Rapid Iron Ore Reduction via Atmospheric Pressure Microwave Hydrogen Plasma

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Abstract: Iron and steel making account for ~8% of global CO_2 emissions, with iron ore reduction in blast furnaces being a major source of these emissions. We present a potentially fully carbon-free approach to iron ore reduction based on atmospheric pressure hydrogen plasma excited by microwave energy. By treating fine iron oxide particles with the effluent of an argon-hydrogen plasma, more than 95% reduction can be achieved in a few seconds with promising mass scaling and kinetics faster than thermal reduction at the same particle temperature.

1. Introduction

The iron and steel making industry globally is the largest industrial emitter of CO_2, directly responsible for 2.6 Gt CO_2 emissions per year [1]. Apart from scrap metal, steel is produced from iron ore containing magnetite (Fe_3O_4) or hematite (Fe_2O_3) and other unwanted minerals (gangue materials) that are ground to micron-size particles right after extraction and then sintered into centimeter-sized pellets [2]. In the traditional blast furnace reduction (BFR), coke, refined coal, acts as energy source and reducing agent producing large amounts of CO_2.

Direct reduction of iron ore (DRI)[3] has been developed as a lower-carbon alternative to BFR, however, most DRI processes use natural gas and remain carbon intensive. Direct reduction using hydrogen gas can potentially achieve this goal, if "green" hydrogen from electrolysis is used as reductant. The in-flight reduction of iron ore particles by H_2 developed by the University of Utah, also known as flash iron making, has emerged as a promising technology. However, at the pilot plant scale, the approach still relies on the partial combustion of natural gas and hydrogen as a source of heat and reductant to make it cost effective [4].

Significant efforts involving plasma-enabled iron making have been reported. The Bethlehem falling film reactor (patented in 1979) used an Ar-H_2 thermal plasma arc to reduce solid ore particles that were injected into the plasma arc [5]. Particles were melted and through centrifugal forces induced by a swirl flow transported to the reactor wall, where a liquid film of molten iron ore was formed. Despite its high efficiency of within 15% of commercial approaches at the time [6], it suffered from difficulties in developing high-power plasma arc torches with sufficient lifetime.

Hydrogen plasma smelting reduction (HPSR)[7] was introduced in 1992 and a first pilot plant was recently built by Voestalpine in 2021. It relies on a thermal plasma arc that is run in an argon:hydrogen atmosphere between a carbon cathode and a steel crucible filled with iron ore powder acting as the anode. While this batch process is capable of handling significant amounts of powder, up to 100 g on the laboratory scale, reduction rates are still significantly impacted by transport limitations [8].

Sabat and Murphy proposed that excited species that are readily produced in nonthermal plasmas, such as vibrationally excited hydrogen molecules, atomic hydrogen, and hydrogen ions can play an important role in the reduction of iron ore [9]. Rajput, Sabat, et al. [10] demonstrated the ability of nonthermal hydrogen plasmas to reduce iron ore at low temperatures. They used a low-pressure microwave sustained plasma operated in pure H_2 at pressures of 5.3 and 13.3 kPa and powers of 750 W and 1,500 W, respectively, to treat samples of ~2.5g mass both in the form of ore lumps and pellets. Reduction of more than 90% was achieved only for the highest temperature studied (1,073 K) and required ~1,500 s. Yoo et al. demonstrated the "catalytic" effect of plasma produced excited species [11]. The authors treated hematite powder with an infrared laser as heat source while flowing 0.5% H_2 in argon at atmospheric pressure. If only the infrared laser was used, reduction of the hematite surface was observed after 5 minutes at a surface temperature of 720 K. However, if a weak plasma was created with a microwave power source, the hematite was reduced at temperatures as low as 570 K. While the feasibility of iron ore reduction by non-equilibrium plasma is established, an implementation that allows continuous processing at competitive efficiencies remains a work in progress.

2. Methods

In this work, we have used microwave argon-hydrogen plasma for the rapid reduction of iron oxide powders, schematically shown in Figure 1. A microwave generation unit, consisting of a magnetron, a circulator, and a power supply, is used to generate microwaves at 2.45 GHz, which are then directed by a waveguide to a surfaguide microwave applicator [12]. A quartz tube, through which the argon-hydrogen gas mixture flows, runs transversely to the waveguide and allows microwave energy to interact with the flow. Due to the high microwave energy density in the waveguide and quartz tube, a plasma can be ignited using a sharp tungsten tip. The plasma heats the gas and creates reactive species such as vibrationally excited hydrogen and atomic hydrogen.
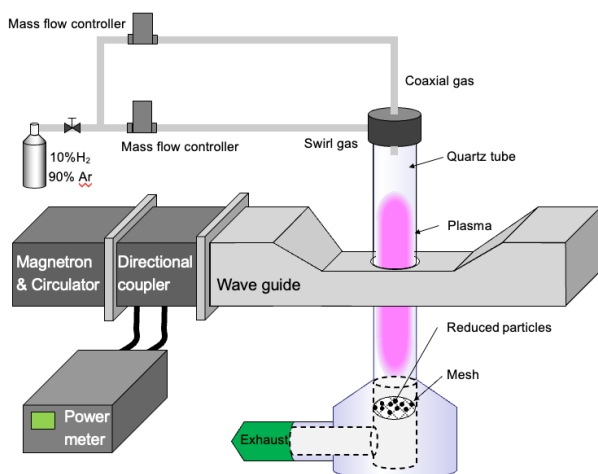
Figure 1: Simplified schematic of the microwave argon-hydrogen plasma to reduce iron oxide particles.

