Low-Temperature Hydrogen Plasma Reduction of Hematite Thin Films

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Abstract: Hydrogen plasma reduction of iron ore is a promising approach for green steel making. We report on the reduction of hematite thin films using an RF-driven hydrogen plasma jet operating near ambient temperatures. The results demonstrate that atomic hydrogen significantly enhances the reduction rate compared to thermal reduction by a factor 1.4 at the same substrate temperature, suggesting the rate limiting step is the interfacial reaction rate of reduction.

1. Introduction

Steel production worldwide totals approximately 2 billion tons annually. Each ton of steel produced accounts for 1.9 tons of CO_2 emission, contributing to about 8% of global anthropogenic CO_2 emissions. Over 70% of these emissions originate from reducing iron ore to pure iron, which is predominantly carried out in blast furnaces using carbon-based reducing agents [1]. Reducing iron ore using H_2 as a reducing agent presents a promising, environmentally friendly alternative for mitigating CO_2 emissions. Recent studies by Kumar et al. found that H_2 microwave plasmas can accelerate the reduction of iron ore by three times compared to thermal reduction at identical gas temperatures. This enhancement was ascribed to the presence of plasma-produced atomic H [2]. In this study, we investigate the effect of H atoms on 300 nm hematite thin films using an atmospheric pressure RF hydrogen plasma jet with gas temperatures near room temperature. This approach allows us to more readily separate thermal and radical-induced effects, measure the H atom flux on the thin film via mass spectrometry, and accurately quantify the role of H-atoms in hematite reduction. Additionally, this work aims to bridge a gap in the literature by focusing on temperatures below 400 °C.

2. Methods

In this study, we used an RF-driven atmospheric pressure plasma jet operating at a frequency of 13.56 MHz and modulated at a frequency of 20 kHz, with a duty cycle of 20% and an average power output of 1.4 watts. The process gas consists of a 4% H_2 and 96% Ar blend, supplied at 1 slm. To prevent oxygen diffusion, 2 slm of Ar sheath flow is employed around the process gas. The substrate was a 300 nm thick hematite thin film deposited on a silicon wafer in-house and was kept on a controlled heated surface at 318 °C. The hematite films were treated with the H_2/Ar plasma jet with a nozzle to substrate distance of 2 mm. For control trials, the films were subjected to the H_2/Ar jet with the plasma turned off. Following the treatment, the thin films were cooled to room temperature under an argon environment. X-ray diffraction (XRD) was performed to assess the quantitative reduction. Additionally, scanning electron microscopy (SEM) imaging is utilized to examine the effects of surface morphology and grain structure on the reduction process.

3. Results and Discussion

Fig. 1 shows a comparison between the thermal reduction of hematite thin films and plasma-assisted reduction at the same substrate temperature. In both scenarios, a fast initial rate of reduction is observed until 40% reduction is achieved, after which the reduction rate significantly decreases. Furthermore, the initial reduction rate for plasma-assisted reduction is 1.4 times faster than the thermal reduction case. This enhancement might be attributed to the increased diffusion rates of H atoms and their higher reduction potential compared to H_2. The quantification of the H atoms is ongoing.

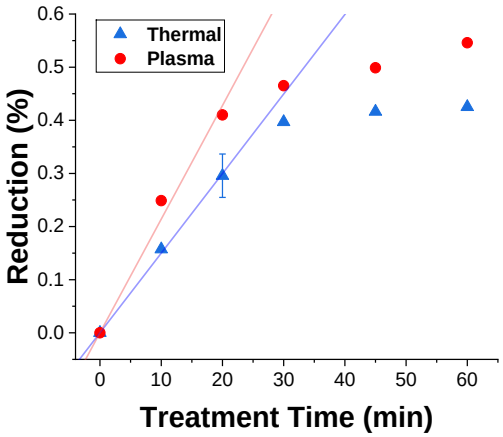

Fig. 1. Comparison between thermal and plasma assisted reduction of a 300 nm hematite film with a substrate temperature of 318 °C.

4. Conclusion

This study demonstrated that atomic hydrogen is capable of enhancing the reduction rate of hematite suggesting the rate limiting step during early stage of reduction is the reaction rate at the interphase of hematite and iron.

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References

[1] Jin, P., et al. *Resources, Conservation and Recycling* 117 (2017): 58-65.
[2] Kumar, S., et al. *Chem. Eng. J.* **472** (2023): 145025.