

Carburization in direct reduction: Effects of various CO-H₂ gas mixtures

Syafinah Fong^{a,*}, Mohammed Liaket Ali^a, Sven Mehlhose^a, Quentin Fradet^a,
Rafiandy Dwi Putra^b, Andreas Schedl^b, Uwe Riedel^a

^a German Aerospace Center (DLR), Institute of Low-Carbon Industrial Processes, Äußere Oybiner Straße 14/16, 02763, Zittau, Germany

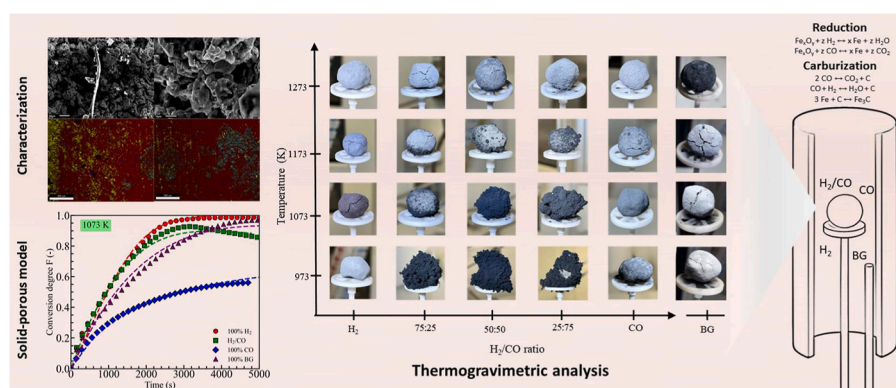
^b Deutsches Biomasseforschungszentrum gemeinnützige GmbH (DBFZ), Thermo-chemical Conversion Department, Torgauer Straße 116, 04347, Leipzig, Germany



HIGHLIGHTS

- Pure H₂ gives fast reduction, full metallization, and a dense uniform α-Fe structure.
- Pure CO exhibits slow reduction and forms iron whiskers at 1273 K with minimal carbon.
- H₂/CO forms carburized structures, which potentially hinder reduction.
- Simulated biogenic gas attains high metallization with controlled carburization.
- The 1D porous-solid model links oxygen removal, carbon uptake, and carbide formation.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:

Direct reduction
Carburization
Biogenic gas
TGA
Sustainable steelmaking

ABSTRACT

Hydrogen and carbon monoxide govern distinct pathways in direct reduction of iron ores, influencing process efficiency and product quality. H₂ enables rapid, nearly CO₂-free reduction, but is strongly endothermic and yields carbon-free direct reduced iron. In contrast, CO enables reduction and supplies in-situ carbon for secondary steelmaking. Balancing these gases, and establishing renewable CO sources such as biomass-derived syngas, is central for decarbonizing steelmaking. Systematic datasets linking carburization with reduction kinetics and product characteristics under industrially relevant conditions remain scarce. Single DR-grade pellets were reduced isothermally (973–1273 K) in H₂/CO atmospheres under moderate flow conditions. Weight evolution was tracked by thermogravimetry, and characterization (SEM–EDS, XRD, nanoindentation) resolved carbon distribution, phase composition, and mechanical properties. Complementary trials with simulated biogenic gas showed slower early reduction than syngas but higher final metallization; only at 973 K did a slight late-stage mass gain indicate controlled carburization. Gas composition and temperature governed the balance between Fe₃C formation and free-carbon deposition. The resulting dataset enabled calibration of a porous–solid model that couples oxygen removal, carbon deposition, and carbide formation, providing a mechanistic basis for optimizing metallization and controlled carburization in hydrogen-rich and renewable CO-containing DR processes.

This article is part of a special issue entitled: Reactive Particle-Gas Systems II published in Particuology.

* Corresponding author.

E-mail address: syafinah.bintimohdfawzifong@dlr.de (S. Fong).

<https://doi.org/10.1016/j.partic.2026.04.014>

Received 25 November 2025; Received in revised form 20 February 2026; Accepted 16 April 2026

Available online 26 April 2026

1674-2001/© 2026 Chinese Society of Particuology and Institute of Process Engineering, Chinese Academy of Sciences. Published by Elsevier B.V. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Steel production accounts for about 7–9% (Worldsteel, 2024) of global anthropogenic CO₂ emissions, largely due to the reliance on the carbon-intensive blast furnace–basic oxygen furnace (BF–BOF) route, making the decarbonization of iron and steelmaking a prerequisite for achieving international climate targets. Analyses indicate that CO₂ emissions from global steel production will jeopardize the 1.5 °C climate target unless steelmaking is rapidly decarbonized through low-emission production technologies (Harpprecht et al., 2022). Compared to the current coke-based BF–BOF route, specific lifecycle greenhouse-gas emissions can be reduced by up to 95% through electrified production technologies such as hydrogen-based direct reduction (H₂-DR), electrolysis-based ironmaking (EW), and secondary recycling routes (Harpprecht et al., 2025). However, realizing these reductions will require faster technological development and large-scale implementation of green ironmaking technologies—particularly H₂-DR—in light of the remaining global carbon budgets. Hydrogen-based direct reduction, followed by melting in an electric arc furnace, has emerged as a cornerstone pathway for decarbonizing primary steelmaking, since it offers near-zero direct emissions and compatibility with renewable energies (OECD, 2025). Long-term projections reinforce this trajectory: according to the analysis of Agora's Net-Zero scenarios by 2050, hydrogen-based DR routes could supply 56–72% of crude steel production (approximately 683–873 Mt), highlighting their potential dominance in future primary steelmaking (OECD, 2025). The remaining production is expected to come from DR-EAF routes with carbon capture and storage (CCS) and from conventional BF–BOF technologies and emerging alternatives. Beyond decarbonization, declining quality of recycled scrap, due to tramp elements such as copper, limits its suitability for high-grade products (e.g., thin-slab casting) (Daehn et al., 2017). As a result, direct reduced iron (DRI) is increasingly required not only as an alternative to the blast furnace, but also as a necessary source of clean virgin iron units in EAF steelmaking, helping reduce tramp-element contamination (Calderon Hurtado et al., 2024). Moreover, the utility of DRI depends not only on metallization degree but also on carbon-oxygen balance: high-carbon DRI with a near-stoichiometric C/O molar ratio (~1) stabilizes the final reduction in the EAF, suppresses reoxidation, and minimizes excess fuel or oxygen requirements (Jess & Depner, 1998). These considerations underscore carburization as a key quality attribute of DRI. On the other hand, carbon-free hydrogen-reduced pellets have been shown to exhibit higher strength and lower fines generation than carbon-containing DRI (Pousette & Kojola, 2024).

While the exclusive use of hydrogen offers the potential for near-zero direct emissions and improved mechanical integrity of the produced DRI, it also presents challenges. The reduction of iron oxides with hydrogen is globally endothermic, with enthalpy requirements that cause local cooling in the shaft furnace unless compensated by higher gas temperatures or external heat. By contrast, CO-based reduction is mildly exothermic and, through reactions such as the Boudouard equilibrium ($2\text{CO} \rightleftharpoons \text{CO}_2 + \text{C}$), not only stabilizes the heat balance but also introduces carbon into the solid. The resulting hydrogen-derived DRI is essentially carbon-free, yet carbon is indispensable in the downstream EAF not only for energy efficiency but also for the fundamental oxygen balance, since residual FeO in the charge must be reduced via reactions such as $[\text{C}] + \text{FeO} \rightarrow \text{Fe} + \text{CO}$, which also generates CO bubbles that sustain slag foaming (Kieush & Schenk, 2025), improving arc stability and electrical efficiency (Echterhof, 2021). If carbon is absent in the DRI, it must be added ex-situ through injection or charge carbon. However, such sources often introduce impurities (sulfur, ash) that increase slag volumes, flux demand, and refractory wear, while also providing carbon less efficiently due to limited dissolution and reaction kinetics (Hornby & Brooks, 2021). By contrast, in-situ carburization during DR distributes carbon within the porous iron matrix, most favorably as cementite (Fe₃C). This provides a cleaner carbon source with low impurity levels,

improved reactivity during melting, and partial thermal compensation of hydrogen's endothermicity. Nevertheless, excessive free carbon deposition can hinder reduction by blocking pores, lowering pellet strength, and causing dusting, underscoring the need to optimize conditions so that just enough in situ carbon is introduced to satisfy EAF requirements without compromising metallization or process stability.

Despite its industrial significance for both process performance and downstream steelmaking, carburization during direct reduction has received far less systematic investigation than overall reduction kinetics and metallization, largely due to the experimental difficulty of decoupling concurrent reduction and carbon-forming reactions. Existing studies have demonstrated carbon deposition via Boudouard reaction (Kazemi & Du, 2016), CH₄ cracking (Kar & Safarian, 2025), and Fe₃C formation under reducing conditions (Kumar, Alatalo, et al., 2022; Perrone et al., 2024). In addition to the Boudouard reaction, alternative pathways for carbon deposition have been identified. Grabke et al. (Grabke et al., 2001) showed that in CO–H₂ mixtures, hydrogen not only serves as a reductant but can also promote carburization via the reaction $\text{CO} + \text{H}_2 \rightleftharpoons \text{H}_2\text{O} + \text{C}$. This route was found to enhance carbon deposition relative to the Boudouard mechanism, highlighting the complex and kinetically coupled nature of carburization in mixed-gas environments. Collectively, these studies reveal multiple carburization pathways, yet existing comparisons remain fragmented and typically limited to isolated parameters—temperature, CO–H₂ ratio, or CO₂ addition—without systematically exploring their interacting effects across the relevant operating range. Moreover, most laboratory experiments are conducted at high gas flow rates to minimize external mass-transfer resistance, whereas industrial shaft furnaces operate in a counter-current configuration, exposing pellets to gradually changing gas compositions and temperatures. In addition, most existing laboratory studies report only bulk weight changes or total carbon uptake, providing limited resolution of the partitioning between Fe₃C and free carbon and little insight into how these phases evolve alongside metallization. This lack of phase- and morphology-specific information limits the value of existing studies for both process optimization and model validation.

The scarcity of phase- and morphology-resolved characterization further compounds the difficulty of understanding the carburization process. Only a handful of studies have resolved carbon phases and morphology with SEM–EDS, XRD, or microhardness testing. Spatially resolved Fe₃C formation after hydrogen reduction has been demonstrated in recent work (Perrone et al., 2024), while combined TGA, SEM–EDS, XRD, CHNS, and XPS analyses have been used to reveal how trace water vapor suppresses carbon uptake and alters carbide formation (Soodmand et al., 2025). Previous investigations have also suggested that carburization via solid carbon can proceed markedly faster than gas-phase mechanisms, emphasizing the need to capture both gas–solid and solid–solid interactions in realistic models (Higashi et al., 2024). Accurate quantification of carbon phases (Fe₃C and graphite) remains challenging, as conventional approaches based on XRD and TGA mass balance are sensitive to peak overlap, phase heterogeneity, and the low abundance of minor carbon species (Ahmed et al., 2022). Huang et al. (Huang et al., 2012) investigated microhardness during the initial reduction phase (up to 9 min) and reported a sharp decline in peripheral microhardness followed by recovery after 7 min due to the sintering of the newly formed metallic iron, an effect that did not occur in the continuously weakening core and mantle. Boechat et al. (Boechat et al., 2018) extended this analysis to higher reduction degree (up to 30%) and confirmed an initial hardness drop throughout the pellet and a subsequent peripheral strengthening associated with metallic iron formation, confirming the non-uniform mechanical response during progressive reduction. Collectively, these studies highlight the importance of spatially and phase-resolved analysis, yet systematic data linking carburization products to pellet integrity remain scarce.

Consequently, the current understanding of how CO–H₂ ratios, temperature, and major products such as H₂O and CO₂ govern carbon partitioning and final metallization remains incomplete. Another

limitation is the scarcity of systematic investigations involving renewable CO-containing gases (e.g., syngas from biomass pyrolysis or waste gasification) in direct reduction. Comprehensive reviews have emphasized both the opportunities and challenges of integrating biomass into iron and steelmaking, particularly regarding its conversion efficiency, gas composition control, and metallurgical compatibility (Mousa et al., 2016). Biomass-derived syngas has been shown to effectively reduce iron oxide pellets (Guo et al., 2016), and later work by the same authors demonstrated that iron ore–biomass composite pellets reduced with simulated biomass syngas exhibit distinct reduction kinetics and phase evolution compared with conventional CO–H₂ systems (Guo et al., 2017). The influence of direct biomass utilization on the metallurgical performance and formation mechanisms of iron ore pellets has also been investigated, showing that biomass addition significantly modifies pellet microstructure, porosity, and phase evolution during reduction (Sheng et al., 2025). Together, these studies underscore the potential of biomass as both a gaseous and a solid carbon source for defossilized ironmaking, yet experimental insight into how renewable carbon sources affect carburization dynamics, carbon phase formation, and final DRI quality remains limited. Addressing these gaps requires systematic validation and robust modeling under realistic reduction conditions.

From a modeling perspective, traditional approaches such as the shrinking-core model (Salucci et al., 2024) and grain model (Valipour et al., 2006) have been widely applied to direct reduction. The former assumes a sharp reaction front separating unreacted and fully reduced zones, whereas the latter idealizes the pellet as an assembly of uniform grains with fixed or homogenized porosity. These simplifications overlook the gradual and spatially distributed progression of reduction and carburization, where oxygen removal, carbon deposition, and carbide formation occur concurrently within an evolving pore structure. More recent efforts have extended reduction models for shaft furnaces but still treat carburization in a simplified way or omit it altogether, leaving them unable to capture the complexity of carbon-phase formation (Immonen & Powell, 2024). Other detailed shaft-furnace models have made important progress by incorporating gas-phase carbon-deposition reactions and capturing their influence on overall reactor behavior. However, because these approaches do not resolve the spatially heterogeneous distribution of carbon within pellets or its coupling with solid-phase reduction and pore evolution, the underlying carburization mechanisms remain only partially represented (Hamadeh et al., 2018; Marsigny, Letz, et al., 2025). Some newer approaches have begun to address carbon behavior: for example, Soodmand et al. (Soodmand et al., 2025) consider the effect of water vapor on carburization in CO–H₂ mixtures, and the thermodynamics-guided model by Büyüksulu et al. (Büyüksulu et al., 2025) enables cementite/graphite formation when it is thermodynamically permissible. Although these studies represent important progress toward integrating carbon chemistry, they are not yet systematically validated across the broad temperature and gas-composition ranges relevant to direct reduction. These contributions complement earlier porous-solid and kinetic models that explicitly addressed gas transport, distributed porosity, carbon deposition, and Fe₃C formation in DR pellets (Fradet, Ali, & Riedel, Fradet, Ali et al., 2022; Ali et al., 2022). Complementarily, a kinetic mechanism has been proposed that accounts for carbon deposition and Fe₃C formation in various H₂/CO atmospheres (Ali et al., 2022). What remains largely absent in the literature, however, is systematic validation of such models across a wide and industrially relevant range of temperatures and gas compositions. The aim of the present work is therefore not to introduce a fundamentally new model, but to provide a comprehensive experimental validation matrix—linking conversion behavior, carbon evolution, and microstructural changes—to establish a more robust mechanistic basis for reduction–carburization in DR-grade pellets.

The present work addresses this gap through a combined experimental and modeling approach. Isothermal reduction of DR-grade pellets is studied at 973–1273 K at moderate total flow rates (300 mL/min), under various CO–H₂ gas mixtures, including a representative biomass-

derived gas composition. Weight changes are monitored by thermogravimetric analysis, and phase-morphology-property relationships are resolved through SEM–EDS, XRD, LOM, nanoindentation-derived Vickers hardness (via the Oliver–Pharr method), and cementite-selective etching imaged by light optical microscopy. This comprehensive dataset enables the calibration and validation of an advanced one-dimensional porous–solid model that explicitly couples oxygen removal, Fe₃C formation, and carbon deposition under realistic transport regimes. This study thus establishes a predictive framework to optimize carburization while preserving metallization and pellet strength in future H₂–DR–EAF steelmaking.