Iron oxide powder was suspended on a 400 mesh stainless steel grid about 7.25 inches (~19 cm) downstream of the plasma. In some experiments, shorter distances were explored but the thermal stability of stainless steel mesh proved to be a limiting factor. The mesh allows the flow to effectively pass through the powder. The plasma effluent carrying hot hydrogen gas including vibrationally excited hydrogen molecules and atomic hydrogen reacts with the iron ore to produce iron. The temperature of the mesh/particles was determined using optical emission spectrometry by fitting the blackbody spectrum of the red glowing mesh. For typical experiments, a 90% Ar - 10% H_2 mixture was used as the reducing gas. High purity (>96% by weight) magnetite and hematite particles with an average particle size <5μm were used. Tests were performed with 10 mg and 500 mg iron oxide powder on the mesh. The reduced particles were analyzed using X-ray diffraction to calculate the reduction percentage and the weight-% of different phases present in the samples.

3. Results

In initial trials, a flow rate of 45 slm and microwave power of 1.67 kW were used to reduce the 10 mg magnetite powder. X-ray diffraction patterns of the treated powder are shown in Figure 2. Even after 2 seconds of plasma exposure, most of the magnetite is transformed into wüstite (FeO). Within 8 seconds, the iron oxide is almost completely reduced to elemental iron, yielding a reduction degree of 97%. Throughout the reaction, the mesh/particle temperature remains at ~ 1,300-1,350 K (1,027-1,077 °C).

A comparison between the microwave reduction and thermal reduction in a furnace revealed that the microwave plasma reduces iron oxide powder about four times faster than thermal reduction at the same temperature and gas flow rates. This strongly suggests that excited gas species

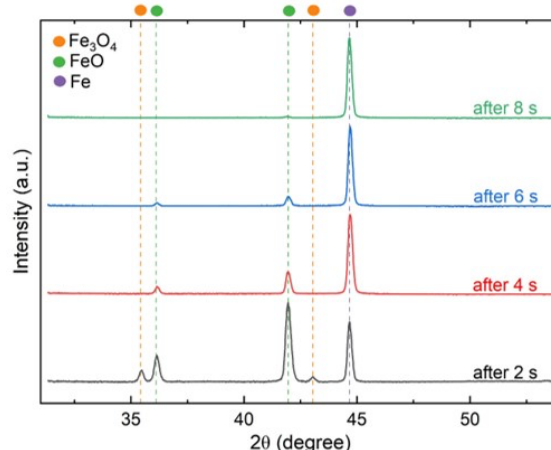produced by the plasma are important for speeding up the reduction process.

Figure 2: X-ray diffraction patterns of 10 mg of magnetite powder after different treatment times with the argon-hydrogen (90:10) microwave plasma at 1.67 kW power and 45 slm flow.

The mass scaling of the microwave plasma reduction was tested as well. In addition to 10 mg samples, we also tested 100 and 500 mg samples. As expected, the reduction of larger powder mass took longer than for the 10 mg samples. However, the scaling with larger sample mass was quite favorable. A 10 mg sample of powder was reduced by more than 95% in 8 s, while achieving the same reduction degree for 500 mg required about 40 s. Hence, reducing 50 times more iron oxide powder required only 7 times more time. This suggests that the microwave plasma technology has significant potential for scale-up.

Our champion result to date is the reduction of 500 mg of magnetite to 92% Fe within 40 s. This corresponds to a specific energy consumption of ~ 170 GJ$_{electric}$/ton Fe. In comparison, the specific energy consumption of the conventional BFR reduction route, including blast furnace operation, coke production, and iron ore pellet making, is ~16 GJ/ton Fe. Given that improvements in specific energy consumption can be expected with scale-up from our current table top device, this is a very encouraging result.

Additional experiments were performed with comparing hematite and magnetite powders. The reduction kinetics for both types of iron oxide were essentially identical. This is not surprising because the hydrogen reduction from Fe_2O_3 to Fe_3O_4 has a negative Gibbs standard free energy change at the temperatures of our reduction process and the fractional oxygen removal is small compared to the reduction from FeO to Fe [10].

4. Conclusion

In this presentation, we discuss results for the reduction of iron oxide using an atmospheric pressure argon-hydrogen microwave plasma. Small 10 mg samples of

magnetite and hematite are reduced on timescales of ∼ 8s. Compared to thermal reduction performed in a furnace under otherwise similar conditions, the plasma reduction proceeds ∼4 times faster, suggesting that excited hydrogen species produced by the plasma aid the reduction.

Larger samples of 500 mg magnetite powder, i.e. 50 times larger mass, require only 7 times longer reduction time to achieve a reduction degree > 90%. The energy efficiency of the current table top device is within a factor of ∼10 of the incumbent blast furnace technology, while it can be entirely carbon-free when operated with renewable electricity and with green hydrogen. This suggests that the microwave plasma technique discussed here may have significant potential for carbon-free ironmaking.

5. Acknowledgments

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