ON THE REDUCTION OF METAL OXIDES IN
NON-EQUILIBRIUM HYDROGEN PLASMAS

by

Hunter James Sceats
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Golden, Colorado

Date __________________________

Signed: _______________________________

Hunter J. Sceats

Dr. Patrick R. Taylor
Thesis Advisor

Golden, Colorado

Date __________________________

Signed: _______________________________

Dr. Angus A. Rockett
Professor and Department Head
Metallurgical and Materials Engineering
ABSTRACT

Metal oxides are some of the most widely-used source materials for the primary production of metals. However, the technologies currently used for the reduction of metal oxides can produce deleterious byproducts. Hence, there exists a need to develop improved processes for reducing metal oxides. Atomic hydrogen, consisting of dissociated hydrogen radicals, has the potential to be such a reagent: due to its high chemical potential, atomic hydrogen is naïvely predicted to be able to reduce even the most stable metal oxides. Additionally, the primary byproduct of these reductions (water) is chemically benign.

This research investigates the efficacy of atomic hydrogen (produced in a low-pressure microwave-frequency plasma) as a reducing agent for several metal oxide systems: copper oxide, molybdenum dioxide, titanium dioxide, and neodymium oxide. In situ thermogravimetric analysis is used to quantify the kinetics of the reduction reactions, while optical emission spectroscopy is employed to characterize the plasma. The experimental results indicate the existence of a finite depth-of-reaction in samples exposed to atomic hydrogen; i.e., only a thin surface region is affected by the hydrogen radicals. An analytical model is developed describing the evolution of this depth-of-reaction and its dependence on the plasma parameters. In order to avoid this depth-of-reaction constraint on the reduction, thin films of titanium and neodymium oxide were prepared on a variety of substrates by sol-gel and thermal oxidation techniques; ex situ analysis of these thin-films was conducted by means of grazing-incidence X-Ray diffraction and X-Ray photoelectron spectroscopy. A greater degree of reduction is observed in samples exposed to atomic hydrogen than in those exposed only to molecular hydrogen, but complete reduction is found to be substrate-dependent; atomic hydrogen is unlikely to be useful for the large-scale reduction of stable metal oxides.
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Figure D-40

XRD pattern for a thin film of Nd$_2$O$_3$ grown on a Ti substrate, exposed to atomic H under 200 W of applied power at 22 Torr, with flow rates of 650 SCCM H$_2$ and 10 SCCM Ar for 21 minutes. Reference patterns: TiH$_2$/98-016-4602; SiO$_2$/01-073-3461; TiO$_2$/98-020-0391; Ti/98-005-2522. The incident angle for this measurement was $\omega = 0.5^\circ$.
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CHAPTER 1
INTRODUCTION

Metal oxides are one of the most widely-used sources of the metals employed in industrial society today. As such, there is a need for the continuous improvement of the means by which metal oxides are reduced to their respective metals. This chapter provides an introduction to the methods currently used to produce a selection of metals from their oxides while identifying some of the drawbacks to those methods. Atomic hydrogen, as can be produced in nonequilibrium hydrogen plasmas, is subsequently introduced as an alternative means of reducing metal oxides. A brief justification of reasons to investigate an atomic-hydrogen based reduction approach is provided, and a scope of research for investigating the feasibility of this method is indicated. This chapter concludes by providing an overview of the structure of the dissertation as a whole.

1.1 Production of Metals from Oxides

Metals are one of the most important groups of materials in modern industrial civilization: attractive because of their strength, ductility, toughness, hardness, and formability, they are employed in large quantities for varied uses. The annual primary production of some of the most commonly-used metals is presented in Table 1.1. Given the size of the primary metals industry and the ubiquity of its products, the methods of production of these metals is of great significance to society.

Table 1.1: Annual primary production of some common metals in 2017, measured in metric tons (per year). Data obtained from (“Mineral Commodity Summaries 2018” 2018)

<table>
<thead>
<tr>
<th>Metal</th>
<th>Production (×10^6 tons)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron</td>
<td>1.2×10^9</td>
</tr>
<tr>
<td>Aluminum</td>
<td>6.0×10^7</td>
</tr>
<tr>
<td>Copper</td>
<td>2.0×10^7</td>
</tr>
<tr>
<td>Zinc</td>
<td>1.3×10^7</td>
</tr>
<tr>
<td>Lead</td>
<td>4.7×10^6</td>
</tr>
<tr>
<td>Nickel</td>
<td>2.1×10^6</td>
</tr>
<tr>
<td>Magnesium</td>
<td>1.1×10^6</td>
</tr>
<tr>
<td>Titanium</td>
<td>1.7×10^5</td>
</tr>
</tbody>
</table>
Primary metals are produced from ores which can be processed to yield the metals of interest. These ores contain the metallic elements within a variety of ore-bearing minerals. Metal oxide ores are one of the most common ore types: per (Rosenqvist 1983), iron, manganese, chromium, titanium, uranium, tin, and the metalloid silicon are produced predominantly from oxide ores. The most common ore of aluminum, bauxite, is an aluminum hydroxide bearing mineral, which is transformed to the intermediary product of aluminum oxide through the Bayer process. A portion of primary copper and nickel production begins with oxide ores. Some magnesium is also produced from a magnesium oxide intermediate (obtained through the calcination of dolomite) via the Pidgeon process (Vignes 2011a). In order to produce each of these metals from their respective ores, the metal species in these oxides must undergo a process of reduction in which their oxidation state is decreased. The reduction of metal oxides is accomplished in a variety of ways. Broadly, this process of reduction is accomplished either by applying an electrical potential or by introducing an appropriate reducing agent such as carbon, hydrogen, or another metal.

The current methods employed for the production of metals from oxide ores can have deleterious side effects such as the production of unwanted byproducts. An example of one such unwanted byproduct (carbon dioxide) occurs during the carbothermic reduction of iron oxide, both in the production of pig iron and in the production of directly-reduced iron. The carbothermic reduction of iron oxide to produce pig iron is conducted in blast furnaces, counter-current shaft furnaces which produce a molten metal product. Carbon sources are provided both by metallurgical coke and by auxiliary fuels injected through the tuyères of the blast furnace; more than half of the steel manufactured globally in 2011 was produced using pig-iron from blast furnaces (Vignes 2011b). The carbothermic reduction of iron oxides is also conducted in
direct reduction processes, in which iron oxide is reduced to solid iron directly, without passing through the liquid state. A variety of direct reduction processes exist, including the well-known Midrex process. The Midrex process involves the solid-state reduction of iron oxide by a combined carbon monoxide/hydrogen feed-gas in a vertical shaft furnace (Vignes 2011b). Both direct reduction processes (at least, those which do not rely entirely on hydrogen gas as the reducing agent) as well as the reduction processes carried out in blast furnaces result in the emission of carbon dioxide as a byproduct. This can be understood by examining the overall reduction reaction:

$$\text{Fe}_2\text{O}_3(s) + 3\text{CO}(g) = 2\text{Fe}(s) + 3\text{CO}_2(g)$$

These carbon dioxide emissions are considered deleterious by some because of a proposed causal connection between increases in the carbon dioxide concentration of the atmosphere and increases in the average global temperature via the greenhouse effect. The global iron and steel industry is directly responsible for as much as 7% of anthropogenic carbon dioxide emitted annually (Y. Kim and Worrell 2002), a point which has motivated some political entities to propose the introduction of carbon taxes and tariffs to disincentivize the magnitude of those emissions (The Economist 2017). Should these carbon taxes and tariffs be enacted, an incentive will be created for investigating new methods of reducing iron oxide which reduce the emission of carbon dioxide.