2. Experimental

2.1. Materials

DR-grade pellets used in this study had a diameter between 12 and 13 mm, and a mass between 4.0 and 4.2 g. The true density was determined using a pycnometer, giving a value of 5.06 g/cm³. The envelope density was measured with a mechanical tapping apparatus with sand particles as the displacement medium. Pellet porosity was then calculated from the ratio of the envelope density to the true density, yielding an average porosity of approximately 29.5%. The chemical composition of the unreduced pellets is summarized in Table 1.

2.2. Preparation of simulated biogenic gas (BG)

The simulated biogenic gas employed in the reduction experiments was derived from the pyrolysis process of biogenic residues. The composition of the gas was determined using a thermodynamic equilibrium calculation approach. This method provides a rigorous framework for modeling and simulating the transformation of biomass constituents during thermochemical conversion processes. The equilibrium state of the system is based on the minimization of the total Gibbs free energy of all possible chemical, leading to the determination of the most thermodynamically stable product distribution under specified conditions. The simulation was using FactSage 8.3 (Bale et al., 2016), a well-established software suite for thermochemical calculations. FactSage was selected for this study owing to its comprehensive and validated thermodynamic databases, as well as its ability to accurately model complex gas–solid–liquid equilibria in multi-component systems.

In this study, green cuttings from landscape maintenance activities were selected due to their regional availability and lower ash content compared to agricultural by-products. The feedstock was characterized for its elemental compositions (C, H, O, N, S, Cl, Al, Ca, K, Mg, Na, P, Si) using standard analytic procedures. The compositions data were used as the inputs of the simulation. To replicate inert conditions characteristic of biomass pyrolysis process, nitrogen flow was introduced as additional input to model the inert condition of biomass pyrolysis process.

The simulation was carried out at a temperature of 973 K and a pressure of 1 atm. The allowed product set included major gas species (H₂, CO, CO₂, CH₄, H₂O, N₂, etc.) and condensed phases, including solid carbon (graphite) representing char, as well as stable Ash phases (oxides and carbonates). Under these conditions, the calculated equilibrium gas phase contains a negligible H₂O fraction. Although H₂O was included as a possible gaseous species, it is thermodynamically consumed via the reaction with solid carbon. The major components of the simulated pyrolysis gas obtained under these conditions are presented in Table 2.

It should be noted that actual biomass-derived syngas compositions may vary depending on feedstock characteristics and process conditions;

Table 1
Chemical composition of the pellets used.

Composition	Fe ₂ O ₃	Fe ₃ O ₄	FeO	Gangue
Content (wt%)	85.9	9.2	0.15	4.75

Table 2
Major pyrolysis gas composition produced from the equilibrium simulation.

Composition	H ₂	CH ₄	N ₂	CO	CO ₂
Content (vol%)	53	3	1	33	10

the present study therefore considers one representative equilibrium-based composition.

2.3. Reduction procedure

Isothermal reduction experiments were carried out in a Linseis PT1600 thermogravimetric analyzer equipped with a vertical reaction tube consisting of a cylindrical main section (inner diameter: 30 mm). The sample chamber was first evacuated to remove air and then purged with nitrogen gas. The furnace was heated at a rate of 30 °C/min under nitrogen flow. Once the desired temperature was achieved, the system was held isothermally for 20 min, to ensure a stable thermal equilibrium of the sample. After the dwelling, the nitrogen gas was switched to a reducing gas mixture of a predetermined composition. All experiments were conducted using a consistent gas mixture flow rate of 300 mL/min. The gas flow rate is a critical parameter in iron ore pellet reduction experiments, as shown for example in Marsigny et al. (Marsigny, Letz, et al., 2025), in that it directly influences the gas composition at the vicinity of the pellets. Given that systematically repeating each experiment at various flow rates would be prohibitive, the most effective approach is to incorporate this external mass transfer limitation directly into the computational model in order to determine the gas compositions, as described in Subsection 2.5. Each reduction run was maintained for 3 h. The 3 h isothermal duration was selected to ensure a consistent end-stage across atmospheres and to capture late-stage microstructural and carbon-transfer processes that can continue after the main mass-loss stage. Selected tests were repeated with a shorter duration of 2 h to check reproducibility. Upon completion of the experiment, the furnace was switched off, and the sample was passively cooled to 150 °C under a continuous flow of nitrogen. Buoyancy effects were corrected using a blank run. Variations in gas composition and reduction temperatures were introduced to study their effects on reduction and carburization. An overview of the reduction experiments is given in Table 3. Specifically, all compositions ranging from pure H₂ to pure CO, with an increment of 25%, were tested at temperatures of 973, 1073, 1173, and 1273 K. Simulated biogenic gas, as described in the previous section, was also tested at these four temperatures. After completion of the reduction, pellets reduced for 3 h were subjected to various characterization analyses, except for the samples reduced in pure H₂ at 1173 K, 50/50 H₂/CO at 1173 K, and 100 BG at 1173 K, for which 2 h-reduced pellets were used.

Table 3
Matrix of reduction experiments carried out and product analyses (T:TGA experiment, S: SEM, E: EDS, X: XRD, H: Hardness test, L: LOM)^a.

Item	973 K	1073 K	1173 K	1273 K
100% H ₂	T	T	T + S + E + H + L + X	T
75% H ₂ /25% CO	T	T	T + X	T
50% H ₂ /50% CO	T + S + E + H + L	T	T + S + E + X	T + S + E
25% H ₂ /75% CO	T	T	T + X	T
100% CO	T + S	T	T + X	T + S + E
Biogenic gas	T	T	T + S + E	T

^a Powder XRD was also performed on solid carbon deposits formed at 973 K under syngas mixtures with H₂/CO ratios of 75/25, 50/50, and 25/75.

2.4. Post-reduction analyses

2.4.1. Sample preparation

Each reduced pellet was sectioned into halves using a low-speed diamond saw, with the rotating blade partially immersed in a diluted Cool 3 (Buehler) coolant bath to reduce frictional heating and minimize microstructural damage. As Cool 3 contains organic components, a minor carbon residue from the cutting process cannot be fully excluded. For hardness testing and light optical microscopy (LOM) only, cross-sectional pellets were hot mounted in epoxy resin, ground using progressively finer grinding disks, and polished with diamond suspension. For each pellet, three representative positions: surface, mid-radius, and core, were selected across the cross-section (Fig. 1) to capture radial variations in microstructure and hardness.

2.4.2. SEM-EDS

Scanning Electron Microscopy coupled with Energy-Dispersive X-ray Spectroscopy (SEM-EDS) was utilized to examine the surface morphology and elemental composition of the samples. A thin platinum coating (5 nm) was applied via sputtering, a vacuum process in which high-energy argon ions dislodge Pt atoms from a target, depositing them evenly on the sample surface to improve conductivity and imaging quality. SEM imaging was performed using a JSM-6510 (JEOL) operating at an accelerating voltage of 20 kV with a working distance of 11 mm in secondary electron mode. Elemental composition was determined using an integrated EDS detector (EDAX AMETEK Element) operated at 20 kV with a live time of 100 s. Semi-quantitative results were corrected using the ZAF method to account for atomic number (Z), absorption (A), and fluorescence (F) effects, with minimum detection limits (MDL) and associated error percentages were reported by the analysis software.

2.4.3. XRD

Phase composition of the reduced pellets and carbonaceous deposits was analyzed by X-ray diffraction (XRD). Powder XRD of the carbonaceous deposits was performed using a Bruker D8 Advance diffractometer with Co K α radiation ($\lambda = 1.78897 \text{ \AA}$) operated at 35 kV and 40 mA. Loose carbon deposits remaining after the 973 K syngas TGA tests were collected for XRD analysis. Diffraction patterns were collected over a 2θ range of 10–75°, with a step size of 0.017° and a counting time of 2 s per step.

For solid XRD, one half of each reduced pellet was ground to obtain a flat base, ensuring parallel alignment of the cross-sectional surface with the diffractometer stage. Measurements were carried out on a Bruker D8 Discover II diffractometer equipped with Co K α source ($\lambda = 1.78897 \text{ \AA}$) operated at 40 kV and 0.5 mA (I μ S tube). Data were acquired over a 2θ range of 20–105°, with a step size of 0.01°, using a VANTEC-500 area detector (three frames per measurement, 1 h 23 min per frame). Phase identification was performed by matching the diffraction peaks with reference data from the ICDD PDF-5 (Powder Diffraction File) database, version 2025.

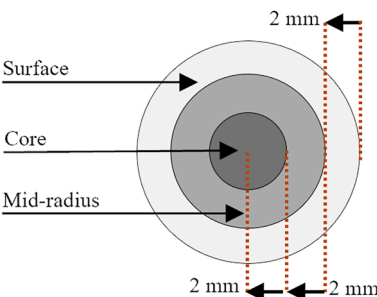


Fig. 1. Division of surface, mid-radius and core in a pellet.

2.4.4. Nanoindentation hardness testing

Hardness measurements were conducted on the polished cross-section of the reduced pellets using an Anton Paar NHT3 nanoindenter equipped with a Berkovich diamond indenter. Indentations were performed in depth-controlled mode to a maximum penetration depth of 300 nm, with a 10 s hold at the maximum depth. Measurements were taken at three positions across the cross-section: approximately 600 μm below the pellet surface, at half of the pellet radius, and at the pellet center, to evaluate the hardness variation from the outer region toward the core. The near-surface position was chosen below the pellet surface to minimize edge and polishing artefacts while still representing the subsurface region. Indentation locations were selected on visually intact metallic regions to avoid pores and obvious defects, and a minimum of 12 indents were measured at each position. The instrumented Vickers hardness (HV_{IT}) values were automatically calculated by the instrument software from the load-displacement data according to the Oliver-Pharr method.

2.4.5. Light optical microscopy (LOM)

Microstructural observations were performed on polished and etched cross-sections of the pellets to reveal the cementite distribution. The polished surfaces were pre-etched with nital (3 vol% HNO_3 in ethanol) for 1 min, then rinsed with ethanol and dried. Subsequently, the samples were etched with picral (4 vol% picric acid in ethanol) for 3 min to selectively reveal the cementite phase. After etching, the surfaces were immediately rinsed with ethanol and dried. Optical micrographs were captured using a Neophot 32 (Carl Zeiss Jena) equipped with a digital camera. Imaging conditions were adjusted to obtain optimal contrast between the iron matrix and cementite phase.

2.5. Kinetic modelling approach

We model single-pellet DR-carburization using a one dimensional porous–solid model developed in an earlier work (Fradet et al., 2022). The model represents the pellet as a porous continuum where gas diffusion, porosity evolution, and solid-state reactions are locally coupled, avoiding the sharp-interface assumptions of classical models. In this study, it is applied as a reaction–transport framework and calibrated against the experimental data to capture the interplay between reduction, carburization, and phase evolution.

2.5.1. Governing equations

The local conservation equations for gas and solid species in the porous–solid pellet allow direct coupling of chemical source terms with evolving porosity and diffusivity, thereby capturing the interplay between reduction and carburization in a transport-limited pellet. The governing equations are as follows:

For gaseous species i :

$$\frac{\partial \epsilon C_i}{\partial t} = -\nabla \cdot (-D_i^{\text{eff}} \nabla C_i) + \dot{s}_i, i \in \text{gas species}, \quad (1)$$

and for solid species j :

$$\frac{\partial (1 - \epsilon) \rho_j X_j}{\partial t} = M_j \dot{s}_j, j \in \text{solid species}. \quad (2)$$

Porosity evolution follows directly from the volumetric balance of solids:

$$\frac{\partial \epsilon}{\partial t} = -\sum_j \frac{M_j}{\rho_j} \dot{s}_j, j \in \text{solid species}. \quad (3)$$

In these equations, the symbols refer to the following terms:

- ϵ – local porosity (–), varying with time and radius as solid phase evolve
- C_i – molar concentration ($\text{mol} \cdot \text{m}^{-3}$) of gas species i

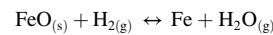
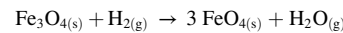
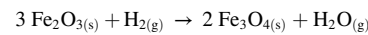
- X_j – mole fraction (–) of solid species j
- D_i^{eff} – effective diffusivity ($\text{m}^2 \cdot \text{s}^{-1}$) of gas species i
- $\rho_{i/j}$ – local density ($\text{kg} \cdot \text{m}^{-3}$) of species i or j
- $\dot{s}_{i/j}$ – net chemical production rate ($\text{mol} \cdot \text{m}^{-3} \cdot \text{s}^{-1}$) of the species i or j due to surface reactions.
- M_j – Molecular weight ($\text{kg} \cdot \text{mol}^{-1}$) of the solid species j

Further details on the expressions and their closure as well as the boundary and initial conditions used in the simulations are provided in [Section S2.5 of the Supplementary Materials](#).

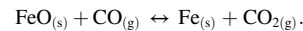
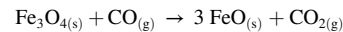
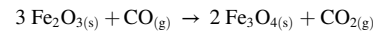
2.5.2. Reaction set and kinetics

The chemical source term is governed by a reaction mechanism that captures the coupled reduction and carburization pathways relevant under various gas mixtures. The reactions are grouped into five categories:

(1) hydrogen-based reduction

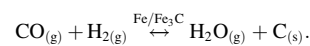
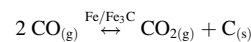
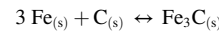


(2) CO-based reduction



Only the FeO–Fe step is treated as reversible because at the relevant temperatures (973–1273 K) and $\text{H}_2/\text{H}_2\text{O}$ or CO/CO_2 ratios, only FeO and Fe can be stable species over the course of reduction. By contrast, the $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4$ and $\text{Fe}_3\text{O}_4 \rightarrow \text{FeO}$ transitions remain far from equilibrium under these conditions. This is clearly illustrated in the classical Chaudron or Baur–Glässner equilibrium diagrams (Ali et al., 2022).

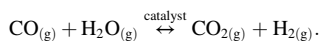
(3) Carburization and carbon deposition



Both metallic iron (Fe) and cementite (Fe_3C) catalyze the Boudouard reaction ($2 \text{CO}_{(g)} \leftrightarrow \text{CO}_{2(g)} + \text{C}_{(s)}$) and the hydrogen-assisted CO reduction ($\text{CO}_{(g)} + \text{H}_{2(g)} \leftrightarrow \text{H}_2\text{O}_{(g)} + \text{C}_{(s)}$). Early kinetic studies (Olsson & Turkdogan, 1974; Xu & Brown, 1989) established that Fe surfaces strongly promote carbon nucleation, while later investigations demonstrated that the $\text{Fe} \leftrightarrow \text{Fe}_3\text{C}$ transformation modifies catalytic activity and selectivity during continuous carbon deposition and filamentous growth (Bonnet et al., 2003; Grabke, 1995; Zhang et al., 2008). Under CO-rich/ H_2 -containing direct reduction atmospheres, Fe evolves to Fe_3C , and both phases can coexist; treating Fe and Fe_3C as parallel catalytic sites therefore reflects this simultaneous presence and dynamic switching of active phases (Kirchner et al., 2020). Including Fe and Fe_3C as parallel catalytic sites in the modeling reflects this evolution of the surface under DR-carburization conditions.

(4) Water–gas shift reaction

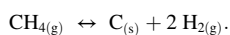
The water–gas shift (WGS) reaction was included as a surface-mediated step:



This reaction is treated as an instantaneous equilibrium to maintain thermodynamic consistency of the H_2/CO ratio. The inclusion of WGS is justified by its well-documented occurrence on iron catalysts (Grabke, 1995; Grabke et al., 1993; Zhang et al., 2008), both in industrial and laboratory contexts, where it plays a key role in adjusting the CO/H_2 ratio and influencing carburization equilibria.

