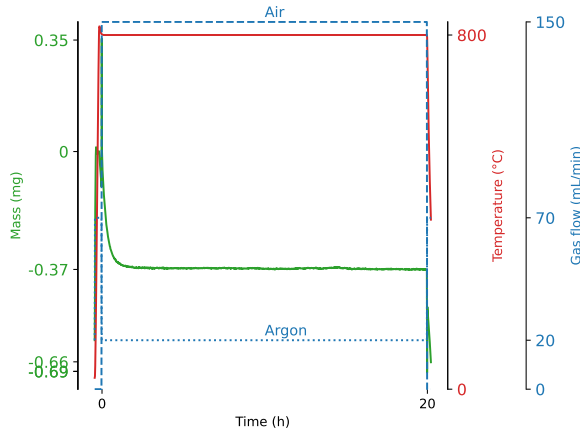


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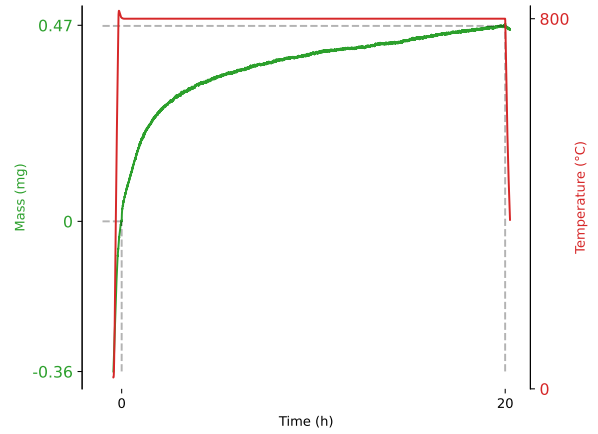


Figure A.26: Corrected test 13

Test 14

N°	Composition	D [μm]	m_0 [mg]	Sample holder	$\dot{V}_{air}$ [mL/min]	T_{ox} [°C]	t_f [h]
14	Fe-7Si	20	25	A	150	1100	6

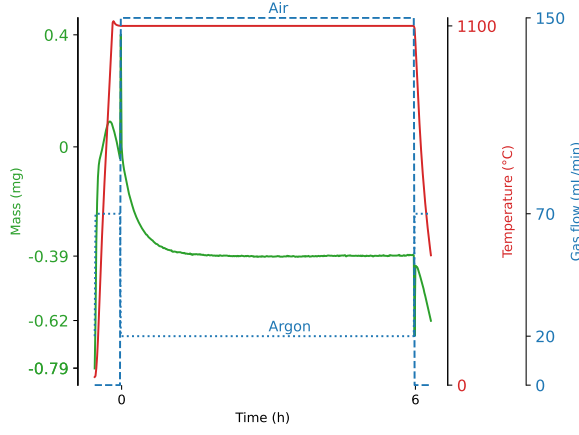


Figure A.27: Blank test 14

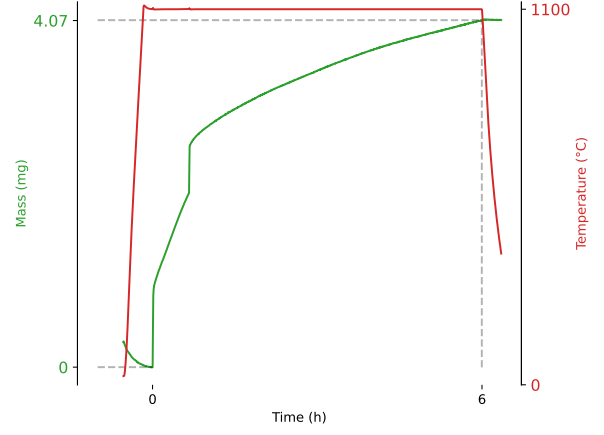


Figure A.28: Corrected test 14

Test 15

N°	Composition	D [μm]	m_0 [mg]	Sample holder	$\dot{V}_{air}$ [mL/min]	T_{ox} [°C]	t_f [h]
15	Fe-7Si	20	31.7	A	150	1200	6