The production of the rare-earth metals via a molten-salt electrolysis technique can also result in the production of deleterious species, such as fluorinated hydrocarbons. The rare-earth ore minerals are generally not oxides: monazite and xenotime are rare-earth phosphates, while bastnaesite is a rare-earth fluorocarbonate. During the course of processing these ores, however, rare-earth oxides are often produced as an intermediate (Gupta and Krishnamurthy, n.d.). These
intermediate oxide products are often reduced to their respective metals by electrowinning in a lithium fluoride/rare-earth fluoride molten salt. These electrowinning cells make use of a carbon anode. Reactions between the carbon anode and the fluoride salt can result in the formation of perfluorocarbons (PFCs) such as CF₄ and C₂F₆. Efforts to reduce the emission of PFCs are underway since they are considered to be potent greenhouse gases (Liu et al. 2014). The molten-salt electrolysis of rare-earth oxides also faces current-efficiency limitations, as well as limitations in the solubility of the rare-earth oxides within the fluoride melts (Anderson 2015). Thus, there exists an incentive for investigating alternative methods of reducing the rare-earth metals to their oxides.

Some refractory metals—such as tungsten and molybdenum—are produced by reduction of their oxides by hydrogen. Once again, these metal oxides are intermediate products formed during the processing of predominantly non-oxide ores (e.g., wolframite and scheelite, iron-manganese and calcium tungstates, in the case of tungsten and molybdenite, a sulfide, in the case of molybdenum). In many respects, hydrogen is an attractive reducing agent due to the benign nature of the byproduct of this reduction reaction: water. While water is an improvement over some of the reduction byproducts discussed previously, the reduction of these metal oxides by hydrogen must be carried out at elevated temperatures for efficient industrial operation. In the so-called “second-stage” reduction of molybdenum dioxide to molybdenum, molybdenum dioxide powder is placed in boats and loaded into a push-pull tube furnace. The furnace is maintained at a temperature in the range of 1000 to 1100 degrees Celsius. The gaseous environment in the furnace is maintained with a continuously flowing, countercurrent, hydrogen gas stream possessing a frost point of approximately -20 degrees Celsius. The residence time of the powder within the furnace is approximately two to three hours (Kangsadan 2004). These
stringent operating requirements—high temperatures, pure reagent gas streams, and relatively long residence times—impose conditions which make the production of these refractory metals more expensive. Hence, the development of reduction technique which avoids or loosens some of these limitations would constitute a process improvement for the production of refractory metals.

The methods of production for lightweight structural metals such as titanium and zirconium are expensive due to the high stability of the oxides of these metals. These metals are generally won from their oxides by means of the Kroll process. This is a two-stage reduction process. For the case of titanium, the first stage involves the carbochlorination of titanium dioxide, often in a fluidized bed, resulting in the production of a volatile TiCl$_4$(g) species. This volatile chloride species is introduced into a retort heated to approximately 900 degrees Celsius and partially filled with molten magnesium. The magnesium acts to reduce the titanium chloride, resulting in the formation of titanium-magnesium metal sponge via the reaction:

$$\text{TiCl}_4(\text{g}) + 2\text{Mg}(\text{l}) = \text{Ti}(\text{s}) + 2\text{MgCl}_2(\text{l})$$

This sponge must be vacuum distilled, crushed, and re-melted to produce titanium metal ingots (Vignes 2011a). The Kroll process is highly energy-intensive, consuming approximately 100 kilowatt hours per kilogram of titanium produced (Klausner 2015). Furthermore, a continuous process would be preferable the batch-reaction Kroll process. Thus, there is clearly a potential for the development of alternative methods for the production of metals such as titanium and zirconium.

1.2 Atomic Hydrogen in Non-Equilibrium Plasmas

Atomic hydrogen describes the state of dissociated hydrogen radicals which are not bonded in molecules of H$_2$. These hydrogen atoms have a high chemical potential, as can be
ascertained by considering their large free energy of formation of \( \Delta G_{f,600^\circ C}^\circ = 172.6 \) kilojoules per mole (Roine 2002). With regard to the reduction of metal oxides, employing dissociated hydrogen in the place of molecular hydrogen results in a large increase in the thermodynamic potential for a reduction reaction to proceed. Considering the reduction of titanium dioxide by both molecular and atomic hydrogen, it is possible to write:

\[
\begin{align*}
\text{TiO}_2 + 2\text{H}_2(g) &= \text{Ti} + 2\text{H}_2\text{O}(g), \quad \Delta G_{\text{rxn,600^\circ C}}^\circ = 385.8 \text{ kJ/mol} \\
\text{TiO}_2 + 4\text{H}(g) &= \text{Ti} + 2\text{H}_2\text{O}(g), \quad \Delta G_{\text{rxn,600^\circ C}}^\circ = -304.5 \text{ kJ/mol}
\end{align*}
\]

Clearly, the much more negative Gibbs free energy of reaction for the reaction of titania with atomic hydrogen indicates that atomic hydrogen is capable of reducing metal oxides which cannot be effectively reduced by molecular hydrogen. In addition to the high chemical potential of this species (a thermodynamic consideration), atomic hydrogen should also be highly reactive from a kinetic perspective: it is a radical species which possesses an unfilled electronic orbital, and is therefore amenable to forming new chemical bonds (Daniel Edward Bullard 1993). Thus, preliminary examination of atomic hydrogen indicates some of its attractive features as a reducing agent: it produces water as a reaction byproduct just like molecular hydrogen, but it should be capable of reducing a wider range of metal oxides than is molecular hydrogen; furthermore, the fact that it is a chemical radical should improve the rate of these reduction reactions.

Atomic hydrogen can be formed in several ways. The first involves thermal dissociation of molecular hydrogen: at temperatures of approximately 3500 degrees Celsius, atomic hydrogen becomes the predominant hydrogen species, with molecular hydrogen accounting for a smaller fraction of the total hydrogen content at increased temperatures, as shown in Figure 1.1 on the next page.
Atomic hydrogen can also be produced in non-equilibrium plasma discharges by applying electrical fields to hydrogen gas; these discharges are discussed further in Chapter 3. These plasmas are capable of dissociating between 40% and 90% of the hydrogen present in the discharge per (Shaw 1959), at gas temperatures of only several hundred degrees Celsius (Daniel Edward Bullard 1993). This points to several advantages of employing a non-equilibrium plasma to produce atomic hydrogen over a thermal dissociation method, including the potential for higher thermal efficiency as well as less stringent requirements for materials of construction, given the lower temperatures involved.

Figure 1.1: Speciation of hydrogen at a pressure of 1 bar; calculated using (Roine 2002).
1.3 Justification for Research

Given the importance of metals to industrial society and the large fraction of metals which are won either from oxide ore minerals or from metal oxide intermediates, the development of a technique which improves on current reduction methods—by lowering the production of harmful byproducts, improving the rates of reaction, or by lowering energy requirements—would be a contribution to the metallurgical industry. Preliminary thermodynamic analysis suggests that even the most stable metal oxides can be reduced in conditions readily achievable in a nonequilibrium hydrogen plasma. For example, if a hydrogen plasma discharge operating at 7.6 Torr exhibits 1% dissociation (i.e., one out of every one-hundred hydrogen molecules is dissociated into two hydrogen atoms) then there will be a partial pressure of approximately $2 \times 10^{-4}$ atmospheres of atomic hydrogen within the discharge. Examination of Figure 1.2 indicates that under these conditions, titanium hydride should be the stable titanium species for the range of water partial pressures depicted in the figure. Thus, this analysis predicts that titanium dioxide placed within the reactor should have a thermodynamic potential to convert to titanium hydride. Titanium hydride has important uses in its own right (e.g., as a sintering aid and as a metal-foaming agent) and can also be converted to titanium metal via a vacuum-degassing process (Ivasishin and Moxson 2015).

Given the attractive features of a non-equilibrium hydrogen plasma-based reduction process, it is important to validate the effectiveness of such a process. This research attempts to confirm the feasibility of an atomic-hydrogen-based reduction process, and in doing so, to add to the fundamental knowledge-base of the relevant physico-chemical processes.
1.4 Scope of Research

This research investigates the reduction behavior of metal oxides in non-equilibrium hydrogen plasmas. As discussed in Chapter 3, the qualification “non-equilibrium” restricts this discussion to low-pressure plasmas (below 70 Torr) which possess gas temperatures in the range of several hundred degrees Celsius. The reduction of metal oxides in equilibrium or thermal plasmas (i.e., those with much higher gas temperatures on the order of several thousand degrees Celsius, generally occurring at pressures of approximately one atmosphere) is not discussed. This restricts the content of this research to situations in which an appreciable population of metastable excited species (such as dissociated hydrogen atoms) are produced; it does not include situations in which atomic hydrogen is the thermodynamically-stable hydrogen species.