(5) Methane cracking reaction

Methane decomposition and its reverse hydrogenation were implemented to capture the dynamic interplay between surface carbon and gas-phase CH_4 :



All reactions are treated as global steps, with source terms written as first-order expressions with regards to the gaseous reactant concentration and the solid-phase mole fraction. For example, for the global reduction of hematite by hydrogen, $3 \text{Fe}_2\text{O}_{3(\text{s})} + \text{H}_{2(\text{g})} \rightarrow 2 \text{Fe}_3\text{O}_4_{(\text{s})} + \text{H}_2\text{O}_{(\text{g})}$,

The source term $\dot{s}$ is formulated as:

$$\dot{s} = k C_{\text{H}_2} X_{\text{Fe}_2\text{O}_3}, \quad (4)$$

where C_{H_2} is the local hydrogen concentration, $X_{\text{Fe}_2\text{O}_3}$ is the mole fraction of hematite, and k is the rate constant. The rate constants were defined according to the Arrhenius law, with activation energies initialized from literature values (Ali et al., 2022). The corresponding pre-exponential factors were determined by calibration against the experimental TGA data of this work. For reactions considered reversible, both forward and backward rates are computed in this global form, and the net rate is obtained as their difference. The water–gas shift reaction is treated separately as an instantaneous equilibrium to ensure thermodynamic consistency of the gas composition. The calibrated kinetic parameters are valid within the experimental temperature window investigated (973–1273 K) and for the specific iron ore pellets utilized in this study.

2.5.3. Calibration and validation

The main evaluation criterion for model validation is the global conversion degree F , given by:

$$F = \frac{m_0 - m(t)}{m_0 - m_\infty}. \quad (5)$$

Here, m_0 represents the initial mass of the pellet, $m(t)$ is the mass at a given time t , and m_∞ corresponds to the theoretical mass after complete reduction in the absence of carburization. The value of F ranges from 0, corresponding to the initial state of the iron oxides, to 1, corresponding to the complete reduction of iron oxides according to Table 1 into metallic iron. Gangue phases remain inert throughout the process and are not included in the conversion definition. Because thermogravimetric analysis records the total mass evolution of the sample, the measured signal reflects both oxygen removal through reduction and mass uptake due to carburization. As a result, the experimentally determined conversion degree reflects the net mass balance rather than pure metallization. A pellet may therefore reach full reduction while still exhibiting an F value below unity if simultaneous carbon deposition increases its mass.

In addition to matching the global reduction curves, the model outcomes were directly compared with phase-resolved and morphology-

resolved experimental data, including spatial phase profiles from XRD, carbon and oxygen distributions from SEM-EDS, and microstructural features observed by light optical microscopy. These product analyses are not used in parameter fitting; instead, they provide an independent validation layer, ensuring that the model qualitatively reproduces the observed evolution of iron, wüstite, Fe_3C , and carbon-rich regions.

3. Results

3.1. Thermogravimetric analysis

Fig. 2 shows the mass change of single pellets reduced in H_2 , H_2/CO mixtures, CO , and simulated biogas at four temperatures (973–1273 K). The pellets in all atmospheres initially exhibit a continuous mass loss up to a certain reaction time, after which the curves either level off to a plateau or show a subsequent mass gain, depending on the gas composition and temperature. While most oxygen removal occurs during the earlier stage, the remaining isothermal exposure can still influence the end-state though continued microstructure sintering and in H_2 – CO -containing atmospheres, time-dependent carbon transfer (carburization and carbon deposition); therefore, the characterized products reflect the specified holding time (3 h, and 2 h for the stated 1173 K cases). At lower temperatures (973 and 1073 K), the mass loss is slower and CO -containing gases displays a minimum point followed by a strong mass gain. At higher temperatures (1173 and 1273 K), the mass loss is more pronounced, close to 30%, i.e. the theoretical mass after complete reduction. In H_2 , the curves reach a constant mass within a short reaction time, while syngas cases display a slow, almost linear, mass uptake. For simulated biogas, while the rate of mass loss of the earlier stage is close to the 25/75% H_2/CO , no subsequent mass uptake is noticeable except for 973 K and the final mass change is systematically higher than syngas cases. The underlying TGA mass-change data used to generate Fig. 2 are provided in the Supplementary csv file.

The visual appearance of the reduced pellets varies with gas composition and temperature, as displayed in Fig. 3. For all H_2 , syngas, and CO atmospheres, the reduction time was 3 h. Pellets reduced in pure hydrogen at 973 K appeared smooth and intact with no visible surface cracking. Surface cracks developed particularly at higher temperatures, but the pellets retained their structural integrity. With increasing CO fraction, dark surface deposits became more pronounced, particularly at 973–1073 K. Increasing the temperature progressively diminished these deposits, and at 1273 K only minor traces were visible. Pellets reduced in pure CO showed no distinct surface layers, apart from a thin, dust-like film covering parts of the surface. For simulated biogenic gas, the pellet reduced at 973 K for 3 h was covered by a dark surface deposit. At 1073–1273 K (2 h), no surface deposits were observed, and the pellets exhibited more pronounced cracking.

3.2. Microstructure (SEM-EDS)

Fig. 4 shows the cross-sectional SEM microstructures of the pellets under the selected reduction conditions. The unreduced pellet (Fig. 4(a)) displays a porous matrix composed of loosely packed grains, consistent with previous observations by Hessling et al. (Hessling et al., 2024) and Prasad et al. (Prasad et al., 2022). Rounded and irregular pores of varying sizes form a continuous open network from the surface to the core, typical of a partially sintered indurated pellet.

After reduction in pure H_2 at 1173 K (Fig. 4(b)), the pellet exhibits a comparatively compact and well-consolidated microstructure throughout the pellet cross-section. The matrix appears relatively uniform, with reduced connectivity, only a few isolated micropores, and no distinct morphological gradient evident from surface to core at the scale of observation. Narrow cracks are visible in the core, consistent with localized stress induced by internal gas pressure, volume contraction during oxygen removal, and phase transformation effects, in agreement with the mechanisms described by Kim et al. (Kim et al., 2021).

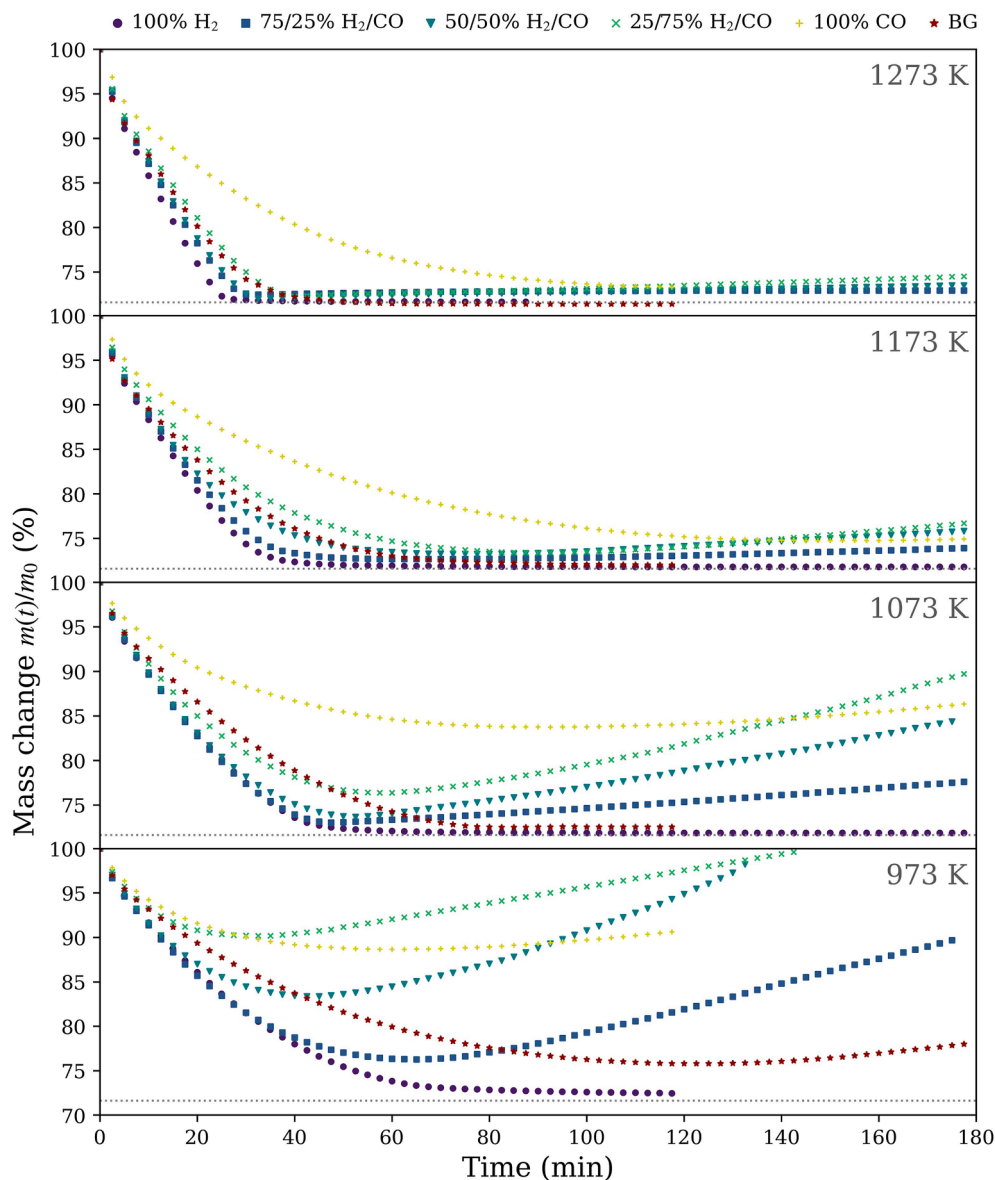


Fig. 2. Mass change of single DR-grade iron oxide pellets during isothermal reduction in H_2 , H_2/CO mixtures (75/25, 50/50, 25/75), pure CO, and simulated biogenic gas at four temperatures (973, 1073, 1173, and 1273 K). The dotted gray lines at 71.6% represent ideal reduction, meaning the complete oxygen removal from the iron oxides according to the composition shown in Table 1, without any carbon uptake or gangue conversion.

However, these cracks cannot be attributed solely to the reduction process, since pre-existing internal pellet heterogeneities and residual sponge-iron porosity may enhance crack visibility during sectioning. The cross-section was examined in the as-cut condition (without grinding and polishing), and parallel saw marks from sectioning are evident on the surface, indicating increased ductility of the metallic iron matrix. Unlike the brittle oxide precursor, the metallic phase deformed slightly under the cutting blade rather than fracturing, leaving visible streaks on the surface. This behavior reflects the transition from brittle to ductile behavior response commonly reported for high-purity hydrogen-reduced pellets (Mendoza et al., 2025) and is consistent with the smoother surface features associated with the formation of more ductile metallic constituents (Meyers & Tantevee, 1986).

In the 50/50 H_2/CO -reduced pellets at higher temperatures (1173–1273 K), the cross-sections (Fig. 4(c and d)) show a uniformly granular matrix throughout the pellet. The surface and core appear similarly coarse, composed of irregular particle clusters separated by open voids, and no pronounced morphological gradient is evident from the surface to the core at the scale of observation. No visible sectioning

streaks are observed on the as-cut surface, reflecting the harder, less ductile nature of the carburized metallic phase. No comparable core cracks are observed, consistent with the more open and granular microstructure that reduces internal stress concentration and mitigates the mechanical effects of shell core mismatch, although spatially heterogeneous cracking elsewhere in the pellet cannot be excluded.

At 973 K (Fig. 4(e)), the 50/50 H_2/CO -reduced pellet exhibits a heterogeneous microstructure. The surface is rough and granular, with numerous pores of varying sizes. In the mid-radius, smoother streaked areas alternate with isolated granular zones, indicating uneven reduction and partial metallic coalescence. Toward the core, the matrix becomes relatively smoother and more compact than the outer regions, although small voids, fragmented clusters, and cracks persist. Faint parallel sectioning marks are visible on the as-cut surface, less pronounced than those observed in the H_2 -reduced pellet.

The pellet reduced in simulated biogenic gas at 1173 K (Fig. 4(f)) exhibits a coarse and porous morphology composed of irregular metallic clusters separated by interconnected voids. The surface contains partially coalesced particles forming a semi-sintered layer, reflecting

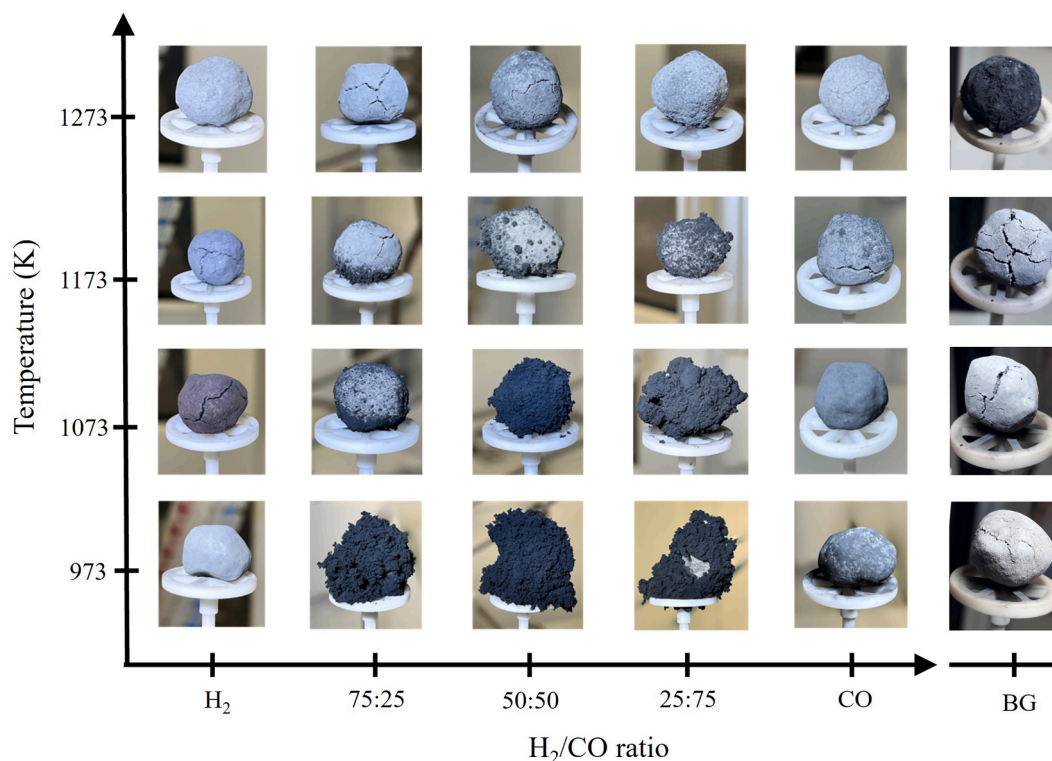


Fig. 3. Photographs of reduced pellets after isothermal reduction–carburization under various H_2/CO atmospheres at 973–1273 K. Rows correspond to temperatures (top to bottom: 1273, 1173, 1073, 973 K) and columns to gas atmospheres (left to right: 100% H_2 , 75:25 H_2/CO , 50:50 H_2/CO , 25:75 H_2/CO , 100% CO, and BG). The images illustrate the temperature- and gas-dependent evolution of pellet morphology.

more advanced reduction near gas–solid interface. The mid-radius appears more granular, consisting of loosely packed particles and elongated voids that maintain gas-transport pathways. Toward the core, the matrix becomes smoother and more consolidated, with fewer open pores and faint linear streaks from sectioning, suggesting enhanced interparticle bonding within the metallic matrix, and no distinct core cracks are observed in the examined section. Overall, the H_2 -reduced pellet exhibits the greatest degree of consolidation, the high temperature 50/50 H_2/CO -reduced pellets remain comparatively coarse and porous, and the simulated biogenic gas-reduced pellet shows an intermediate level of consolidation with residual porosity.