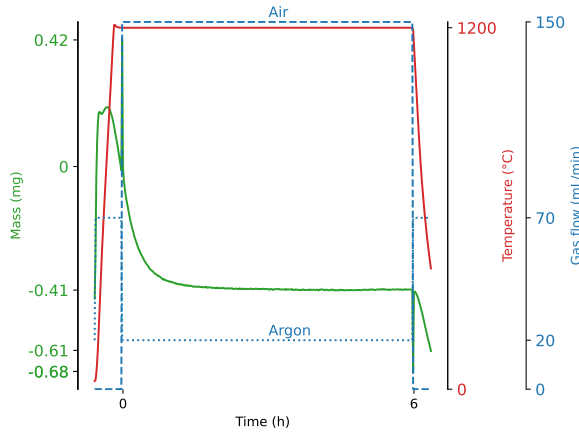


Figure A.29: Blank test 15

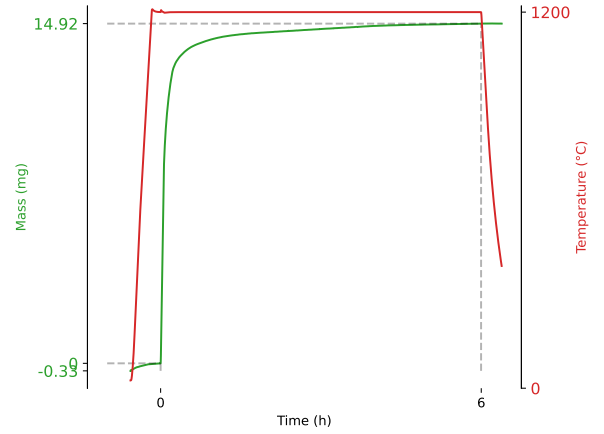


Figure A.30: Corrected test 15

Test 16

N°	Composition	D [μm]	m_0 [mg]	Sample holder	$\dot{V}_{air}$ [mL/min]	T_{ox} [°C]	t_f [h]
16	Fe-7Si	20	31.5	A	150	1100	20

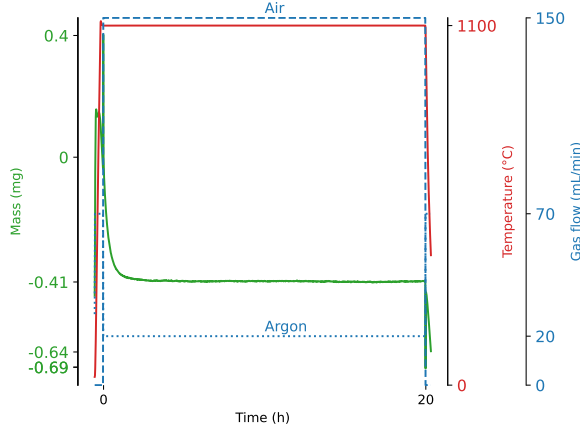


Figure A.31: Blank test 16

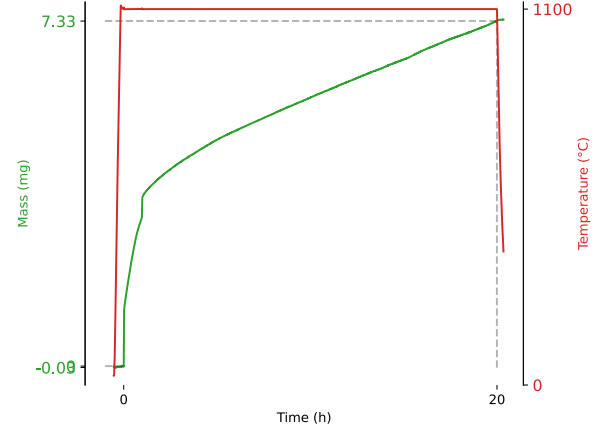


Figure A.32: Corrected test 16

Test 17

N°	Composition	D [μm]	m_0 [mg]	Sample holder	$\dot{V}_{air}$ [mL/min]	T_{ox} [°C]	t_f [min]
17	Fe-7Si	20	36.1	A	150	1100	40