This work attempts to evaluate the efficacy of these non-equilibrium hydrogen plasmas at reducing metal oxides. This efficacy is evaluated in several ways. First, it is important to
determine which metal oxides can be reduced to their respective metals (or hydrides, as discussed previously) by application of a non-equilibrium hydrogen plasma. Second, given the superficial nature of reduction observed in previous experimental studies employing atomic hydrogen (discussed in more detail in Chapter 2), it is incumbent on this research to determine the maximum thickness of a metal oxide layer that can be reduced by these non-equilibrium plasmas. Third, this research should indicate the rates of reduction achievable in these plasma discharges, thereby allowing for a comparison with other reduction methods, including the comparison between atomic and molecular hydrogen.

These studies focus on the reduction behavior of several representative metal oxide systems. The first, cupric oxide, is a classic oxide system; the reduction of cupric oxide by molecular hydrogen has been studied extensively in the past (see (Patrick R. Taylor 1978; J. Y. Kim et al. 2003; Rodriguez et al. 2003; Jelić, Tomić-Tucaković, and Mentus 2011; Yamukyan, Manukyan, and Kharatyan 2009)). Hence, the investigation of the reduction behavior (specifically, the kinetics of the reduction reaction) of copper oxide will allow for the direct comparison between atomic and molecular hydrogen. That being said, copper metal is not produced from copper oxide by reduction with hydrogen on an industrial scale; copper is generally won from oxide ores by hydrometallurgical means.

The second oxide system of study, molybdenum dioxide, provides another aspect to this research by investigating an oxide which is reduced by molecular hydrogen on an industrial scale. The reduction process employing molecular hydrogen must be carried out at high temperatures (in the range of 1100 degrees Celsius). Preliminary thermodynamic analysis (discussed further in Chapter 4) indicates that the reduction of molybdenum dioxide by atomic hydrogen should be possible at considerably lower temperatures. Thus, the investigation of the
reduction of molybdenum dioxide by atomic hydrogen sheds insight on the possible implementation of a microwave-induced discharge as a means of effecting a process improvement of immediate industrial interest.

The third and fourth systems of study, titanium dioxide and neodymium oxide, are oxide systems which cannot be reduced to their respective metals by molecular hydrogen under readily attainable conditions, as can be seen by examining the Gibbs free energies of reduction. Thus, these systems provide a test of the efficacy of atomic hydrogen at reducing highly stable metal oxides. This satisfies the research goal of attempting to determine which metal oxides are amenable to processing by atomic hydrogen, while also providing insight into the superficial nature of the reduction reaction. Given that both neodymium and titanium readily form hydrides, studies of these systems will also involve investigation into the mechanism of hydride formation and the utility of a plasma-based process for producing these metal hydrides.

**1.5 Organization of Dissertation**

This dissertation is organized in eleven chapters. Chapter 1 constitutes an introduction to the research, delineates the scope of investigation to be conducted, and provides motivation for this course of inquiry. A review of the literature relevant to the reduction of metal oxides by atomic hydrogen is presented in Chapter 2. Chapter 3 consists of a brief overview of the background knowledge necessary for understanding the physical phenomena relevant to the processing of materials in non-equilibrium hydrogen plasmas. Chapter 4 outlines the theoretical considerations relevant to the metal oxide systems investigated in the course of this research, including a thermodynamic analysis of systems involving metastable concentrations of atomic hydrogen as well as kinetic analyses of the relevant reactions. Details of the methods and procedures employed in the experiments are specified in Chapter 5 while the experimental
reactors are characterized in Chapter 6. Chapter 7 through 10 present the experimental results and discussion for each of the systems studied (copper oxide in Chapter 7, molybdenum dioxide in Chapter 8, titanium oxide in Chapter 9, and neodymium oxide in Chapter 10). Chapter 11 is a conclusion to the dissertation, in which the contributions of this research are summarized, its shortcomings are identified, and recommendations for future research are enumerated. Additional supporting data and derivations not essential to the main lines of discussion are presented in the appendices.
CHAPTER 2
LITERATURE REVIEW

A survey of the literature was conducted to review previous investigations into the use of atomic hydrogen as a reducing agent. The knowledge gained from this review served to motivate the specific goals of this research. Note that this discussion is constrained to consider atomic hydrogen produced in low-pressure, non-equilibrium hydrogen plasmas, in contrast with the more extensive research which has been conducted on the applications of high-pressure, “thermal” plasmas. This distinction is discussed further in chapter 3.

2.1 Atomic Hydrogen as a Reducing Agent

Chemists and physicists have studied low-pressure hydrogen plasmas for an extended period of time, starting as early as the 19\textsuperscript{th} century with spectroscopic studies of discharge tubes, e.g., (Ferry 1898). Investigations into the properties of these plasmas relevant to extractive metallurgy—specifically, the capacity of these discharges to reduce metal oxides—are relatively more recent, beginning with (Wood 1922).

Many previous investigators such as (D R Sadedin 2006), (Daniel Edward Bullard 1993), and (Sabat et al. 2014) have pointed to atomic hydrogen as an attractive reducing agent due to the highly negative Gibbs free energy of reaction for these reductions. Consider, for example, the reduction of molybdenum dioxide by molecular and atomic hydrogen, respectively (Roine 2002):

\[
\text{MoO}_2 + 2\text{H}_2(\text{g}) = \text{Mo} + 2\text{H}_2\text{O(}\text{g}), \quad \Delta G^{\circ}_{\text{rxn}}(298 \text{ K}) = 76.34 \text{ kJ/mole}
\]

\[
\text{MoO}_2 + 4\text{H}(\text{g}) = \text{Mo} + 2\text{H}_2\text{O(g)}, \quad \Delta G^{\circ}_{\text{rxn}}(298 \text{ K}) = -736.80 \text{ kJ/mole}
\]

Clearly, the reduction with atomic hydrogen has a negative standard Gibbs free energy of reaction while the reduction with molecular hydrogen is positive. This highly negative free energy of reaction has proved sufficient to spark the interest of the aforementioned studies in the use of
atomic hydrogen as a reductant for the so-called “refractory oxides.” Here, the refractory nature of these oxides refers to the difficulty encountered in reducing them due to a highly negative standard Gibbs free energy of formation and not in the context of, e.g., thermally insulating oxides which are resistant to degradation at high temperatures. That being said, the argument based on comparing the Gibbs free energies of reaction with molecular and atomic hydrogen is naïve in the sense that the configuration resulting from the reduction with atomic hydrogen can react via the “reverse” re-oxidation reaction:

$$\text{Mo} + 2\text{H}_2\text{O}(g) = \text{MoO}_2 + 2\text{H}_2(g), \quad \Delta G^\circ_{\text{rxn}}(298 \text{ K}) = -76.34 \text{ kJ/mole}$$

The significance of this re-oxidation reaction will be subsequently revisited.

Brief summaries of past investigations into the utilization of atomic hydrogen as a reducing agent are provided next. These summaries are grouped based on the nature of the oxide studied: non-refractory oxides (i.e., those which can be reduced by molecular hydrogen under the conditions investigated, as predicted by a negative standard Gibbs free energy of reaction with molecular hydrogen gas), refractory oxides (those which are unable to be reduced by molecular hydrogen, possessing a positive standard Gibbs free energy of reaction with \( \text{H}_2 \) under the conditions investigated), and volatile oxides (those which are volatile in their standard state, or possess a suboxide or hydroxide which has an appreciable partial pressure relative to the pressures at which the experiments are conducted).