Fig. 5 presents the SEM-EDS elemental maps of the unreduced pellet and for representative reduction conditions illustrating the effects of temperature and gas atmosphere. In the unreduced pellet (Fig. 5(a)), Fe (dark red) and O (cyan) are uniformly distributed across the surface, mid-radius and core. Minor gangue elements (Si, Al, Ca, Mg, and Ti) occur as discrete, sparsely distributed spots without evident segregation. Al is slightly less frequent at the surface, with no clear localization trend for the other gangue elements. Overall, this distribution is characteristic of an indurated pellet, where gangue minerals are homogeneously incorporated within the iron oxide matrix.

In the H_2 -reduced pellet (Fig. 5(b)), a marked decrease in O signal is observed across all three regions, with Fe remaining predominant. Minor C (yellow) is detected, as the cross-sections were examined in the as-cut condition, some contribution from the cutting coolant cannot be fully excluded. The decrease in oxygen indicates extensive reduction to metallic iron, consistent with the high reducibility of iron oxides in hydrogen atmospheres.

For the 50/50 H_2/CO -reduced pellet at 1273 K (Fig. 5(c)), Fe remains dominant across the cross-section, and oxygen is detected only at trace levels, indicating near-complete oxide reduction. Carbon appears as coarser, consolidated agglomerates, indicating increased carbon mobility and coalescence at elevated temperature and stronger interaction with the metallic iron surface. At 1173 K (Fig. 5(d)), oxygen

signals remain very low, consistent with an advanced reduction state. Carbon is present as fine, uniformly dispersed particulates across all regions, and Ca occurs mainly as very fine particulates overlying the granular Fe matrix, with only a few coarser features. At 973 K (Fig. 5(e)), oxygen is more clearly detected, forming irregular patches of varying size and intensity that indicate incomplete oxide reduction at this lower temperature. Carbon distributes across the cross-section, accumulating as larger irregular deposits at the surface and as finer particulates or patch-like features toward the mid-radius and core. Overall, the progression from 973 to 1273 K shows a clear decrease in residual oxygen content and a shift from surface-localized carbon deposition at low temperature to increased carbon mobility and coalescence within the metallic phase at higher temperature, consistent with the behavior reported by Iguchi and Endo (2004). The simulated biogenic gas-reduced pellet at 1173 K (Fig. 5(f)) exhibits a nearly carbon-free matrix, with only trace signals that may partly arise from surface contamination during sectioning. The lack of carbon reflects the low carburizing potential of the simulated biogenic gas, which results from its high H_2/CO ratio and the CO_2 present, both of which suppress carbon deposition. Although a moderate CO_2 content in the gas mixture can stabilize cementite by retarding its decomposition into iron and free carbon, excessive CO_2 levels (>7–8%) have been reported to markedly decrease the rate of cementite formation (Kumar, Ahmed, et al., 2022).

Fig. 6 shows higher-magnification SEM images of the CO-reduced surface. The surface morphologies reflect the end-state after the specified isothermal hold (3 h). At 973 K, the surface is covered by a dense, finely grained metallic iron layer intermixed with carbon derived from CO dissociation, giving the pellet a compact but weakly sintered morphology (Fig. 6(a)). This fine carbon-bearing film partially blocks pore opening and reduces surface permeability, thereby restricting the penetration of the reactive gas into the underlying oxide. Consequently, reduction proceeds primarily at the surface, while the interior remains partially unreduced, consistent with the lower normalized mass loss measured at this temperature.

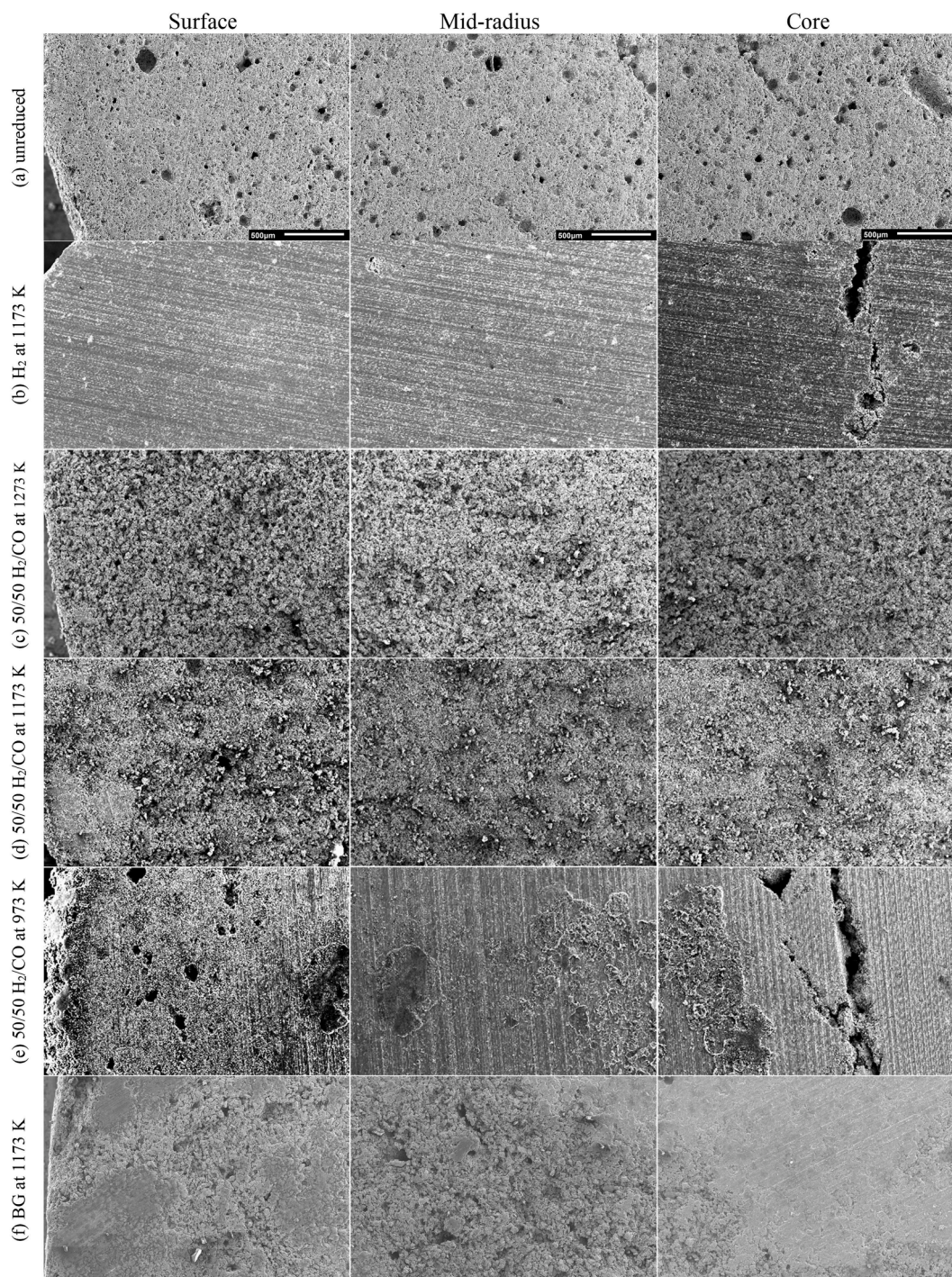


Fig. 4. Cross-sectional SEM micrographs of the unreduced at reduced pellets under different gas atmospheres and temperatures: (a) unreduced, (b) 100 H₂ at 1173 K, (c) 50/50 H₂/CO at 1273 K, (d) 50/50 H₂/CO at 1173 K, (e) 50/50 H₂/CO at 973 K, (f) 100 BG at 1173 K. Each row represents one reduction condition, with the surface, mid-radius, and core regions shown from left to right.

At 1273 K, the surface morphology in Fig. 6(b) becomes considerably coarser, with larger, rounded iron grains formed by coalescence and surface diffusion. The broader pore openings and smoother grain contours indicate enhanced grain coarsening and early-stage sintering under high-temperature CO reduction, while the structure remains characteristically porous (El-Geassy et al., 1996). Despite the coarsening, small patches of carbon film remain on the surface. The appearance of elongated iron whiskers (Fig. 6(c)) is characteristic of pure CO reduction at elevated temperatures (1173–1273 K) (Yi et al., 2015), where the exothermic FeO + CO reaction and the increased vacancy

mobility enable directional diffusion of Fe atoms toward the localized nucleation sites. These whiskers often span across pore cavities, forming bridges that can obstruct gas pathways and promote abnormal swelling (Purohit et al., 2025). In the present work, swelling was not quantified (no in-situ measurement), and no pronounced macroscopic distortion was observed by visual inspection. The Si detected on the whisker surface (Table 4) suggest local enrichment from gangue-derived phases. Previous studies report that Si segregation can modify whisker-tip energetics and promote thicker or more irregular whisker morphologies, particularly in Si-rich, low CaO systems (Lei et al., 2023; Wang & Sohn,

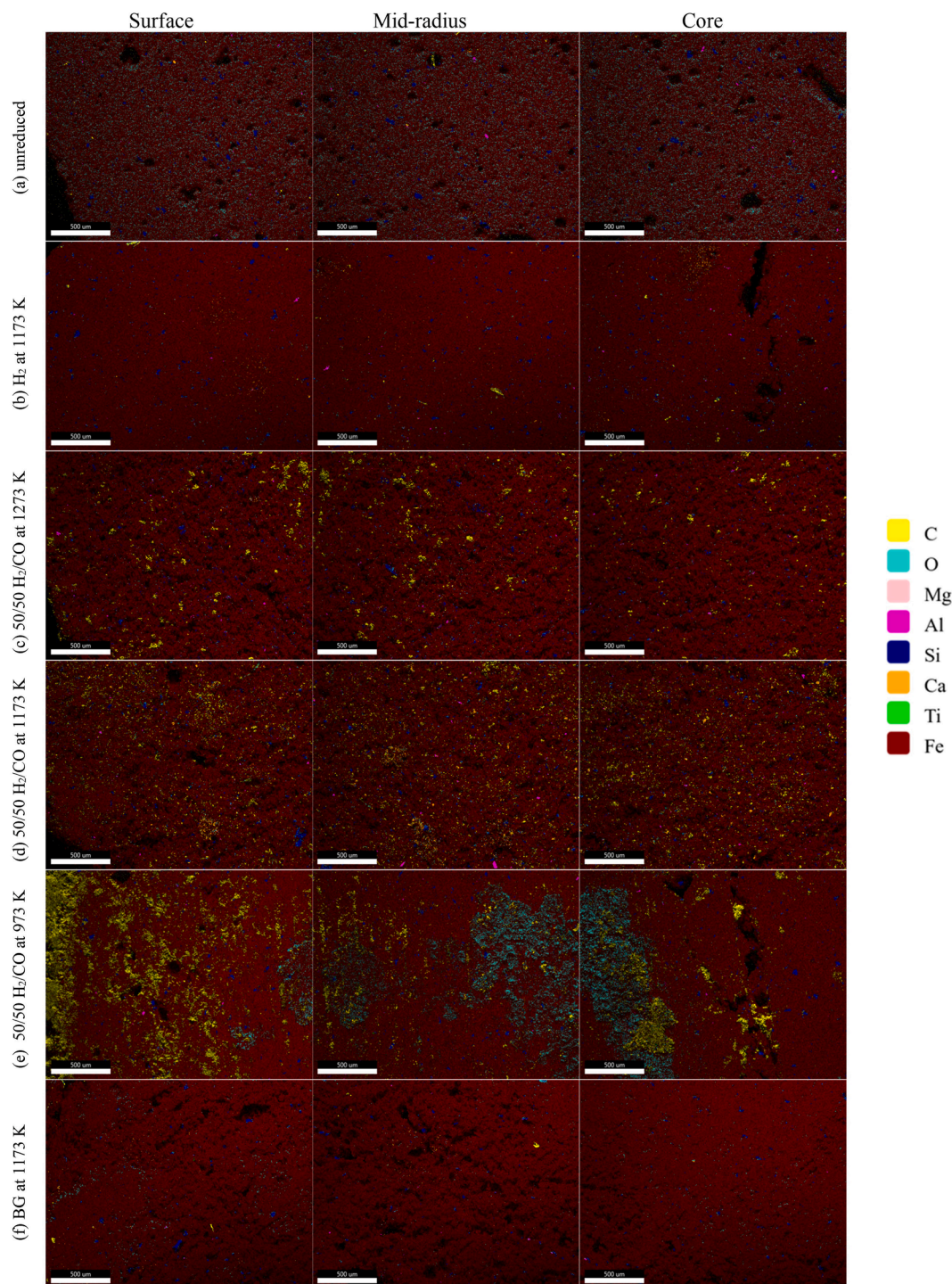


Fig. 5. SEM-EDS elemental maps of the unreduced pellet and samples reduced under various gas atmospheres and temperatures: (a) unreduced, (b) 100 H₂ at 1173 K, (c) 50/50 H₂/CO at 1273 K, (d) 50/50 H₂/CO at 1173 K, (e) 50/50 H₂/CO at 973 K, (f) 100 BG at 1173 K. For each condition, maps from the surface, mid-radius, and core (left to right) illustrate radial changes in elemental distribution.

2011). In the present work, the observed whisker remains relatively slender, but the Si enrichment indicates that similar mechanisms may be active.

3.3. Phase analysis (XRD)

The XRD patterns of reduced pellets and of carbonaceous deposits are shown in Fig. 7, while the references can be appreciated in the Supplementary Fig. S1. For each of the tested pellets, three

measurements were taken: the core, the mid area, and the surface. Fig. 7 (a) reveals a consistent reduction across the pellet reduced in the hydrogen environment at 1173 K. As the pellet is predominantly composed of iron, with three distinct peaks, it facilitates the identification of the residual gangue material, SiO₂ and CaO, notably. Traces of magnetite resulting from partial re-oxidation can be observed, but wüstite is not detectable from this analysis. Fig. 7(b–e) systematically show major differences between the surface measurement and the latter two, i.e. the mid area and the core. Besides the traces of magnetite also

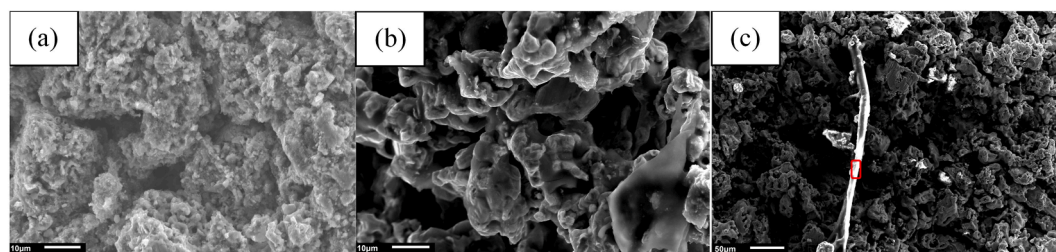


Fig. 6. Highly magnified SEM images of the pellet surface after pure CO reduction: (a) finely grained and compact surface 973 K; (b) coarser, rounded iron grains with wider pore openings at 1273 K; (c) elongated Fe whisker at 1273 K.

Table 4

Chemical composition from EDS spot analysis performed directly on the Fe whisker, taken at the location marked by the red rectangle in Fig. 6(c).

Elements	Fe	O	C	Si	Al	Ca	Mg
Weight (%)	22.4	41.6	11.3	23	0.6	0.7	0.5

present in the CO-containing conditions, wüstite is clearly identified in significant amounts for the pure CO case with peaks at 49.5° in the core and mid area. On the surface for the same case, or for the syngas cases, high amount of wüstite is unlikely because the peak at 49.5° corresponds to SiO_2 and the one at 72.5° is associated with cementite. All pellets reduced with CO-containing gases contain cementite (or the mineral cohenite), but in varying amounts. Fe_3C content increases with the CO proportion up to 75%, and then decreases for pure CO. In all cases, the conversion to cementite is much more advanced on the surface than in the mid area or in the core. A large amount of carbon is identified on the surface of the syngas cases, with a peak at 31° . In the core and mid area, there may be some carbon, but its peak overlaps with that of SiO_2 and cementite, making a quantification challenging. It is not possible to identify from the XRD analysis the type of carbon because of the simultaneous presence of too many species. Comparing CO with the syngas cases, the carbon content on the surface is much smaller.