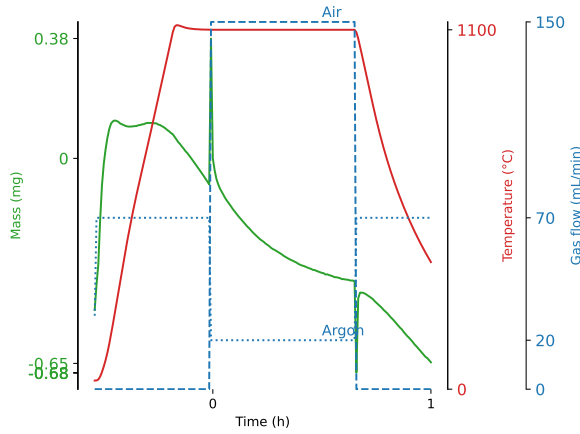


Figure A.33: Blank test 17

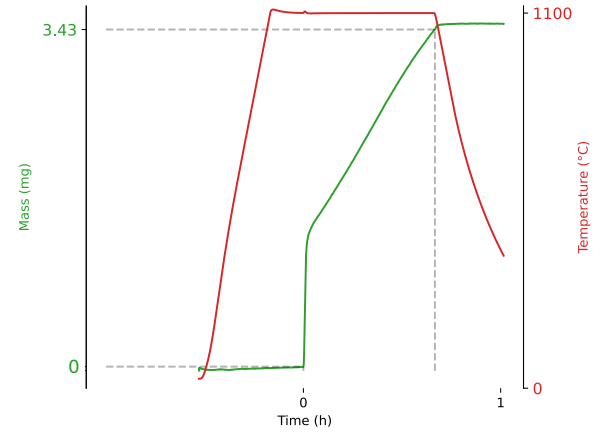


Figure A.34: Corrected test 17

A.2 TGA: Oxidation level and Oxygen mass fraction

T [°C] - t_f - m_0 [mg]	30s	1m	5m	30m	1h	3h	6h	20h
540 - 3h - 49.2	0.19	0.20	0.27	0.34	0.38	0.42		
800 - 6h - 46.8	0.12	0.14	0.25	0.59	1.04	1.85	2.28	
800 - 20h - 30.0	0.12	0.16	0.31	0.81	1.32	2.10	2.51	3.26
900 - 6h - 49.1	0.14	0.18	0.36	0.81	0.97	1.27	1.55	
900 - 20h - 29.2	0.21	0.21	0.28	0.51	0.61	0.88	1.26	2.56
1000 - 6h - 22.7	3.17	3.29	3.57	3.99	4.27	5.05	5.78	
1000 - 20h - 30.4	3.26	3.46	3.64	3.94	4.21	4.98	5.72	7.97
1100 - 40m - 36.1	3.95	7.12	8.99	17.08	19.81			
1100 - 6h - 31.5	4.22	6.63	8.05	13.48	21.12	26.03	30.45	
1100 - 20h - 27.9	4.25	7.47	9.22	16.00	23.74	28.63	33.13	48.55
1200 - 6h - 31.7	5.57	14.73	64.42	90.66	93.82	96.61	98.17	

Table A.1: **Oxidation level values (Equation 3.1)** for tests 7 to 17 (see Table 3.6) at various times after the start of oxidation. Red color gradient indicates oxidation level (white = low, red = high).

T [°C] - t_f - m_0 [mg]	30s	1m	5m	30m	1h	3h	6h	20h
540 - 3h - 49.2	0.15	0.16	0.19	0.23	0.25	0.27		
800 - 6h - 46.8	0.03	0.05	0.11	0.27	0.48	0.87	1.07	
800 - 20h - 30.0	0.05	0.07	0.14	0.39	0.63	1.00	1.19	1.54
900 - 6h - 49.1	0.06	0.09	0.17	0.39	0.47	0.61	0.74	
900 - 20h - 29.2	0.11	0.11	0.15	0.25	0.31	0.44	0.62	1.23
1000 - 6h - 22.7	1.31	1.55	1.68	1.88	2.01	2.36	2.69	
1000 - 20h - 30.4	1.26	1.63	1.71	1.85	1.97	2.33	2.67	3.68
1100 - 40m - 36.1	1.35	3.20	4.12	7.56	8.67			
1100 - 6h - 31.5	1.44	3.03	3.72	6.06	9.20	11.10	12.75	
1100 - 20h - 27.9	1.44	3.34	4.21	7.11	10.21	12.06	13.70	18.88
1200 - 6h - 31.7	1.81	5.87	23.47	30.30	31.03	31.66	32.01	

Table A.2: **Global oxygen mass fraction [wt.%]**, computed based on mass increase for TGA tests 7 to 17 (see Table 3.6) at various times after the start of oxidation. Red color gradient indicates oxidation level (white = low, red = high).

Appendix B

Modelling

B.1 1D and 2D diffusion model, linear regression

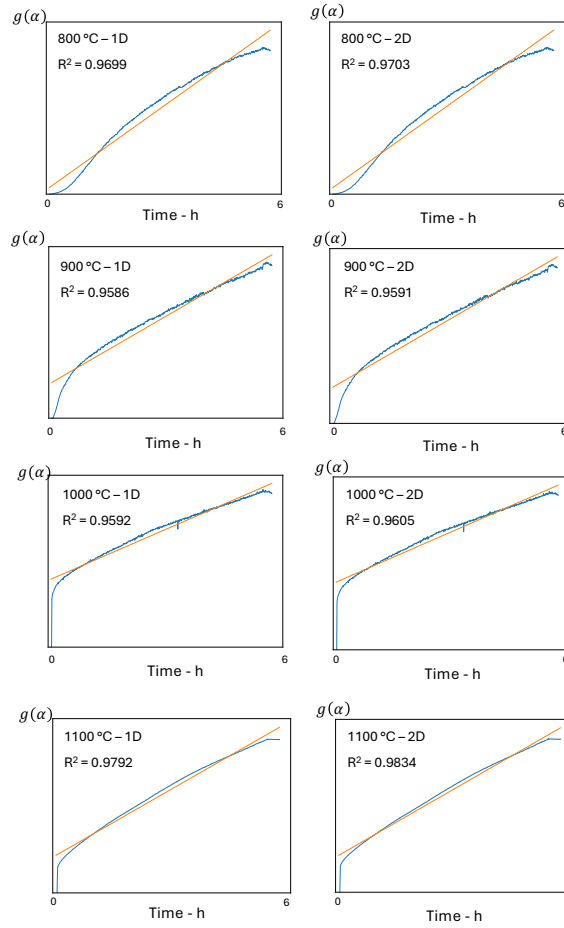


Figure B.1: Linear regression for 1D and 2D model at 800 °C, 900 °C, 1000 °C and 1100 °C.

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