### 2.2 Reduction of Non-Refractory Metal Oxides

The communication in (Wood 1922) represents one of the earliest (possibly the earliest) report of the reducing capabilities of atomic hydrogen. This discovery was incidental to Wood’s interests in the spectroscopic properties of hydrogen discharges: a small amount of wax containing tin oxide fell into the discharge chamber and was partially reduced to tin metal. Wood
also remarks on the ability of atomic hydrogen to cause some solids to incandesce; he attributes this effect to a catalytic reaction in which the solid (remaining chemically unchanged during the course of the reaction) induces atomic hydrogen to recombine into molecular hydrogen, thereby releasing a great deal of energy. This recombination can be represented using a generic metal oxide “MeO” and can be quantified by writing using data from (Roine 2002):

$$2\text{H}(g) + \text{MeO} = \text{MeO} + \text{H}_2(g), \quad \Delta H^\circ_{\text{rxn}}(298 \text{ K}) = -435.68 \text{ kJ/mole}$$

Wood also reports that an oxidized piece of copper was reduced to provide a shiny metallic surface in his discharge. These early studies in the reduction of non-refractory oxides were continued by (Bonhoeffer 1924), replicating Wood’s results in reducing the oxides of copper and tin and extending the metals studied by successfully reducing the oxides of bismuth, lead, mercury, and silver. These early studies were qualitative in nature and did not attempt to quantify either the rate or extent of reaction, or the dependence of these variables on experimental parameters.

(Sakamoto and Ishibe 1980) provides a more recent study in which non-refractory oxides of copper, nickel, and iron were successfully reduced in an electron-cyclotron resonance (ECR) hydrogen plasma. Sakamoto used a clever experimental technique in which he grew oxide layers on metals to produce thin-film interference fringes; knowledge of the refractive index of the oxide layer allowed him to quantify the thickness of the oxide film, and the rate of disappearance of the fringes allowed him to evaluate the rate of reaction. While the authors provide a detailed description of the plasmas parameters and experimental parameters they employed, it is not clear to what extent the removal of this oxide layer corresponds to in-situ solid state reduction or whether the oxide layer is merely removed or modified by, e.g., sputtering. Furthermore, no results are reported regarding the morphology or chemical composition of the film either before
or after reduction. That is to say, the qualitative appearance/disappearance of colors on the samples was employed as a proxy for the oxidation/reduction of the sample without more rigorous investigation.

The investigation of the reduction of non-refractory metal oxide thin films was continued by (Sawada et al. 1999) with their study of the reduction kinetics of cuprous oxide thin films in an atmospheric pressure helium/hydrogen discharge. The authors used Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS) to quantify the depth of reduction after different exposure times. They assumed: (1) diffusion of atomic hydrogen through the reduced product layer was the rate-limiting step of the reaction; (2) there was negligible recombination of atomic hydrogen within the copper layer; and (3) the movement of the reaction interface was much slower than the diffusion of hydrogen. Using these assumptions, Sawada et al. thereby derived a kinetic equation describing the depth of the reduced layer with respect to time:

\[ x_i = \left( \frac{D_H C_{H_0}}{C_{Cu_2O}} \right)^{1/2} t \]  

where \( x_i \) is the depth of the reduced layer, \( D_H \) is the diffusion coefficient of atomic hydrogen in the reduced product layer, \( C_{H_0} \) is the molar concentration of atomic hydrogen at the surface of the product layer, \( C_{Cu_2O} \) is the molar concentration of cuprous oxide within the film, and \( t \) is the time of reaction. Their data agreed roughly with this model, as depicted in Figure 2.1. The authors attribute the slight delay in the onset of reduction to a nucleation effect. They also report the presence of XPS peaks indicative of O-H bonds at the reaction interface, from which they conclude the reduction mechanism takes place in two distinct steps: (1) the reaction of oxygen ions with hydrogen to form hydroxide ions followed by (2) the reaction of hydrogen with the
hydroxide ions to form water (presumably with the attendant reduction of the copper ion occurring at this step). The fact that there was a detectable build-up of these hydroxide ions does seem to contradict the assumption that the diffusion of hydrogen atoms was the rate-limiting step of this reaction.

![Figure 2.1: Reduction kinetics of thin films of cuprous oxide exposed to hydrogen plasma; adapted from (Sawada et al. 1999). Experimental parameters: 200 W of applied RF power, 50 SCCM H₂, 5000 SCCM He, electrode temperature of 100 °C; conducted at “atmospheric pressure.”](image)

Sabat et al.’s studies of the reduction kinetics of iron oxide (Rajput et al. 2014), cobalt oxide (Sabat et al. 2015), and copper oxide (Sabat, Paramguru, and Mishra 2016) in non-equilibrium hydrogen plasmas are some of the most recent investigations of the reduction of non-
refractory oxides by atomic hydrogen. The review paper (Sabat et al. 2014) also provides a thorough overview of experimental investigations and theoretical considerations to date.

The investigation of the reduction of iron oxide (Rajput et al. 2014) consists of a study of the effects of varying the applied microwave power (750 W-1900 W), the hydrogen flowrate (100 SCCM-500 SCCM), the reactor pressure (12 Torr to 56 Torr), the sample temperature (300 °C to 1150 °C), and the sample dimensions (3 mm thickness to 9 mm thickness) on the kinetics and extent of reduction of hematite pellets. The kinetics of the reaction are measured by weighing the samples after different exposure times and by a semi-quantitative comparison of the intensity of XRD peaks of the iron and the various iron oxides (Fe$_2$O$_3$, Fe$_3$O$_4$, and FeO). The authors conclude that: while the surrounding (gas-phase) temperature in the gas phase does not have a strong influence on the rate of reduction, the interface (pellet) temperature does influence the rate of reduction; hydrogen utilization is improved at low flowrates; increasing the pressure increases the extent of reduction “to a certain degree”; and the microwave power density (the ratio of input power to plasma volume) is the key controlling parameter which affects the interface temperature.

The study (Rajput et al. 2014) exhibits loosely controlled experimental variables (i.e., within a given experiment under nominally constant conditions, the applied power varied from 800 W to 1300 W) and some of the authors’ conclusions are not convincingly supported: their discussion regarding activation energy employs a novel $k'$ factor (representing the ratio of the percent reduction per cubic meter of hydrogen passed through the reactor) which they assert functions as an effective proxy for the Arrhenius rate constant, despite the fact that the other parameters (i.e., flow rate, pressure, and applied power) “were allowed to vary while keeping the temperature constant.” It does not seem justified to conduct an Arrhenius-type rate analysis while
flow rate and pressure are allowed to vary, since variations in these parameters could affect the mass transfer of products and reagents to/from the pellet, thereby confusing the effects of changing the temperature with the variation of the other parameters. Furthermore, the manner in which the hydrogen flowrate and pressure were varied does not allow for a clear understanding of the effects of changing these parameters. The pressure was allowed to increase throughout the course of the reaction, producing a transient effect which was not accounted for. Similarly, the effect of flow rate variations was studied by delivering a constant volume of hydrogen at different rates with correspondingly varied times (i.e., higher flowrates were delivered for shorter time periods to expose the sample to a constant volume of hydrogen, after which the extent of reaction was measured). This arrangement does not allow for an explicit measurement of the effect of a higher flow rate on the extent of reaction after a given period of time. A consideration of these experimental weaknesses leads one to conclude that the study (Rajput et al. 2014) does not provide sufficient information for the development of a mathematical model for understanding the reduction process.

Sabat et al.’s investigations continue in (Sabat et al. 2015) with the experiments on the reduction of cobalt oxide $\text{Co}_3\text{O}_4$. The authors employed the same experimental apparatus as in the previous study, varying the chamber pressure (14 Torr to 22 Torr), interface temperature (550 °C to 766 °C), and hydrogen flowrate (70 SCCM to 150 SCCM) and examining the impact of these variables on the rate of reduction. Since these experiments were conducted at a constant applied power of 750 W, it seems reasonable to assume that the interface temperature was varied by adjusting the flowrate of cooling water applied to the sample holder, although this is not explicitly stated. The rate of reduction was quantified by removing the samples from the reactor and measuring their weights after set periods of time had elapsed. These experiments exhibited
similar temporal variations of both temperature and pressure to those present in the authors’ study (Rajput et al. 2014).