3.4. Etched microstructure (LOM): cementite (Fe_3C) revelation

Fig. 8 shows the optical micrograph of H_2 - and 50/50 H_2/CO -reduced pellets before and after etching. Before etching (Fig. 8(a) and (c)), both polished cross-sections appear uniformly bright under reflected light, with visible polishing marks and isolated dark pores corresponding to residual voids. Fig. 8(b) exhibits a uniform dark tone without radial contrast, indicating a homogeneous metallic ferrite ($\alpha\text{-Fe}$) matrix (Kumar, Ahmed, et al., 2022). In contrast, the 50/50 H_2/CO -reduced pellet (Fig. 8(d)) reveals a distinct optical gradient within the surface region (~ 2 mm from the edge). The edge layer appears bright but slightly less intense than the adjacent cementite-enriched band, which is distinctly brighter, followed by a darker inner ferritic zone with dispersed bright Fe_3C clusters located toward the inner boundary of this ~ 2 mm region, closer to the mid-radius. This sequence reflects progressive carbon diffusion and phase transformation during reduction: the bright cementite-enriched band corresponds to cementite (Fe_3C) formed by carbon diffusion into metallic iron, the slightly dimmer edge layer suggests the onset of cementite decomposition, and the darker inner zone with bright inclusions represents a ferritic matrix containing discrete cementite particles. The observed contrast aligns with the topochemical mechanism described by Kumar et al. (Kumar, Alatalo, et al., 2022), where prolonged exposure at $650\text{--}700^\circ\text{C}$ promotes the breakdown of Fe_3C from the edge inward, producing ferrite and graphitic carbon through sequential transformation $\text{Fe}_3\text{C} \rightarrow \text{Fe(C)} \rightarrow \alpha\text{-Fe} + \text{C}$. The dispersed bright clusters likely represent Fe_3C formed at favorable nucleation sites during inward carbon diffusion, reflecting the heterogeneous nucleation and growth nature of carburization in the metallic matrix.

3.5. Hardness profile

As shown in Fig. 9, the hardness varies distinctly across the pellet radius for both reduction conditions. The reported values represent local microhardness measured on polished cross-sections at defined radial positions. For clarity, the data point referred to as “near-surface” corresponds to an indentation location approximately $600\text{ }\mu\text{m}$ below the external pellet surface (see Methods). The outermost $<600\text{ }\mu\text{m}$ layer was therefore not probed, and any hardness variations within this region are not captured by the present measurements. For the pellet reduced in pure H_2 at 1173 K , the hardness decreases from the near-surface region ($\sim 351\text{ HV}$) to the mid-radius ($\sim 286\text{ HV}$) and remains similar at the core ($\sim 293\text{ HV}$). The higher hardness in the near-surface region ($\sim 600\text{ }\mu\text{m}$) is consistent with a more advanced reduction state and stronger consolidation in the outer pellet region under high temperature conditions. In contrast, the comparable hardness at mid-radius and core indicates a largely uniform mechanical response once reduction is essentially complete.

For the pellet reduced in 50/50 H_2/CO at 973 K , the hardness increases from a relatively softer near-surface region ($\sim 228\text{ HV}$) to a pronounced maximum at the mid-radius ($\sim 354\text{ HV}$) and remains at a similar level toward the core ($\sim 335\text{ HV}$). Considering the modest difference between mid-radius and core, the main feature is the lower near-surface hardness relative to the interior. The elevated interior hardness is consistent with a higher fraction of hard phases, most notably cementite (Fe_3C) and residual oxides. The lower near-surface hardness may reflect a combination of limited consolidation and local decarburization of Fe_3C in the outer pellet region during prolonged gas exposure, together with free-carbon deposition that does not translate into higher load-bearing hardness.

Overall, these results demonstrate that hardness in direct-reduction pellets is governed by the coupled effects of consolidation and phase constitution. High-temperature hydrogen reduction yields a largely uniform interior response with slightly higher hardness in the outer region, while low-temperature H_2/CO produces a pronounced radial gradient characterized by a softer near-surface region and a comparably high hardness across the interior (mid-radius to core), indicating spatially heterogeneous reaction and phase evolution.

3.6. Modelling results

The kinetic model was validated against the experimentally measured conversion curves $F(t)$ for single DR-grade pellets reduced under the gas atmospheres and temperatures described in Subsection 2.2 & 2.3. Across the full range of conditions, the model reproduces the characteristic ranking of gas reactivity— $\text{H}_2 > \text{H}_2/\text{CO} > \text{CO}$ —and captures the progressive shift in controlling mechanisms with temperature and gas compositions. The simulations match both the rapid hydrogen-driven initial reduction and the slower approach to equilibrium observed in CO-containing atmospheres, as well as the mixed reduction–carburization behavior characteristic of syngas. For the simulated biogenic gas mixture, the model correctly predicts the high final degree of reduction achieved at elevated temperature and the moderated

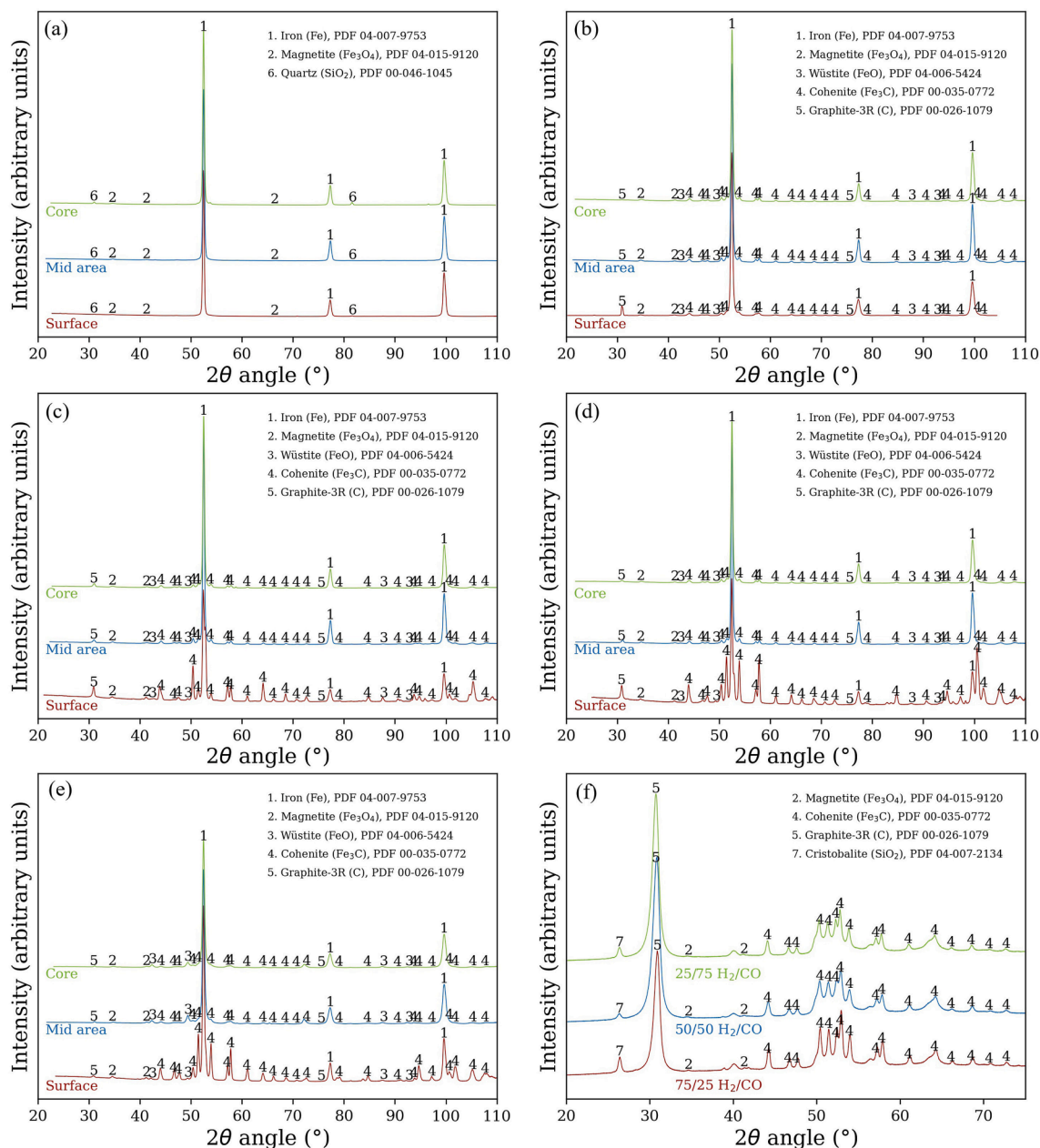


Fig. 7. XRD patterns of the reduced pellets at 1173 K under (a) H_2 (b) 75/25 H_2/CO , (c) 50/50 H_2/CO , (d) 25/75 H_2/CO , and (e) CO. Panel (f) shows the XRD pattern of the solid carbon deposits collected from syngas reduction at 973 K.

carburization arising from the CO_2 -buffered carbon activity. These trends demonstrate that the model consistently reflects the coupled effects of intrinsic kinetics, gas transport, and carbon chemistry that govern the experiments. The all-encompassing validation of the 24 tested conditions is provided in the [Supplementary Figs. S2 and S3](#), where comparisons between experimental and simulated data are presented. The overall conclusion is that the model is thoroughly validated and predictive across the examined temperature and gas-composition range. In all cases, the agreement is satisfactory and the model captures the defining kinetic features of each gas atmosphere, supporting its use as a mechanistic framework for interpreting the reduction and carburization pathways discussed in [Section 4](#). Minor deviations can be observed at very high metallization levels, particularly in the plateau region under certain conditions. In this regime, the reaction rate decreases and the conversion becomes more sensitive to late-stage structural evolution (e.g., local densification, sintering, pore restructuring)

and to small net mass-balance effects under simultaneous reduction and carburization. While these effects are not explicitly resolved in the present formulation, they do not indicate a systematic loss of model validity. The dominant trends and controlling mechanisms remain well captured across the validated range. A limitation of the present approach is that the parameter set inevitably contains apparent kinetic coefficients that incorporate unresolved microstructural effects, leading to a degree of overfitting. Nonetheless, achieving consistent agreement across the full matrix of temperatures and gas compositions represents a meaningful step toward a kinetic description robust enough for future implementation in shaft-furnace simulations. While the present study uses product characterization (XRD, SEM, SEM-EDS) only for qualitative consistency checks, future work will extend model validation to quantitative phase-fraction data following recent developments by Büyüksü et al. ([Büyüksü et al., 2025](#)), thereby strengthening the predictive capability of the model.

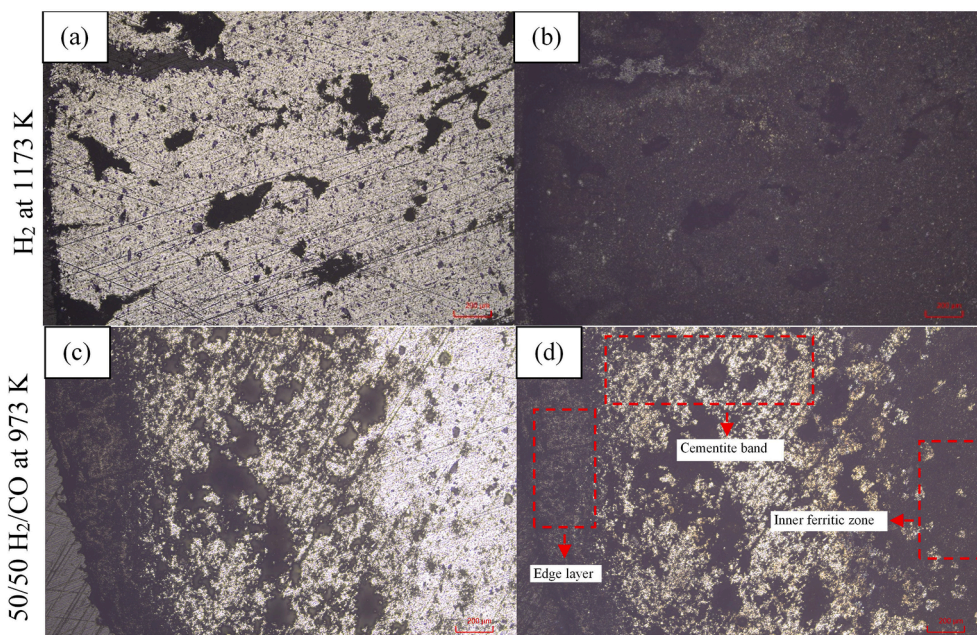


Fig. 8. Optical micrographs of pellets reduced in (a,b) H_2 at 1173 K and (c,d) 50/50 H_2/CO at 973 K. Images (a) and (c) correspond to the polished surfaces before etching, whereas (b) and (d) show the same regions after etching, revealing microstructural contrast.

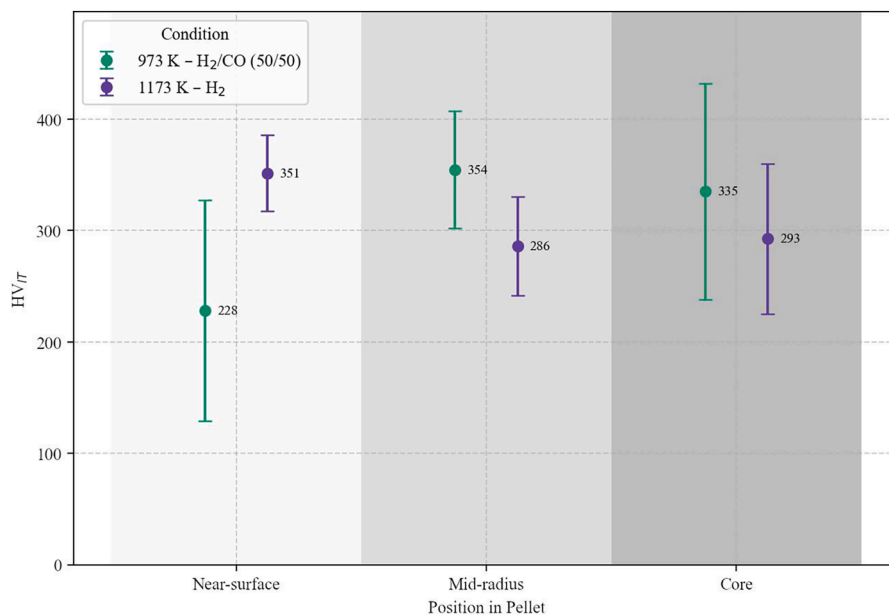


Fig. 9. Instrumented Vickers hardness (HV_{IT}) measured at the near-surface, mid-radius, and core of pellets reduced in H_2/CO (50/50, 973 K) and H_2 (1173 K), showing the radial hardness variation obtained from depth-controlled nanoindentation.

