Experimental and thermodynamic limits of dissociative metal oxide reduction using microwave hydrogen plasma

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Abstract: We investigate the limits of dissociative metal oxide reduction using a hydrogen plasma. Six metal oxides exhibiting different reduction potentials with hydrogen are studied. It is found that nickel, iron, and zinc oxides are reduced to their metallic forms. Chromium oxide is reduced to a mix of Cr, CrO_x, and Cr_2O_3 particles, whereas manganese and silicon oxides are only partly reduced to lower oxidation state oxides. Thermodynamic calculations, using the Gibbs minimization approach to predict the equilibrium composition, agree with the experimental results, explaining the observed process limitations.

1. Introduction

Metal and alloy production from mineral oxides accounts for around 10% of global CO_2 emissions due to dependence on carbon-based reducing agents and energy sources [1]. Hydrogen plasma-based reduction is investigated as an alternative to carbon-based processes. Here, we investigate the process limits of dissociative metal oxide reduction using microwave hydrogen plasma. In dissociative reduction, a metal oxide is dissociated into gaseous metal and oxygen atoms, which are reacted with hydrogen to form solid metal and water vapor [2]. Theoretical and experimental investigations of six metal oxides, namely NiO, Fe_3O_4, ZnO, Cr_2O_3, MnO_2, and SiO_2, are carried out to identify the boundaries of the applicability of this process.

2. Methods

Metal oxide particles aerosolized in an Ar:H_2 mixture (90:10 volume %) are passed through the active plasma zone of a microwave atmospheric pressure plasma. The particles collected at the reactor exhaust, using a 500-mesh filter, are analyzed by X-ray diffraction (XRD), transmission electron microscopy (TEM), Raman spectroscopy, and X-ray photoelectron spectroscopy (XPS). Thermodynamic equilibrium calculations based on the Gibbs minimization approach are used to predict the gas phase composition in the plasma and the particle formation from the gaseous phase components.

3. Results and Discussion

Figure 1 shows the XRD spectra of untreated iron oxide particles and nanoparticles (NPs) formed after the plasma treatment. It is found that the iron oxide particles undergoing dissociative reduction are transformed to metallic NPs. Similarly, nickel and zinc oxides are reduced to their metallic NPs after plasma treatment. However, chromium oxide, Cr_2O_3, is only partly reduced to metallic Cr NPs along with Cr_2O_3 and CrO_x phase in the products. On the other hand, MnO_2 and SiO_2 are only reduced to MnO and to an amorphous $SiO_{x<2}$ matrix, with few embedded Si nanocrystals, respectively.

Thermodynamic calculations reveal strong agreement with experimental results. At a temperature of at least 2000 K, all oxides, except SiO_2, are predicted to exist predominantly as gaseous metal atoms in the plasma. However, whether the gaseous metal condenses to metal or metal oxide NPs depends on (i) the thermodynamic equilibrium product at condensation temperatures and (ii) the competition between oxidation kinetics on one hand with condensation and cooling rate on the other.

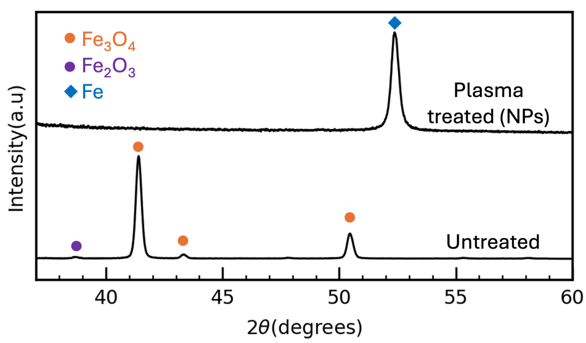

Fig. 1. XRD patterns of untreated iron oxides particles and NPs formed after plasma treatment.

4. Conclusion

We find that that the process can reduce NiO, Fe_3O_4, and ZnO completely to their respective metallic nanoparticles. Cr_2O_3 is reduced partially to a mix of Cr, CrO_x and Cr_2O_3 particles due to incomplete dissociation (~90%) in plasma and reoxidation in the downstream region of the reactor. MnO_2, though reduced to gaseous Mn in the plasma, recondenses to MnO at ~1800 K. On the other hand, SiO_2 dissociates to ~99% SiO and ~1% Si in the plasma zone, leading to an amorphous $SiO_{x<2}$ matrix in the products.

Acknowledgment

This work is supported by the University of Minnesota under the Doctoral Dissertation Fellowship and the Minnesota Environment and Natural Resources Trust Fund.

References

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