Sabat et al. also construct a model in (Sabat et al. 2015) describing the kinetics of the reaction by appealing to the assumption that the chemical reaction is the rate-limiting step for the overall heterogeneous kinetics. This analysis results in the equation

\[ X = \frac{kC_{H_2}}{4H\rho_B(1-\varepsilon)}t \]  \hspace{1cm} (2.2)

where \( X \) is the extent of reaction, \( k \) is the rate constant for the chemical reaction, \( C_{H_2} \) is the concentration of hydrogen, \( t \) is the elapsed reaction time, \( H \) is the initial height of the pellet, \( \rho_B \) is the molar density of the initial oxide, and \( \varepsilon \) is the initial porosity of the pellet. However, the authors seem to contradict their assumption that the chemical reaction is the rate-limiting step of the overall mechanism when they conclude that their calculated activation energies of 26.2 kilojoules per mole (presumably, kilojoule per mole of cobalt) and 13.3 kilojoules per mole are too low for chemical reaction to be the rate-limiting step, indicating instead that some form of diffusion is the rate-limiting step.

Sabat et al. also study the reduction of copper oxide in their publication (Sabat, Paramguru, and Mishra 2016). The authors varied the applied microwave power (600 W to 750 W) and the hydrogen flow rate (50 SCCM to 150 SCCM), with pressures in the range of 6.7 Torr to 20.3 Torr. The authors measured the sample-gas interface temperature, the reactor pressure, and the mass change of the sample. The mass change of the samples was measured by removing the samples from the reaction chamber after set exposure times and weighing them on an analytical balance. These samples were also characterized using X-ray diffraction. These
experiments exhibited the same transient evolution of temperature and pressure present in [10] and [11].

Sabat et al. assert that the reduction reaction occurs stepwise, via the sequential reduction from CuO to Cu₄O₃ to Cu₂O to Cu. They base this conclusion on the X-ray diffraction patterns taken at intervals during the reaction. However, the peaks corresponding to the two intermediate oxides are much weaker in intensity than those corresponding to CuO and to Cu, such that the direct conversion from CuO to Cu seems to predominate. Furthermore, it is not clear whether these X-ray diffraction patterns are produced by grinding the entire sample to produce a homogeneous powder or if they are obtained from a surface analysis of the intact sample. The authors calculate an activation energy of the reaction for the overall reduction reaction of 75.6 kilojoules per mole (presumably kilojoules per mole of copper), asserting that the participation of atomic hydrogen has contributed to the lowering of the activation energy relative to that for the reduction of copper oxide by molecular hydrogen. However, the authors did not make an attempt to measure the activation energy of the reaction with molecular hydrogen in their experimental setup; rather, they merely referenced the values obtained by other authors, which were obtained using different samples, geometries, and experimental protocols.

Sabat et al. make numerous references to the presence of an “induction period” (i.e., an initial period during which the rate of reaction is quite slow). Due to the low-temporal resolution of the reaction kinetics (i.e., the mass change is evaluated every 300 seconds, while the overall reaction can be completed in as little as 900 seconds), the existence of the induction period is not convincingly proven. Additionally, the authors refer to a connection between the induction period and the autocatalytic behavior of the reaction (where an autocatalytic reaction refers to one which experiences a period of increasing rate during the course of the reaction) as resulting
from the formation of active sites for the adsorption and dissociation of molecular hydrogen, following (J. Y. Kim et al. 2003). However, they do not take into account the transient temperature and pressure effects on the rate of reaction (resulting from the initial heating of the reactor following ignition of the plasma). They only briefly mention the exothermic nature of the reduction reaction. The authors attempt to fit their data to Avrami-Erofeev kinetic model of the form

\[ [-\ln(1 - \alpha)]^{1/n} = k_{\text{app}} \times t \]  

(2.3)

where \( \alpha \) is the fractional extent of reduction, \( k_{\text{app}} \) is the apparent rate constant, \( t \) is the elapsed time, and \( n \) is the Avrami parameter, determined by the authors to have a value of about 3. The authors also present optical emission spectra in the range of 306 nanometers to 320 nanometers. They assert that the observed emission peaks in this region indicate that a hydroxyl species is being formed during the induction period.

2.3 Reduction of Refractory Metal Oxides

McTaggart discusses the reduction of refractory metal oxides in his monograph (McTaggart 1967). He references the partial reduction of TiO\(_2\) and V\(_2\)O\(_5\) to lower valency forms (i.e., suboxides) in hydrogen plasmas. He also refers to qualitative changes in color that can be observed upon the exposure of MoO\(_3\) and WO\(_3\) to atomic hydrogen (e.g., MoO\(_3\) turns a blue color when exposed to atomic hydrogen). Additionally, McTaggart describes the formation of “hydrogen bronzes” upon the exposure of certain refractory oxides to hydrogen plasmas. These hydrogen bronzes are golden colored compounds that possess metallic conductivity; they are named in analogy to the “bronzes” formed by the implantation of alkali metal ions into certain metal oxide structures (e.g., WO\(_3\)). ZrO\(_2\), TiO\(_2\), and HfO\(_2\) formed hydrogen bronzes (the former two with approximate stoichiometries of H\(_{0.2}\)Zr\(_{1.0}\)O\(_{1.7}\) and H\(_{0.2}\)Ti\(_{1.0}\)O\(_{1.3}\)) upon exposure to
hydrogen discharges, whereas ThO₂, Al₂O₃, and BeO₂ did not. These bronzes were only formed in microwave discharges, not in radio-frequency (RF) discharges.

Bullard’s dissertation (Daniel Edward Bullard 1993) and publications [15], [16] provide an in-depth description of his work investigating the reduction of both TiO₂ and of FeTiO₃ in non-equilibrium hydrogen plasmas. In these studies, thin beds of packed powder (about 5 millimeters in thickness) were exposed to hydrogen plasmas with applied microwave powers in the range of 400 W to 1200 W and pressures in the range of 6 Torr to 26 Torr. The temperature of the powder beds was measured using both a pyrometer and a shielded, grounded thermocouple and ranged from about 500 °C to about 900 °C. The extent of reaction was quantified by means of ex situ X-ray diffraction using a semi-quantitative external-standard-based method. This method has some weaknesses in that it is unable to specify the exact degree of reduction of a sample (i.e., it can only identify the relative proportions of TiO₂ and Ti₂O₃) and it cannot identify non-stoichiometric or amorphous phases. In particular, this means that it cannot distinguish between phases of the form TiO₂-y and TiO₂-x, where 0<y<0.5 and 0.5<x<1. A mass-spectrometer also provided kinetic information regarding the production of water vapor during the course of the reaction.

Qualitatively, Bullard describes the formation of a thin black layer (at most 1 millimeter in thickness) at the surface of the powder bed. Below this lay a gray layer, underneath which lay the unreacted starting material; this arrangement is depicted in Figure 2.2.

The black layer is reduced to at most 60% (by weight) Ti₂O₃; the XRD signal of the initial TiO₂ decreases over time. Since the sum of the fractional contributions of the components (TiO₂ and Ti₂O₃) does not always equal unity, Bullard concludes that the remainder of the layer
consisted of some non-stoichiometric (or possibly amorphous) titanium oxide, which he labels TiO$_{2-x}$. Bullard concludes that the active species within the plasma are responsible for the formation of the black layer, while molecular hydrogen is responsible for the lower degree of reduction observed in the underlying gray region. He also suggests that the water vapor produced in the underlying gray region prevents an increased degree of reduction past Ti$_2$O$_3$ by means of the re-oxidation reactions, e.g.

$$2\text{Ti}_3\text{O}_4 + \text{H}_2\text{O}(g) = 3\text{Ti}_2\text{O}_3 + \text{H}_2(g)$$

Bullard notes that the thickness of the black surface layer remained constant with reaction time and was fully formed after approximately five minutes of exposure to the plasma; this period corresponds to the time during which he observed the largest water signal on the mass spectrometer. On the other hand, the thickness of the underlying gray layer increased with reaction time. For a constant reaction time, the thickness of the gray layer increased with pressure, applied power, and sample temperature. When the gray layer has displaced the entirety of the unreacted white layer, the Ti$_2$O$_3$ signal from the black surface layer began to decrease in intensity, as depicted in Figure 2.3. Bullard interprets this as the further reduction to a nonstoichiometric oxide phase of the form TiO$_{2-x}$ with 0.5<x<1. This reduction is only possible because there is no further production of water vapor from the reduction reaction occurring in the underlying gray region.
Another notable conclusion of Bullard is the influence of the electrical potential of a solid sample undergoing plasma processing: during studies on the chlorination of TiO$_2$ in a nonequilibrium plasma, he found that the reaction did not proceed at an appreciable rate unless a connection was made between the sample holder and an electrical ground (with a corresponding electrode placed above the sample, within the plasma). Bullard also emphasizes that (theoretically) the electric-field-to-pressure ratio determines the degree of dissociation of hydrogen, though he does not find the correlation he expected between this ratio and the rate of reduction.