4. Discussion

The following discussion integrates the experimentally observed reduction behavior of single DR-grade pellets under the four investigated atmospheres—pure H_2 , pure CO, H_2/CO mixtures, and simulated biogenic gas—together with insights from model predictions, XRD analyses, and microstructural characterization. It should be emphasized that the simulated biogenic gas discussed throughout this section refers exclusively to the specific equilibrium-based composition defined in Section 2.2. In addition, the presence and distribution of carbon-bearing phases are supported by XRD and SEM-EDS analyses, their quantitative distinction remains inherently semi-quantitative. Therefore, the phase fractions discussed here are primarily derived from the validated model

and interpreted in a trend-consistent manner. The aim is to clarify how gas composition and temperature govern the interplay between intrinsic reaction kinetics, gas-phase and intraparticle transport, and the development of carburized phases. These coupled mechanisms determine not only the reduction rate but also the extent and distribution of carbon incorporation within the pellet. A key aspect in interpreting the thermogravimetric data is that the measured mass change reflects the combined effects of oxygen removal (mass loss) and carbon uptake (mass gain). Because reduction and carburization proceed concurrently in CO-containing atmospheres, the apparent conversion degree derived from TGA does not directly represent the true metallization state. For example, a pellet showing 90% apparent conversion may in fact be fully reduced but carry a measurable amount of Fe_3C or free carbon. This

discrepancy widens with increasing carbon activity in the gas, particularly under CO and syngas, where the Boudouard reaction contributes to carbon deposition, and to a lesser extent under simulated biogenic gas, where CO₂ moderates carbon activity. Recognizing this mass-balance interplay is therefore essential for distinguishing between genuinely incomplete reduction and carbon-driven offsets in the apparent conversion curves. In addition, the experimental distinction between Fe₃C and free carbon is subject to some uncertainty due to peak overlap in XRD and the semi-quantitative nature of SEM–EDS; therefore, quantitative phase fractions discussed herein are primarily based on model predictions and interpreted in a trend-consistent manner.

4.1. Reduction under pure H₂

Fig. 10 shows the conversion curves and corresponding pellet appearances after reduction in pure H₂ at 973–1273 K. In all cases, the reduction begins with a steep initial rise. At 1073–1273 K, the reaction proceeds smoothly to full metallization within the experimental time-frame, consistent with the XRD results in Fig. 7(a), which show only metallic iron across the pellet cross-section. At 973 K, however, the rate decreases noticeably at the very late stage and the final conversion remains slightly below unity. This indicates that a small fraction of oxygen remains trapped in the pellet interior under these low-temperature conditions. This effect can be most likely attributed to the sluggish oxygen solid state diffusion through the already formed iron product layers surrounding the wüstite (Kim et al., 2021). Self-diffusion coefficients in iron or iron oxide are characterized by high activation energies (Fradet et al., 2025). Solid-state diffusion can therefore become a limiting factor at lower temperatures. Although this mechanism is not explicitly represented in the present model, its omission does not compromise the overall agreement, as it manifests only at the final stages of reduction and only at the lowest temperature investigated.

To better assess the contribution of the combined reduction reactions/internal transport/external transport to the overall reduction process, a sensitivity analysis was performed, the results of which are shown in Fig. 11. The internal diffusion term, the rate of reaction FeO→Fe, and the external flux were artificially halved and doubled to ascertain their impacts on the time taken to reach 50% conversion and the time taken to reach 99.9% conversion. Two temperatures, namely 973 and 1173 K, were chosen to support the analysis. It should be emphasized that the results of the sensitivity analysis are based on the specific conditions of the present study, including the TGA setup or the size and composition of the pellets, and may not be broadly generalizable.

The sensitivity results show that, at both temperatures, the reduction rate is initially most responsive to changes in external mass transfer,

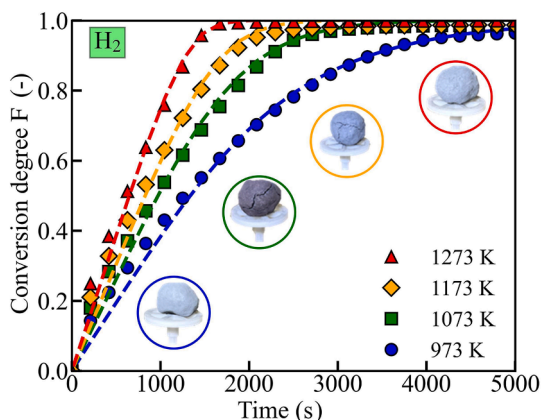


Fig. 10. Experimental and simulated reduction curves for single DR-grade iron oxide pellets reduced under pure H₂ atmospheres at 973–1273 K. Experimental data are shown as discrete symbols, and model predictions as dashed lines.

indicating fast reduction from H₂ and internal diffusion of the H₂/H₂O pair, which barely contribute to the overall kinetics. At the later stage at 973 K, the surface-reaction rate becomes the most sensitive parameter, while the comparatively small response to intraparticle diffusivity indicates that internal transport remains fast relative to the overall kinetics. The gradual deceleration observed in the conversion curve is consistent with the growing limitation by surface-reaction, originating from the decreasing chemical driving force as the oxide concentration diminishes during reduction.

At 1173 K, external mass transfer remains the most influential resistance in the later stage. Surface-reaction sensitivity increases slightly, especially towards the end, where the curve suddenly decelerates. Intraparticle diffusion is a minor contributor at both 973 K and 1173 K. This was further evidenced in our simulations by rather flat H₂/H₂O concentration profiles along the radius.

All in all, pure H₂ reduction proceeds rapidly due to favorable thermodynamics and fast intrinsic kinetics, allowing full metallization under the conditions studied at temperatures ≥ 1073 K, while internal transport resistances play only a minor role. Conversely, H₂-reduction appears very sensitive to constraints related to the external gas flow, i.e. by the delivery of fresh H₂ and removal of H₂O around the pellets. Also, since hydrogen introduces no carbon into the system, the resulting product is fully metallic and carbon-free, which is beneficial for purity but requires external carbon addition in downstream steelmaking processes.

4.2. Reduction under pure CO

Fig. 12 presents the conversion curves of pellets reduced in pure CO at 973–1273 K. Reduction in pure CO is markedly sluggish, showing a slow initial rise in conversion and an early transition into a strongly decelerating regime. At 973, the curves even plateau below 50% conversion. A modest mass gain is detected near the end of the test, reflecting limited carbon formation; as shown later, this deposition is minor compared with the extent of unreduced FeO. Only at 1273 K does the conversion approach $\sim 90\%$, yet the final extent remains significantly below that achieved under pure H₂.

To clarify the relative importance of reaction kinetics and mass-transport phenomena during CO reduction, a sensitivity analysis has been performed, and the results are shown in Fig. 13. At 973 K, the analysis considers the time to reach 20% conversion (Δt_{20}) as the early stage and the interval from 20% to 30% conversion ($\Delta t_{20 \rightarrow 30}$) as the later stage, reflecting the rapid onset of rate deceleration in pure CO. At 1173 K, the early stage has been defined by the time to reach 35% conversion (Δt_{35}), while the later stage spans the interval 35% to 65% conversion ($\Delta t_{35 \rightarrow 65}$).

The sensitivity trends at 973 K show that the early stage is mainly controlled by external mass transfer, meaning the gas film around the pellet limits how fast CO reaches the surface. As reduction proceeds, the dominant resistance quickly shifts toward intraparticle diffusion, indicating that CO/CO₂ transport inside the porous pellet increasingly govern the rate, whereas the surface-reaction step remains of secondary importance. This trend is consistent with the pronounced curvature and incomplete conversion in Fig. 12 and with the SEM image (Fig. 6) at 973 K, which shows a compact, finely textured surface with limited pore opening. At 1173 K, both gas-film and internal diffusion contribute during the early stage, but the surface-reaction rate becomes the most influential parameter in the later stage. Thus, CO reduction evolves from mainly transport-controlled behavior at 973 K to a more mixed regime with stronger chemical control at 1173 K, consistent with the higher maximum conversion levels at elevated temperature.

Fig. 14 presents the modeled radial phase distributions, which provide further insight into the incomplete conversion of CO cases. At 973 K, the model predicts a large fraction of residual FeO in the pellet interior and Fe₃C concentrated near the surface, while free carbon is minimal. Thus, low-temperature carburization occurs mainly as carbide

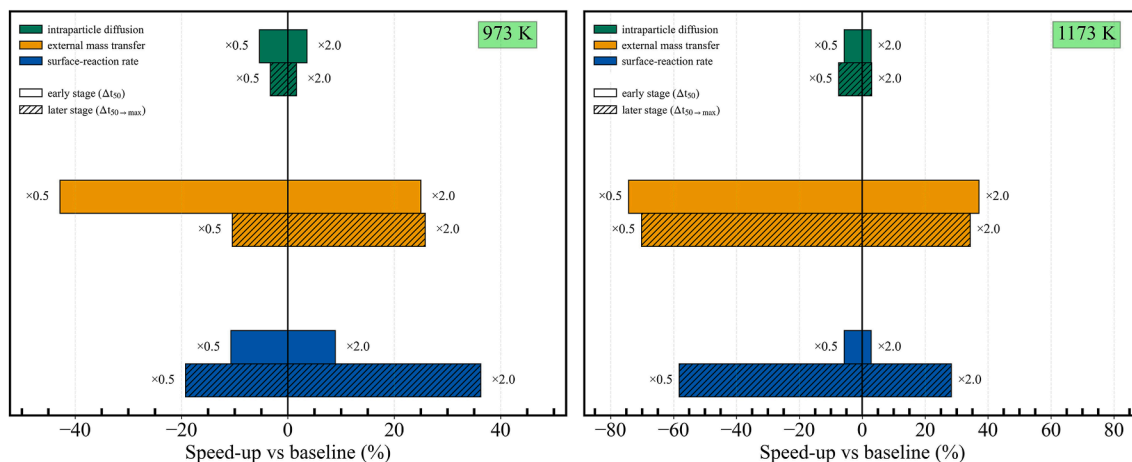


Fig. 11. Sensitivity of iron-ore pellet reduction under pure H_2 , showing relative influence of surface reaction, external mass transfer, and intraparticle diffusion during early (Δt_{50}) and later ($\Delta t_{50 \rightarrow \max}$) stages.

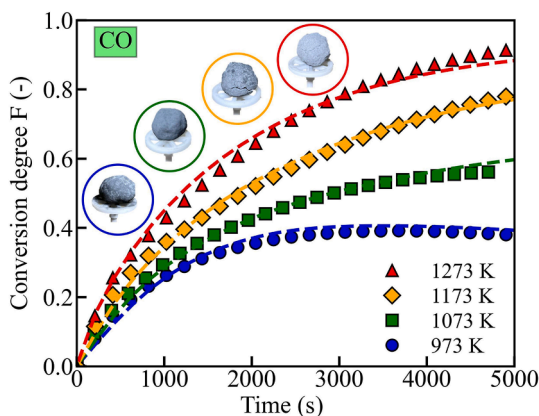


Fig. 12. Experimental and simulated reduction curves for single DR-grade iron oxide pellets reduced under pure CO atmospheres at 973–1273 K. Experimental data are shown as discrete symbols, and model predictions as dashed lines.

formation rather than as pore-blocking free carbon, and the stalled reduction originates from slow kinetics and transport of the CO/CO_2 pair. At 1173 K, the XRD results confirm the presence of Fe_3C together with metallic Fe and with almost no free carbon, consistent with the modeled phase distribution. The SEM morphology becomes more open,

reflecting enhanced reduction progress. At 1273 K, the SEM image (Fig. 6) shows a more open surface structure compared with 973 K, indicating that intraparticle diffusion becomes less restrictive at high temperature, in line with the reduced diffusion sensitivity (Fig. 13). Under these conditions, the reaction kinetics gain prominence, as reflected by the higher sensitivity of the surface-reaction parameter in the later stage. The appearance of elongated whisker-like iron features at 1273 K (Fig. 6) introduces an additional local morphological resistance by partially obstructing gas flow paths, explaining why CO reduction at 1273 K does not reach the same final metallization level as the corresponding H_2 case.

Overall, pure CO atmospheres promote carburization primarily through the formation of Fe_3C , but the degree of metallization remains constrained by the inherently slow CO–wüstite reduction kinetics together with transport limitations. At higher temperatures, the more open surface morphology reduces diffusion resistance, yet the intrinsic chemical step increasingly governs the rate, and the appearance of whisker-like growth introduces an additional microstructural resistance that slows the late-stage approach to full reduction. As a result, pure CO alone does not achieve complete metallization under the conditions investigated. Nevertheless, CO retains practical value as a carburizing component in mixed or simulated biogenic gas atmospheres, where the presence of H_2 accelerates reduction while enabling controlled in-situ carburization of the reduced product, as detailed in the following.

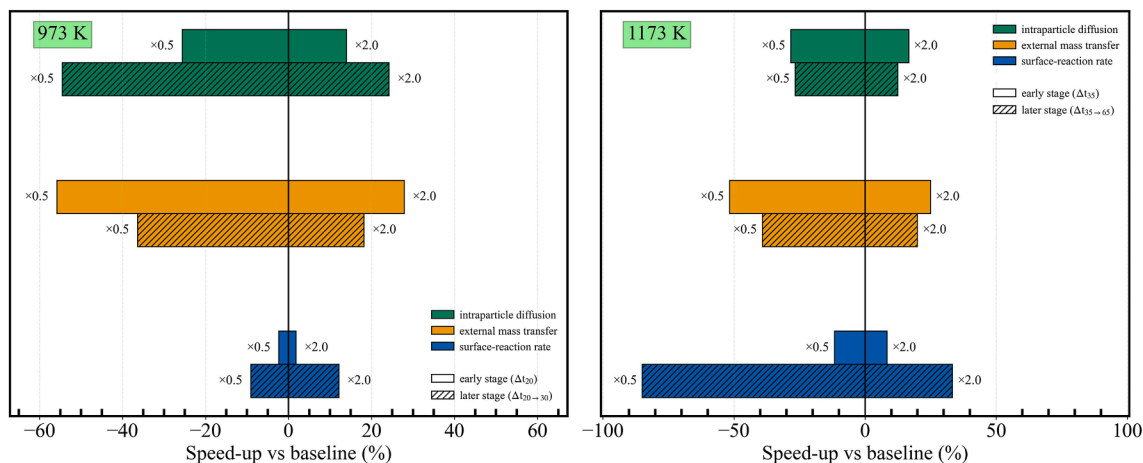


Fig. 13. Sensitivity of iron-ore pellet reduction under pure CO, showing relative influence of surface reaction, external mass transfer, and intraparticle diffusion for representative early and later conversion ranges.

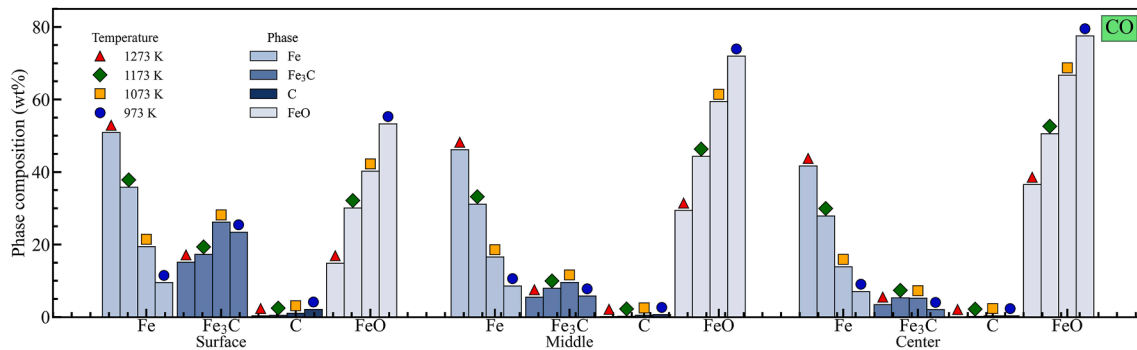


Fig. 14. Model-predicted radial distribution of solid phases (Fe, Fe₃C, C, and FeO) in fully reduced pellets after 5000 s under a CO atmosphere. The bars indicate zone-averaged phase compositions for the surface, middle, and core regions of the pellet.

4.3. Reduction under mixed H₂/CO atmospheres

The reduction in the mixed H₂/CO (50:50) atmosphere, given in Fig. 15, initially proceeds at an intermediate rate between the pure H₂ and pure CO limits. At 973 K, the early-stage reduction follows the hydrogen case closely, with similar times to reach 40% conversion as shown in Table 5. Beyond this point, however, the mixed gas slows markedly, requiring more than twice the time to reach 65% conversion. This deceleration reflects the onset of carbon deposition and the emergence of transport resistance. At 1073 K, this retardation largely disappears: the times to reach 40% and 65% conversion match those for pure H₂, suggesting that carbon deposition is less restrictive. At 1073–1273 K, the rapid reduction step brings the pellets close to full metallization, while the gentle mass increase observed afterward indicates moderate carburization rather than continued oxygen removal. The corresponding experimental and modeled curves for the 25:75 and 75:25 H₂/CO mixtures, which exhibit behavior consistent with the trends discussed here, are included in the Supplementary Fig. S3. The sensitivity analysis in Fig. 16 identifies the rate-controlling mechanisms underlying this behavior. At 973 K, the reduction is governed primarily by the surface-reaction step in both the early and later stages, which contrasts with both CO and H₂ cases discussed previously. This can be explained as follows: in the syngas case, the carburization has a strong contribution to the overall mass change over time.