Figure 2.3: Weight percent TiO$_2$ and Ti$_2$O$_3$ versus exposure time to plasma, as determined by XRD; adapted from (Daniel Edward Bullard 1993). The plasma was maintained with an applied power at 800 W and a total pressure of 26 Torr. Bullard attributes the gradual decline in the Ti$_2$O$_3$ signal to the production of a non-stoichiometric phase of the form TiO$_{2-x}$, with 0.5<x<1.

Huet et al. report on the reduction of thin films of titanium dioxide in atmospheric pressure plasmas consisting of 1 to 10% hydrogen, with the remainder of the gas stream being
composed of helium (Huet et al. 2005). They report reduction to TiO to a depth of four micrometers and reduction to Ti$_2$O$_3$ to five micrometers deeper, as determined by XRD and grazing-angle XRD (GAXRD), following an exposure time of four hours. Sample temperatures investigated were in the range of 707 °C to 817 °C.

Sakamoto and Ishibe’s study (Sakamoto and Ishibe 1980) referenced earlier also investigates the reduction of thin films of molybdenum and titanium oxides. These oxides were grown on their respective metal coupons by means of localized heating in atmosphere. Note that the particular identities of the oxides (i.e., MoO$_3$ versus MoO$_2$, or TiO$_2$ versus Ti$_3$O$_4$) were not determined empirically, nor were they characterized by means other than visual inspection. The titanium oxide film (assumed to be TiO$_2$) was estimated to be 177 nm thick, while no estimate was given for the thickness of the molybdenum oxide film. These films were reduced in a hydrogen plasma of pressure 2x10$^{-4}$ Torr; the samples are attached to a water-cooled copper plate, such that their temperature is estimated to be about 60 °C. The oxide film was removed from the molybdenum sample after six hours of exposure to the plasma while the oxide film was removed from the titanium sample after 15 hours of exposure to the plasma. The authors calculate that the flux of hydrogen ions to the sample surface was about ten times that the flux of neutral atoms to the surface; they estimate that a fraction of only 2x10$^{-3}$ of the active species (ions and hydrogen atoms) incident on the sample result in the net removal of an oxygen atom.

Sadedin et al.’s works (D R Sadedin 2006; Zhang et al. 2007) discuss experimental efforts to reduce pressed tablets of ZnO, TiO$_2$, and ZnFe$_2$O$_4$ in a hydrogen spark discharge; the pressure at which these experiments were conducted is not specified, though another study from Sadedin and Zhang (David Roy Sadedin 2016) which discusses a similar apparatus describes experiments conducted at atmospheric pressure. External heating (beyond that provided by the
spark discharge) was made available by means of a tube furnace; sample temperatures ranged from 150 °C to 570 °C. The authors describe only a partial reduction of the oxides treated, with the plasma-affected region constrained to the surface of the samples: in the case of titanium, the most-reduced form of titanium found was Ti$_2$O$_3$, whereas in the case of ZnFe$_2$O$_4$ the ferrite decomposed to produce some metallic iron, as determined by XRD. A total of about 58% of the oxygen content of the ferrite was removed, as determined by EDS. Note that it is not specified whether this analysis was conducted using external standards, such that the quantitative nature of this conclusion is questionable. Furthermore, this measurement only quantifies the removal of oxygen from the plasma-affected surface region of the sample, which extended to a depth of only 500 micrometers. Visually, the zinc ferrite sample changed from a red color to a light tan color in the center of the sample with a gray-black exterior.

In the case of ZnO, approximately 18% of the oxygen within the plasma-affected surface region was removed (once again measured by EDS). Since zinc possesses no oxides of lower oxygen content than ZnO (and since the authors do not remark on the production of metallic zinc), presumably the removal of this oxygen resulted in the formation of a non-stoichiometric oxide of the form ZnO$_{1-x}$ with 0<x<1. The authors state that the plasma-affected region extended an average of 200 micrometers into the sample, to a depth of at most 400 micrometers. Sadedin also notes that both the TiO$_2$ and ZnO samples exhibited re-oxidation upon exposure to the atmosphere (subsequent to the reduction experiment). For the titanium oxide sample, approximately 95% of the weight lost by the sample (attributed to oxygen removed from it) was regained following 30 minutes in atmosphere at room temperature. For zinc oxide, this re-oxidation behavior exhibited a temperature-dependency for samples reduced at 150 °C, about 90% of the weight lost was regained within 15 minutes, whereas for samples reduced at 570 °C,
only about 5% of the weight lost is regained; the re-oxidation behavior of these oxides is shown in Figure 2.4. Sadedin explains this effect by asserting that at higher temperatures greater mobility of atoms within the lattice allows for the destruction of oxygen vacancies, preventing rapid re-oxidation. At low temperatures, however, atoms cannot move as rapidly such that oxygen vacancies remain following reduction. These oxygen vacancies are then proposed to quickly react with oxygen in the atmosphere, resulting in re-oxidation of the sample. Also of note is the discontinuous nature of the reduction kinetics perceived, shown in Figure 2.5. There, Sadedin depicts a linear rate of reaction for the first three minutes of treatment, at which time the reaction appears to cease to proceed entirely.

Figure 2.4: Re-oxidation behavior of samples treated in a hydrogen spark discharge; adapted from (D R Sadedin 2006). The zinc oxide treated at high temperatures exhibits a lower degree of re-oxidation.
Wood’s communication (Wood 1922) also references the effect of a hydrogen discharge at about 0.5 Torr on aluminum. Upon initially inserting a strip of aluminum foil in the discharge, he observed the secondary emission spectrum (i.e., the Fulcher series) of hydrogen to the exclusion of the Balmer spectrum. This indicates a high concentration of molecular hydrogen and a low concentration of atomic hydrogen, implying that the initial aluminum surface is an effective catalyst in aiding the recombination of atomic hydrogen to form molecular hydrogen. Following a few minutes exposure to the discharge, however, the situation was reversed, such that the Balmer series was prominent and the secondary series had disappeared, implying a decrease in the catalytic activity of the aluminum surface. Following exposure of the aluminum strip to atmosphere, the catalytic activity of the aluminum strip was restored, as indicated by the re-appearance of the secondary spectrum of hydrogen. Given that aluminum readily forms a surface oxide layer upon exposure to the atmosphere, these results indicate that the hydrogen discharge has modified the properties of the surface oxide, perhaps to include removal or reduction of the surface oxide to reveal the underlying metal.

2.4 Reduction of Volatile Metal Oxides

A number of studies have investigated the reduction of metal oxides which are themselves volatile (i.e., possess a high vapor pressure relative to the experimental pressure) or possess suboxides, hydroxides, or hydrides which are volatile, or are volatile in their metallic form. The earliest reference to the reduction of a volatile material in a hydrogen discharge would likely be Wood’s study (Wood 1922), referenced earlier, in which he describes the effect of a hydrogen plasma on zinc oxide: a dark deposit formed on the reactor walls in the vicinity of the zinc oxide sample. This deposit presumably formed by condensation of the volatile intermediate Zn(g), following reduction of the oxide sample to zinc metal.
McTaggart’s communications (McTaggart 1967) and (McTaggart 1964) discuss the reduction of silica in a hydrogen discharge. At pressures of about 2.5 Torr and sample temperatures in the range of approximately 810 °C to 900 °C (these temperatures being determined or estimated by an unspecified technique), SiO₂ plates were etched at a rate of approximately 0.075 grams per hour (with an unspecified flow rate of hydrogen). The plasma discharge was produced by applying 200 W to 650 W of microwave power at a frequency of 2.45 GHz. No reaction was observed when the discharge was maintained by RF power. Concurrent with the etching of the silica sample, a deposit appeared on the walls of the reaction tube near the sample, transitioning in color from nearly colorless, to light amber, dark orange, and finally near-black as the reaction proceeded. “X-ray analysis” (presumably X-ray diffraction) indicated that the wall deposit consisted of elemental silicon as well as some form of SiO₂. Upon oxidizing a sample of the wall deposit material, the resulting mass gain indicated that it consisted
of approximately equal amounts of silicon and silica. McTaggart concludes that the deposit is formed by the disproportionation of SiO(g) at the wall:

$$2\text{SiO}(g) = \text{Si} + \text{SiO}_2$$

and hence that the original silica sample is being partially reduced from SiO$_2$ to form the volatile silicon monoxide. McTaggart also notes that small quantities of polymerized silicon hydrides were found on the walls of the reactor as well as SiH$_4$ which was found downstream in a “liquid-air trap.” Furthermore, he states that only the silica sample placed in the center of the plasma experienced reduction, while the quartz reactor wall showed no evidence of etching.

Bullard also discusses the reduction of SiO$_2$ in a hydrogen plasma in (Daniel Edward Bullard 1993). These observations were incidental to his studies on the reduction of titania and ilmenite: he observed “pinhole” etching of the quartz reactor wall under conditions of high pressure (above 26 Torr) and high applied powers (above 1 kilowatt). Bullard notes the deposition of material on the quartz reactor wall surrounding the area of pinhole etching. EDS and AES analysis of the wall deposits indicate the deposition of reduced silicon in an inner ring about the pinhole and silica in the exterior region. Bullard estimates the temperature at the point of pinhole etching to have been less than 1220 °C. By conducting a Gibbs-energy minimization, he concludes that the volatile intermediary removed from the pinhole and deposited on the wall at these temperatures was likely SiH$_4$(g).

Vesel et al. conducted studies of the removal of metal oxides from oxidized Inconel and stainless steel surfaces, as described in the publications (Mozetič et al. 2015) and (Vesel, Mozetic, and Balat-Pichelin 2016). These involved the application of microwave power at 500 W to produce a hydrogen discharge at a pressure of 0.3 Torr; the hydrogen flow rate was controlled between 110 and 140 standard cubic centimeters per minute (SCCM). Additional heat
was delivered to the samples by means of focused solar radiation; this heated the samples to temperatures in the range of 1130 °C to 1230 °C. Characterization of the samples was conducted by means of SEM, AES, XPS, XRD, and AFM. These analyses indicated the removal of the surface oxide films (on the order of 500 nm to 700 nm in thickness) from the samples. The authors propose that the application of the plasma resulted in the formation of volatile hydroxides, such as \( \text{CrO}_2(\text{OH})_2(g) \), which subsequently evaporated from the sample surface, exposing the reduced metal layer. Since the gaseous products from this reaction were not characterized, it is not clear whether it is appropriate to label this reaction as the reduction of metal oxides (i.e., the oxidation state of the metal species may not have changed).

A number of publications—e.g., (Chang, Chang, and Darack 2003; Chang and Darack 1981), and (Bruno, Losurdo, and Capezzuto 1995)—also reference the use of hydrogen plasmas for the removal of oxide layers in the semiconductor industry. These studies investigate the reduction and volatilization of compounds which possess volatile hydrides, such as gallium-arsenide oxide, silicon oxide, and indium-phosphide oxide. These reactions are generally carried out at low applied RF/MW power (10 W to 400 W), low pressures (0.1 mTorr to 10 Torr), low temperatures (50 °C to 270 °C), and low etch rates (0.1 nm per second to 4 nm per second). They are thus of limited interest for applications relevant to extractive metallurgy and are included only for completeness.

2.5 Synthesis and Overview

A consideration of the experimental studies of the reduction of metal oxides by non-equilibrium hydrogen plasmas yields a number of conclusions. First, it is clear that non-refractory metal oxides may be reduced to their respective metals in these plasma discharges. This is to be expected, given the definition of “non-refractory oxide” employed here; i.e., an
oxide which is amenable to reduction (under the pressures and temperatures described) even by molecular hydrogen. Given this definition, however, the fact that these oxides are reduced by hydrogen plasmas does not demonstrate any particular advantage of plasma-based reduction over reduction with molecular hydrogen: since these oxides can be reduced by molecular hydrogen, the mere fact that they can be reduced in a low-pressure hydrogen discharge does not demonstrate that the active species produced by the plasma have made any significant contribution to the reaction. Hence, for the oxides discussed in section 2.2, any improvements over molecular hydrogen must necessarily be kinetic in nature as opposed to thermodynamic.

In the studies discussed in this review, the kinetic advantages of non-equilibrium hydrogen plasmas over molecular hydrogen have not yet been convincingly demonstrated: most authors did not even attempt to compare the effects of molecular hydrogen on the oxide under study. While Sabat et al. made some attempts to justify the kinetic advantages of hydrogen plasmas over molecular hydrogen in regard to the lowered onset temperature of reduction (Rajput et al. 2014) and lowered activation energy (Sabat, Paramguru, and Mishra 2016; Sabat et al. 2015) of reactions employing hydrogen plasmas, these justifications are not sufficiently supported: direct comparisons between the different methods of reduction are not conducted within the context of the same experimental set-up. Rather, the authors merely compare their experimental results with those obtained by other investigators, thereby inviting the possibility that differences in experimental method and sample preparation could account for the trends they have observed. Thus, for the case of non-refractory oxides, hydrogen plasmas do not supply a thermodynamic advantage over molecular hydrogen, and it is not clear from the literature if they supply a kinetic advantage.
For the case of refractory metal oxides, the experimental results discussed so far are limited in scope and are sometimes contradictory. Only Sakamoto’s communication (Sakamoto and Ishibe 1980) reports complete reduction of a non-refractory oxide to metal. However, his communication provides very little characterization of the initial oxide (i.e., it is identified only by a color change that occurs upon oxidizing a metal coupon in atmosphere) and of the final reduced state (once again, only a qualitative color change). Thus, it is not clear whether the starting reactant was the actual oxide in question (TiO$_2$), nor whether it has actually been reduced (as opposed to removal via, e.g., sputtering). Of the other experimental studies reviewed here, none have reported complete reduction of a refractory metal oxide to metallic form but have only demonstrated partial reduction, either to suboxides or to a non-stoichiometric oxide.

While most authors have made an attempt to estimate the temperature of their samples within the plasma, few have characterized the speciation within the plasma (i.e., extent of ionization, dissociation, etc.), nor have they quantified the chemical composition of the plasma with regard to the presence of oxidizing species. That is to say, while the authors have often reported reagent flow rates, total pressures, and reagent purity (and some have evaluated the ultimate pressures obtained in their vacuum systems), they have not effectively measured the concentration of water or oxygen within their reactors. Bullard’s study (Daniel Edward Bullard 1993) could be a possible exception to this in that he employed a mass-spectrometer capable of detecting water vapor, but he does not report the partial pressure of water within his system: rather, he merely subtracts the background water signal from the transient water found during the course of the reaction to give some idea of the relative rates of reaction over time. He does not attempt to calibrate this signal nor to quantify the amount of water within the system. In controlling an environment for metal oxide reduction, the relative pressure of the reducing and
oxidizing agents is an essential piece of information, since this ratio controls the tendency of the overall reaction to proceed. While these authors may have an idea of the impurities present within their reagent stream, they do not attempt to quantify the leak-rate of their reactors (i.e., the rate at which atmosphere enters the system through imperfect seals). These rates are often small relative to the flow rates of reagents, but they can have an important influence on the concentration of the oxidizing species when dealing with refractory metal oxides.

Another salient feature of the studies of refractory metal oxides is the superficial nature of the reduction: in each of the experiments, the greatest degree of reduction was found only in a thin, often dark-colored surface layer. Below this layer, the degree of reduction was low or nonexistent. The studies by Wood (Wood 1922) and Sakamoto (Sakamoto and Ishibe 1980) were conducted on thin oxide layers of less than one micrometer in thickness, while reports from other investigators described the plasma-affected surface region as being between four micrometers and one millimeter in thickness. Several potential explanations for the superficial nature of this reduction are discussed here: the re-oxidation model proposed by Bullard (Daniel Edward Bullard 1993), the vacancy-mobility model suggested by Sadedin (D R Sadedin 2006), and the hydrogen-recombination model of Legasov (Legasov, Rusanov, and Fridman 1978) and Fridman (Fridman 2008).