Decreasing the reduction rate does not affect strongly the carburization rate; therefore, the net mass change, which is the summation of the reduction rate and carburization rate, severely decreases. At 1173 K, the situation changes: in the early stage, the strongest sensitivity is to external mass transfer, while intraparticle diffusion also contributes

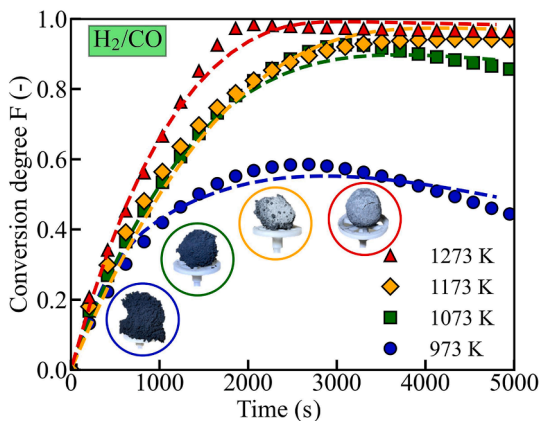


Fig. 15. Experimental and modeled pellet reduction in mixed H₂/CO (50:50) atmospheres at 973–1273 K. The intermediate reactivity between pure H₂ and CO reflects competing reduction and carburization pathways. Experimental data are shown as discrete symbols, and model predictions as dashed lines.

Table 5

Characteristic reduction times for 40% ($t_{40\%}$) and 65% ($t_{65\%}$) conversion of single DR-grade pellets under pure H₂, mixed H₂/CO (50:50), and pure CO atmospheres at 973–1073 K.

Temperature	Gas composition	$t_{40\%}$	$t_{65\%}$
973 K	H ₂	18 min	34 min
	50:50 H ₂ /CO	18 min	80 min
	CO	~	~
1073 K	H ₂	13 min	23 min
	50:50 H ₂ /CO	13 min	23 min
	CO	30 min	79 min

significantly. During the later stage, all processes have similarly large sensitivities, illustrating the complex interplay of transport, reduction, and carburization mechanisms of syngas cases. The strong transport limitation might be attributed to the lower diffusivities of CO and CO₂; the presence of H₂ not compensating for a sufficient internal diffusion at the later stage.

The spatial phase distributions as shown in Fig. 17 are fully consistent with the experimental XRD (Fig. 7(c)) and SEM-EDS observations (Fig. 5(d and e)). At 973 K, the model predicts a strong radial gradient in which metallic Fe and Fe₃C are concentrated near the surface while FeO dominates toward the core, with limited free carbon. This pattern is mirrored in the SEM-EDS maps, which show carbon enrichment and metallic domains near the exterior and FeO-rich regions in the interior, confirming that the reduction front advances only partway into the pellet under low-temperature syngas. At 1173 K, the modeled profiles become more uniform, with metallic Fe prevailing across the pellet thickness and Fe₃C appearing in moderate amounts throughout. The XRD results at 1173 K (Fig. 7(c)) corroborate this state: Fe is the dominant phase at surface, mid-radius, and core, accompanied by clear Fe₃C peaks and barely detectable graphitic carbon, while small FeO peaks persist in the interior—as predicted by the model. The SEM micrographs and EDS maps (Fig. 5(d and e)) further support this interpretation by revealing a porous metallic matrix with dispersed carbonaceous regions rather than a fully compacted or heavily carburized structure. Together, the modeled phase distributions, XRD patterns, and SEM-EDS data present a coherent picture of syngas reduction as a mixed reduction–carburization process that remains incomplete at intermediate temperatures due to residual transport limitations and the coexistence of Fe, Fe₃C, C, and FeO within the pellet.

Overall, syngas reduction reflects the interplay of fast H₂-driven reduction and strong carburization. At 973 K, the process is surface-kinetics-controlled, and carbonaceous species accumulate sufficiently to impede transport and slow the progression of the reduction front. At 1173 K, the rate becomes transport-limited, governed by external and internal gas diffusion, while moderate carburization continues to compete with reduction. Full metallization is achievable at the condition to maintain a sufficient temperature to limit excessive carburization.

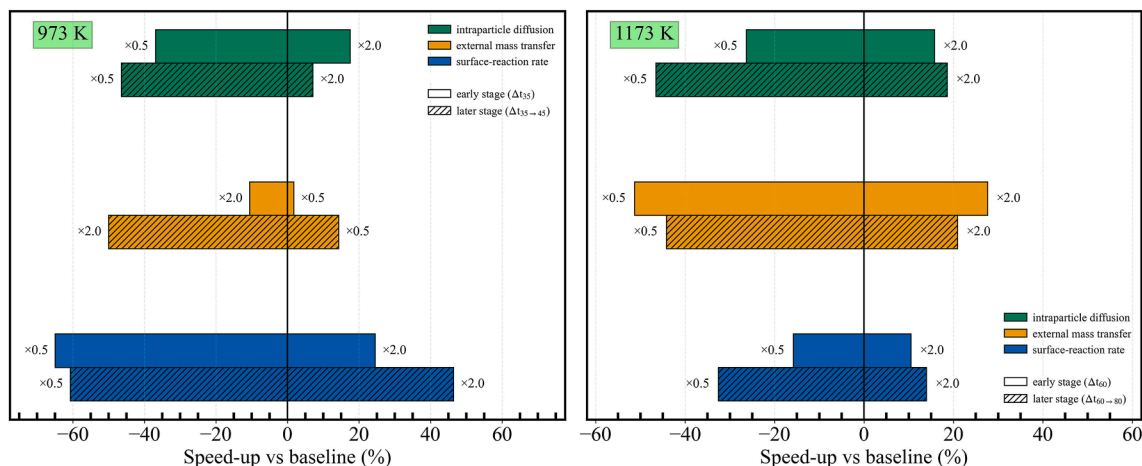


Fig. 16. Sensitivity of iron-ore pellet reduction under pure H_2/CO , showing relative influence of surface reaction, external mass transfer, and intraparticle diffusion for representative early and later conversion ranges.

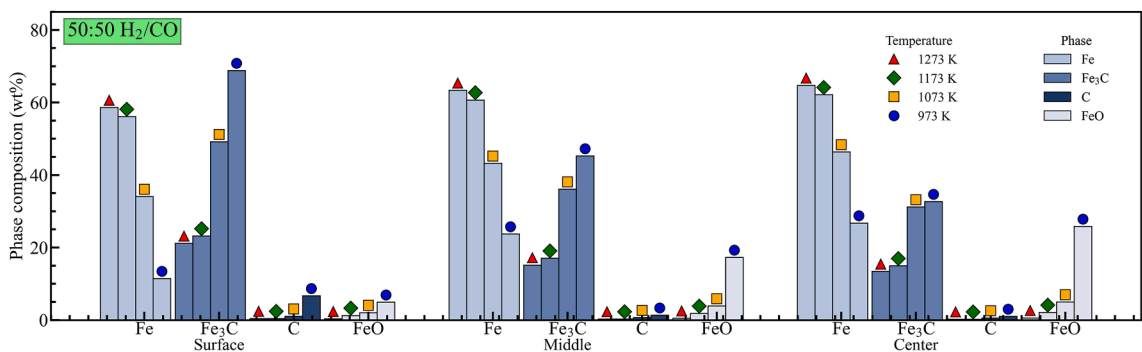


Fig. 17. Model-predicted radial distribution of solid phases (Fe, Fe_3C , C, and FeO) in fully reduced pellets after 5000 s under a 50/50 H_2/CO atmosphere. The bars indicate zone-averaged phase compositions for the surface, middle, and core regions of the pellet.

4.4. Reduction under simulated biogenic gas

Across all temperatures, simulated biogenic gas reduces slower than syngas in the early stage, yet ultimately attains a higher final degree of reduction, although its overall kinetics remain slower than pure H_2 (Fig. 18). At 1073–1273 K, the pellets approach close to full metallization, and the final conversion consistently exceeds that of syngas. This improvement is linked to the inhibiting effect of CO_2 , which strongly reduces carbon deposition at intermediate and high temperatures and helps maintain gas–solid contact during the later stages of reduction. Only at 973 K does the reaction remain incomplete, with the characteristic late-stage mass gain indicating limited low-temperature carbon uptake.

Fig. 19 presents the model-predicted radial phase distributions after 5000 s under BG. At 973 K, the surface becomes strongly carburized, with Fe_3C exceeding metallic Fe, while the intermediate region contains mainly Fe with residual FeO, and the core remains dominated by FeO with negligible carburization. This gradient indicates a carburized shell surrounding an incompletely reduced interior, reflecting slow internal diffusion at low temperature. At 1073–1273 K, the radial differences largely disappear: metallic Fe dominates from surface to center, Fe_3C appears in moderate and spatially uniform amounts, and free carbon is absent. The minor presence of FeO at the later stage can be explained by the formation of an equilibrium according to the reaction $FeO(s) + CO(g) \leftrightarrow Fe(s) + CO_2(g)$; equilibrium that depends on the CO/CO_2 ratio of the simulated biogenic gas and the temperature.

SEM analysis (Fig. 4(f)) at 1173 K confirms that the BG-reduced pellet retains open porosity and does not form extensive carbon-rich

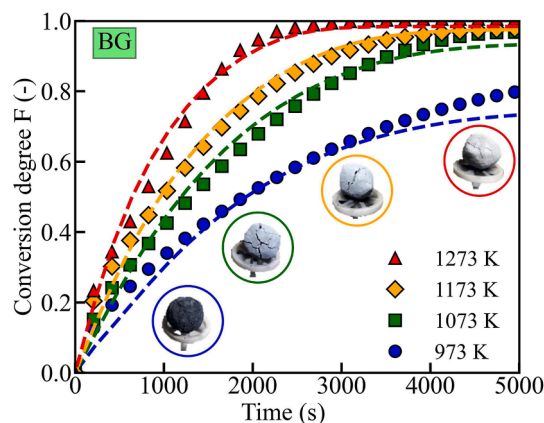


Fig. 18. Experimental and modeled pellet reduction in simulated biogenic gas (H_2 -53%, CH_4 -3%, CO -33%, CO_2 -10%) atmospheres at 973–1273 K. Experimental data are shown as discrete symbols, and model predictions as dashed lines.

surface layers, consistent with the limited free-carbon fraction in the phase distributions (Fig. 19). SEM-EDS (Fig. 5(f)) further shows that the metallic matrix contains only trace carbon, indicating that BG inhibits carbon deposition during reduction. This can be attributed to the elevated H_2/CO ratio together with the CO_2 content, which lowers the effective carbon activity. Although CO_2 can thermodynamically stabilize Fe_3C , increasing CO_2 significantly suppresses its formation by lowering

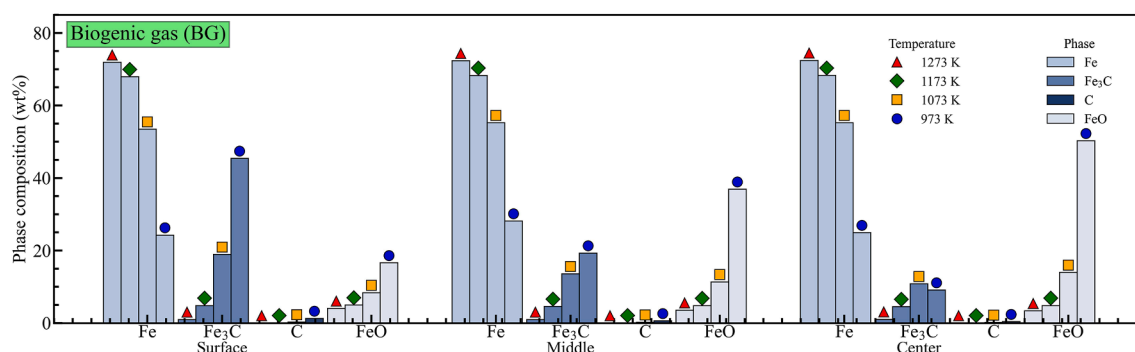


Fig. 19. Model-predicted radial distribution of solid phases (Fe, Fe₃C, C, and FeO) in fully reduced pellets after 5000 s under simulated biogenic atmosphere. The bars indicate zone-averaged phase compositions for the surface, middle, and core regions of the pellet.

carbon activity and shifting equilibria away from cementite (Kumar, Ahmed, et al., 2022). The CO₂ level in the present BG mixture is well below this range, so moderate Fe₃C formation can still proceed.

In summary, BG provides a balanced combination of reduction efficiency and carbon control. Its early-stage kinetics are slower than syngas, but BG achieves a higher final metallization because the presence of CO₂ limits carbon deposition and helps maintain gas access throughout the pellet during the later stages of reduction. Carburization proceeds mainly via Fe₃C and remains moderate, while free carbon remains negligible except at 973 K. These characteristics make BG a promising renewable-gas candidate – alone or in addition to green hydrogen – for DR processes requiring higher reduction and controlled carburization without the complications associated with carbon oversaturation.

5. Conclusions

The combined experimental and modeling work across H₂, CO, H₂/CO mixtures, and simulated biogenic gas provides a coherent picture of how gas composition and temperature govern reduction and carburization in DR-grade pellets. Because the TGA signal reflects the net mass balance of oxygen removal and carbon uptake, and not only metallization extent, interpretation of conversion curves requires coupling with phase-resolved (XRD), microstructural (SEM-EDS/LOM), and model-derived information. Together, these datasets reveal clear trends in both metallization pathways and carbon evolution. It should be noted that these findings are derived from single-pellet, isothermal experiments and therefore provide mechanistic insight at the pellet scale. As such, they form a foundational basis for future scale-up studies and for the development of reactor-scale models relevant to industrial shaft furnace operation.

- Under pure H₂, the iron ore pellets under consideration reduce rapidly across all temperatures. Under pure H₂ at temperatures ≥ 1073 K, complete metallization was achieved within the experimental timeframe, consistent with the XRD results showing Fe as the dominant phase throughout the pellet. At 973 K, the reduction slows in the very late stage and a small unreduced fraction remains, which aligns with the expected slow oxygen solid-state diffusion through iron layers under low-temperature conditions. Sensitivity analysis indicates that external mass transfer dominates early in the reaction, whereas surface kinetics become more influential at the end of the 973 K test. Intraparticle diffusion has only a minor contribution across all the temperatures.
- Under pure CO, reduction proceeds slowly and remains far from completion at 973–1073 K, where the conversion curves plateau well below full metallization. The modeled phase distributions and SEM observations confirm that FeO persists in the pellet interior while Fe₃C forms mainly near the surface, with very little free carbon. Sensitivity analysis shows that reduction at 973 K transitions from

external mass-transfer influence in the early stage to intraparticle-diffusion limitation in the later stage. At 1173–1273 K, the pellet surface becomes more open, but the sensitivity results show that chemical reaction kinetics increasingly govern the later stage. The appearance of whisker-like iron features at 1273 K in SEM provides a consistent morphological explanation for the restricted late-stage approach to full metallization relative to pure H₂.

- Under mixed H₂/CO (50:50), reduction proceeds at an elevated rate, but so does carburization. At 973 K, the early stage resembles hydrogen reduction, but the progression slows once carburization begins, with the coexistence of Fe, Fe₃C, residual FeO, and free carbon in the model and SEM-EDS results. Comparing the syngas case with CO, the carburization appears enhanced by the presence of H₂ through additional reaction pathways. At 1173 K, the spatial phase distributions become more uniform, with metallic Fe dominating and Fe₃C present throughout the pellet. The sensitivity analysis indicates that the rate becomes jointly influenced by external mass transfer, intraparticle diffusion, and surface reaction at high temperature, consistent with the mixed reduction–carburization behavior observed experimentally and in the modeled profiles.
- Reduction under the specific equilibrium-based simulated biogenic gas composition investigated in this study presents a distinct behavior due to its elevated H₂/CO ratio and CO₂ content. Early-stage reduction kinetics are slower than syngas, yet simulated biogenic gas consistently achieves a higher final metallization because CO₂ suppresses carbon deposition and helps maintain open gas pathways throughout reduction. Both the modeled phase distributions and SEM-EDS confirm that, under the present BG composition, carbon incorporation into the product matrix occurs primarily in the form of Fe₃C throughout the pellet while free carbon remains strongly suppressed. Only at 973 K does measurable carbon deposition occur, appearing late in the experiment and coinciding with a low final degree of metallization. Therefore, this specific BG mixture introduces in-situ carbon primarily in the form of Fe₃C, sufficient for carburization without causing excessive free-carbon deposition. In future studies, biogenic gases derived from different biomass feedstocks will be investigated to evaluate feedstock-dependent effects on reduction behavior and carbon-phase evolution.

To summarize, the collective evidence shows that the controlling mechanisms shift systematically across the investigated atmospheres. Hydrogen provides rapid, reaction-controlled metallization with negligible transport resistance and, as expected, no carburization. Thus, although hydrogen reduction is beneficial in terms of kinetics and extent of metallization, it is coupled with drawbacks such as the process endothermicity or the complete absence of carbon in the product. CO and syngas exhibit coupled reduction–carburization behavior, but in different ways: in syngas, the reduction is driven by the presence of hydrogen, but strong carbon deposition can abruptly stop the reduction

process. Whereas in pure CO, both reduction and carburization remain slow and incomplete metallization is governed mainly by slow reaction kinetics and transport resistances rather than carbon uptake. Biogenic gas reduces more slowly than pure hydrogen, but the presence of CO₂ strongly suppresses free-carbon deposition, enabling the reaction to reach a high metallization extent. Biogenic gas reduction forms Fe₃C consistently across the pellet while avoiding heavy carbon deposition, offering a controlled level of in-situ carburization. These trends define a mechanistic window in which hydrogen-rich and renewable CO-containing gases can be tuned to balance fast metallization with controlled carburization, providing a basis for designing next-generation DR processes that satisfy both decarbonization goals and the carbon requirements of downstream EAF steelmaking.

CRedit authorship contribution statement

Syafinah Fong: Writing – review & editing, Writing – original draft, Visualization, Validation, Software, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Mohammed Liaket Ali:** Writing – review & editing, Writing – original draft, Visualization, Validation, Project administration, Methodology, Investigation, Funding acquisition, Data curation, Conceptualization. **Sven Mehlhose:** Formal analysis. **Quentin Fradet:** Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Resources, Project administration, Methodology, Funding acquisition, Formal analysis, Conceptualization. **Rafiandy Dwi Putra:** Methodology, Investigation. **Andreas Schedl:** Supervision, Funding acquisition. **Uwe Riedel:** Supervision, Resources.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

We acknowledge funding by the European Union and by tax revenues on the basis of the budget adopted by the Saxon State Parliament (European Regional Development Fund (EFRE) project “BioFe - Biomassenutzung in der Eisenerzeugung unter wirtschaftlichen und CO₂-mindernden Randbedingungen”). We additionally thank Dr. Florian Praße and Eric Kluge (ZIRKON) for SEM-EDS troubleshooting and instrument support, Dr. Marcus Schreiner and Christian Schmidt (IEC, TU Freiberg) for assistance with XRD analysis, and Matthias Herrmann and Dr. Jana Reinhold (Hochschule Zittau/Görlitz) for support with nano-indentation and cementite etching.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.partic.2026.04.014>.

References

- Ahmed, H., Sandeep Kumar, T. K., Alatalo, J., & Björkman, B. (2022). Effect of carbon concentration and carbon bonding type on the melting characteristics of hydrogen-reduced iron ore pellets. *Journal of Materials Research and Technology*, 21, 1760–1769.
- Ali, M., Fradet, Q., & Riedel, U. (2022). Kinetic mechanism development for the direct reduction of single hematite pellets in H₂/CO atmospheres. *Steel Research International*, 93(12), Article 2200043.
- Bale, C. W., Bélisle, E., Chartrand, P., Decterov, S. A., Eriksson, G., Gheribi, A. E., ... van Ende, M.-A. (2016). Reprint of: FactSage thermochemical software and databases, 2010–2016. *Calphad*, 55, 1–19.
- Boechat, F. O., Da Rocha, L. T., Carvalho, R. M., Jung, S.-M., & Tavares, L. M. (2018). Amenability of reduced iron ore pellets to mechanical degradation. *ISIJ International*, 58(6), 1028–1033.
- Bonnet, F., Ropital, F., Berthier, Y., & Marcus, P. (2003). Filamentous carbon formation caused by catalytic metal particles from iron oxide. *Materials and Corrosion*, 54(11), 870–880.
- Büyüksulu, Ö. K., Yang, F., Raabe, D., to Baben, M., & Ravensburg, A. L. (2025). Using thermodynamics and microstructure to mitigate overfitting in pellet reduction models. *Steel Research International*.
- Calderon Hurtado, F. A., Govro, J., Emdadi, A., & O'Malley, R. J. (2024). The melting behavior of hydrogen direct reduced iron in molten steel and slag: An integrated computational and experimental study. *Metals*, 14(7), 821.
- Daehn, K. E., Cabrera Serrenho, A., & Allwood, J. M. (2017). How will copper contamination constrain future global steel recycling? *Environmental Science and Technology*, 51(11), 6599–6606.
- Echterhof, T. (2021). Review on the use of alternative carbon sources in EAF steelmaking. *Metals*, 11(2), 222.
- El-Geassy, A. A., Nasr, M. I., & Hessien, M. M. (1996). Effect of reducing gas on the volume change during reduction of iron oxide compacts. *ISIJ International*, 36(6), 640–649.
- Fradet, Q., Ali, M., & Riedel, U. (2022). Development of a porous solid model for the direct reduction of iron ore pellets. *Steel Research International*, 93(12), Article 2200042.
- Fradet, Q., Fong, S., Kurnatowska, M., Soria-Verdugo, A., Choisey, L., & Riedel, U. (2025). Thermogravimetric and microstructural analysis of the low-temperature oxidation of iron powders. *Fuel*, 401, Article 135866.
- Grabke, H. J. (1995). Metal dusting of Low- and high-alloy steels. *Corrosion*, 51(9), 711–720.
- Grabke, H. J., Krajak, R., & Nava Paz, J. C. (1993). On the mechanism of catastrophic carburization: ‘metal dusting’. *Corrosion Science*, 35(5–8), 1141–1150.
- Grabke, H. J., Müller-Lorenz, E. M., & Schneider, A. (2001). Carburization and metal dusting on iron. *ISIJ International*, 41(Suppl), S1–S8.
- Guo, D., Li, Y., Cui, B., Chen, Z., Luo, S., Xiao, B., ... Hu, M. (2017). Direct reduction of iron ore/biomass composite pellets using simulated biomass-derived syngas: Experimental analysis and kinetic modelling. *Chemical Engineering Journal*, 327, 822–830.
- Guo, D., Zhu, L., Guo, S., Cui, B., Luo, S., Laghari, M., ... Luo, S. (2016). Direct reduction of oxidized iron ore pellets using biomass syngas as the reducer. *Fuel Processing Technology*, 148, 276–281.
- Hamadeh, H., Mirgaux, O., & Patisson, F. (2018). Detailed modeling of the direct reduction of iron ore in a shaft furnace. *Materials (Basel, Switzerland)*, 11(10), 1865.
- Harpprecht, C., Naegler, T., Steubing, B., Tukker, A., & Simon, S. (2022). Decarbonization scenarios for the iron and steel industry in context of a sectoral carbon budget: Germany as a case study. *Journal of Cleaner Production*, 380, Article 134846.
- Harpprecht, C., Sacchi, R., Naegler, T., van Sluysveld, M., Daioglou, V., Tukker, A., & Steubing, B. (2025). Future environmental impacts of global iron and steel production. *Energy & Environmental Science*, 18(16), 8009–8028.
- Hessling, O., Fogelström, J. B., Kojola, N., & Martinsson, J. (2024). Influence of water content on the kinetics and mechanisms of hydrogen reduction using industrial iron ore pellets at 873 K–1173 K. *ISIJ International*, 64(10), 1493–1502.
- Higashi, R., Maruoka, D., Iwami, Y., & Murakami, T. (2024). Reduction and carburization behaviors of iron oxide composite with iron carbide and free carbon. *ISIJ International*, 64(15), 2107–2114.
- Huang, Z., Yi, L., & Jiang, T. (2012). Mechanisms of strength decrease in the initial reduction of iron ore oxide pellets. *Powder Technology*, 221, 284–291.
- Hornby, S., & Brooks, G. (2021). *Impact of hydrogen DRI on EAF steelmaking*. North Carolina 28208 USA: Charlotte.
- Iguchi, Y., & Endo, S. (2004). Reactions, coalescence of reduced iron particles, and liberation of carbon particles in carbon composite iron ore pellets. *ISIJ International*, 44(12), 1999–2007.
- Immonen, J., & Powell, K. M. (2024). Dynamic modeling of a direct reduced iron shaft furnace to enable pathways towards decarbonized steel production. *Chemical Engineering Science*, 300, Article 120637.
- Jess, A., & Depner, H. (1998). Reduction and carburization of iron-ore in a fluidized bed by CO, H₂ and CH₄. *Steel Research*, 69(3), 77–84.
- Kar, M. K., & Safarian, J. (2025). Carburisation of hydrogen-reduced iron ore pellets by CH₄–H₂ gas mixtures for sustainable steelmaking. *Ironmaking and Steelmaking*.
- Kazemi, M., & Du, S. (2016). Effect of experimental conditions on cementite formation during reduction of iron ore pellets. *Metallurgical and Materials Transactions B*, 47(6), 3519–3526.
- Kieush, L., & Schenk, J. (2025). Influence of carbon material properties on slag-foaming dynamics in electric Arc furnaces: A review. *Steel Research International*, 96(8).
- Kim, S.-H., Zhang, X., Ma, Y., Souza Filho, I. R., Schweinar, K., Angenendt, K., ... Raabe, D. (2021). Influence of microstructure and atomic-scale chemistry on the direct reduction of iron ore with hydrogen at 700°C. *Acta Materialia*, 212, Article 116933.
- Kirchner, J., Baysal, Z., & Kureti, S. (2020). Activity and structural changes of Fe-based catalysts during CO₂ hydrogenation towards CH₄ – A mini review. *ChemCatChem*, 12(4), 981–988.
- Kumar, T. K., Ahmed, H., Alatalo, J., & Björkman, B. (2022). Carburization behavior of hydrogen-reduced DRI using synthetic bio-syngas mixtures as fossil-free carbon sources. *Journal of Sustainable Metallurgy*, 8(4), 1546–1560.
- Kumar, T. K., Alatalo, J., Ahmed, H., & Björkman, B. (2022). Effect of temperature and gas mixtures on cementite formation during the carburization of hydrogen-reduced DRI. *Journal of Sustainable Metallurgy*, 8(4), 1450–1464.
- Lei, J., Zhang, C., An, J., Kong, Y.-q., He, S., Long, H., & Wu, T. (2023). Mechanism study on gas-based reduction swelling behavior of ultra-high grade pellets. *Journal of Materials Research and Technology*, 26, 823–836.

- Marsigny, A., Letz, J.-B., Mirgaux, O., & Patisson, F. (2025). Kinetics of the reduction of iron ore pellets with hydrogen: A parametric experimental and modeling study. *Metals*, 15(9), 1034.
- Mendoza, S., Nusheh, M., Yin, B. H., & Bumby, C. W. (2025). Comparison of the compressive strength and failure mechanism of hydrogen-reduced iron ore pellets from titanomagnetite ironsand and high-grade magnetite concentrates. *Powder Technology*, 454, Article 120715.
- Meyers, M. A., & Tantevee, T. (1986). Stresses induced in iron-ore pellets by hydrogen reduction. *Metallurgical Transactions B*, 17(1), 217–227.
- Mousa, E., Wang, C., Riesbeck, J., & Larsson, M. (2016). Biomass applications in iron and steel industry: An overview of challenges and opportunities. *Renewable and Sustainable Energy Reviews*, 65, 1247–1266.
- OECD. (2025). OECD science, technology and industry policy papers. *OECD science, technology and industry policy papers*.
- Olsson, R. G., & Turkdogan, E. T. (1974). Catalytic effect of iron on decomposition of carbon monoxide: II. Effect of additions of H₂, H₂O, CO₂, SO₂ and H₂S. *Metallurgical Transactions A*, 5(1), 21–26.
- Perrone, A., Cavaliere, P., Sadeghi, B., Dijon, L., Laska, A., & Koszelow, D. (2024). Carburization behavior of high-grade pellets after direct reduction in pure hydrogen. *Journal of Sustainable Metallurgy*, 10(4), 1991–2008.
- Pousette, H., & Kojola, N. (2024). Factors influencing physical and mechanical properties of direct reduced iron ore pellets. *Ironmaking and Steelmaking*.
- Prasad, R., Soren, S., Kumaraswamidhas, L. A., Pandey, C., & Pan, S. K. (2022). Experimental investigation of different fineness and firing temperatures on pellets properties of different iron ore fines from Indian mines. *Materials (Basel, Switzerland)*, 15(12).
- Purohit, S., Pownceby, M. I., & Guiraud, A. (2025). Sticking and swelling of iron ore pellets: Mechanisms and controlling factors. *Journal of Sustainable Metallurgy*, 11(1), 67–87.
- Salucci, E., D'Angelo, A., Russo, V., Grénman, H., & Saxén, H. (2024). Modelling of iron oxide reduction with hydrogen in a small fixed bed. *Chemical Engineering Science*, 292, Article 119934.
- Sheng, H., Yang, Y., Zhan, W., He, Z., Liu, J., & Gao, L. (2025). Exploring the effects of biomass utilization on the metallurgical performance and formation mechanisms of iron ore pellets. *Journal of Analytical and Applied Pyrolysis*, 186, Article 106977.
- Soodmand, A. M., Heidari, A., Azadi, S. K., Iljana, M., Heikkilä, A., Ghosalya, M. K., ... Fabritius, T. (2025). Effect of water vapor on the reduction and carburization of iron ore pellets: Theoretical and experimental approaches. *Metallurgical and Materials Transactions B*.
- Valipour, M. S., Motamed Hashemi, M. Y., & Saboohi, Y. (2006). Mathematical modeling of the reaction in an iron ore pellet using a mixture of hydrogen, water vapor, carbon monoxide and carbon dioxide: An isothermal study. *Advanced Powder Technology*, 17(3), 277–295.
- Wang, H. T., & Sohn, H. Y. (2011). Effect of CaO and SiO₂ on swelling and iron whisker formation during reduction of iron oxide compact. *Ironmaking and Steelmaking*, 38(6), 447–452.
- Worldsteel, Association. (2024). *2024 World Steel in Figures*. Brussels.
- Xu, M.-W. P., & Brown, J. J. (1989). Mechanism of iron catalysis of carbon monoxide decomposition in refractories. *Journal of the American Ceramic Society*, 72(1), 110–115.
- Yi, L., Huang, Z., Jiang, T., Wang, L., & Qi, T. (2015). Swelling behavior of iron ore pellet reduced by H₂–CO mixtures. *Powder Technology*, 269, 290–295.
- Zhang, J., Schneider, A., & Inden, G. (2008). Initiation and growth of iron metal dusting in CO–H₂–H₂O gas mixtures. *Corrosion Science*, 50(4), 1020–1034.