The re-oxidation model proposed by Bullard (Daniel Edward Bullard 1993) (and also discussed by Sadedin (D R Sadedin 2006)) considers the behavior of the water vapor produced by the reduction reaction (written for a generic metal oxide MeO):

\[ \text{MeO} + 2\text{H(g)} = \text{Me} + \text{H}_2\text{O(g)} \]
This reaction is assumed to be thermodynamically feasible in the direction in which it is written; i.e., the standard Gibbs free energy of reaction is negative. However, if this is a refractory oxide as defined earlier, then the re-oxidation reaction also has a thermodynamic potential to proceed:

\[ \text{Me} + \text{H}_2\text{O}(g) = \text{MeO} + \text{H}_2(g) \]

Thus, a net reduction of metal oxide to metal requires that the water vapor product be removed relatively rapidly (presumably, the appropriate relative comparison is the rate at which the re-oxidation reaction proceeds), so as to prevent the re-oxidation reaction. The re-oxidation model proposed by Bullard asserts that at a certain depth below the surface of the sample (i.e., the plasma-sample interface), reduction is prohibited due to the long characteristic time for water molecules to exit the sample. Because the characteristic time necessary for removal of the water grows larger at increasing depths, the water molecules have a longer time period in which they can cause a re-oxidation event. Thus, this model proposes that the efficacy of reducing refractory oxides with atomic hydrogen is limited to a thin surface layer in which diffusion and mass transport of water vapor from the sample can occur quickly.

The vacancy mobility model discussed by (D R Sadedin 2006) asserts that the differential mobility of metal ions and oxygen atoms within the lattice can prevent the progression of the extent of reduction beyond a superficial surface layer in refractory oxides. Given that the temperatures of reduction in these cold plasmas are relatively low, the rate at which metal ions diffuse through the lattice may be limited. This prevents the elimination of oxygen vacancies formed by reduction events. If the rate of oxygen (or water) diffusion from the gaseous phase into the sample is relatively fast, oxygen molecules may react with these vacancies, thereby returning the metal oxide to its original unreduced state. As supporting data for this model, Sadedin references the temperature dependence of re-oxidation behavior (Figure 2.4) as well as
the sudden manner in which the reduction reaction stops (Figure 2.5), stating that this suddenness “may not be consistent with water vapor re-oxidation being the cause.” The microstructural explanation of this model is not proven, however. To do so would require a demonstration of variations in reduction behavior consistent with changes in oxygen- and metal-mobilities across different oxides, and such a demonstration has not yet been provided.

The hydrogen-recombination model was first mentioned as an explanation for the limited penetration depth of reduction by Legasov et al. in their 1978 publication (Legasov, Rusanov, and Fridman 1978); this publication was communicated in the Russian language and has received relatively little attention in the Western literature. The model is described in English by Fridman (another author of the 1978 publication) in (Fridman 2008). Bullard also mentions this model in (Daniel Edward Bullard 1993), but he does not evaluate the implications of this model quantitatively, in contrast to Fridman and Legasov. The hydrogen-recombination model considers the loss of atomic hydrogen radicals within the superficial product layer by means of heterogeneous recombination of the form:

\[
2\text{H}(g) + \text{MeO} = \text{MeO} + \text{H}_2(g)
\]

Since molecular hydrogen is unable to reduce refractory metal oxides, this recombination results in a loss of the active species as one proceeds deeper into the solid, until the atomic hydrogen concentration is so low that the reaction can proceed no further. Quantitatively, Fridman and Legasov assert that the concentration profile of atomic hydrogen within a one-dimensional solid should be given by the solution of the equation:

\[
D_H \frac{\partial^2 n_H}{\partial x^2} - kn_H^2 = 0 \quad (2.4a)
\]

with boundary conditions:
\[-D_H \frac{\partial}{\partial x} n_H|_{x=0} = \Phi\]  \hspace{1cm} (2.5b)

and

\[\frac{\partial}{\partial x} n_H|_{x=\infty} = n_H|_{x=\infty} = 0\]  \hspace{1cm} (2.6c)

where \(n_H\) is the concentration of atomic hydrogen, \(D_H\) is the diffusion coefficient of hydrogen within the solid, \(k\) is the rate coefficient for the (second-order) recombination reaction (Fridman utilizes a more complicated expression for \(k\) which has been simplified here), and \(\Phi\) is the flux of atomic hydrogen incident on the surface of the solid, Fridman asserts that the solution to this equation is given by:

\[n_H(x) = \left[\left(\frac{2D_H k}{3\Phi^2}\right)^{1/6} + x \left(\frac{k}{6D_H}\right)^{1/2}\right]^{-2}\]  \hspace{1cm} (2.7a)

Fridman then asserts that the effective penetration depth of atomic hydrogen is given by:

\[\delta = \left(\frac{8\pi D_H^2}{k\Phi}\right)^{1/3}\]  \hspace{1cm} (2.8b)

though in another formulation he simplifies this to yield:

\[\delta = \left(\frac{D_{H,0}}{\Phi r_0}\right)^{1/3} \frac{-E_a^D}{e^{3T_0}}\]  \hspace{1cm} (2.9b)

in which \(r_0\) is the “critical reactive distance between H atoms in the matrix” and an Arrhenius model for the diffusion coefficient has been employed with \(D_{H,0}\) the pre-exponential factor, \(E_a^D\) the activation energy for diffusion of hydrogen atoms within the lattice, and \(T_0\) the temperature of the surface region of the solid (presumably converted to dimensions of energy by means of Boltzmann’s constant \(k_B\)).

Thus, there exist several explanations for the superficial nature of the extent of reduction observed in refractory metal oxides, but none of these has been convincingly supported by experimental investigation. The case of volatile metal oxides is perhaps simpler. While there are
sometimes multiple mechanistic interpretations for a given reaction—e.g., (McTaggart 1964) proposed that a SiO(g) intermediary was responsible for the volatilization of silica, in contrast with (Daniel Edward Bullard 1993) who proposed that a SiH₄(g) intermediary was responsible—and occasionally some ambiguity if reduction has actually occurred (in the case of the proposal of (Mozetič et al. 2015) that the Cr₂O₃ oxide film is removed by the formation of an unprocessed volatile CrO₂(OH)₂(g) species), it is clear that the oxide does react and there is general agreement on the identity of the solid deposits of this reaction. Furthermore, there is no unexplained “surface-affected” region as in the case of non-volatile refractory oxides since there is a continuous removal of the product layer, exposing a fresh oxide surface as the reaction proceeds.

2.6 Outstanding Questions

Thus, several outstanding questions concerning the reduction of metal oxides in non-equilibrium hydrogen plasmas have yet to be answered convincingly. First, it is unclear if the kinetics of the reduction of non-refractory metal oxides are improved by the application of a hydrogen plasma discharge. Are the rates of these reactions improved by the use of a hydrogen plasma instead of conventional molecular hydrogen treatment? If so, what is the mechanism by which these improvements are achieved? In the case of refractory metal oxides, it is unclear if these materials may be reduced to their respective metals by application of a hydrogen discharge. Which metals can be produced from their oxides by means of non-equilibrium hydrogen discharges? Is there a theoretical framework that can be employed to predict the metal oxides which are amenable to this reduction process, given that a traditional equilibrium thermodynamic analysis is inappropriate because of the inherently non-equilibrium nature of the hydrogen plasma? Can a mechanistic explanation of the superficial nature of the reduction observed in
refractory metal oxides be constructed, and can it be used to solve for the maximum penetration depth of reaction under a given set of experimental parameters, thereby determining the maximum particle size of an oxide particle that can be reduced within a reactor? For the case of volatile oxides, there is some ambiguity in terms of mechanisms as well as in the practical utility of this technique. Can the products of this reaction be effectively captured? In the case of, e.g., SiO$_2$, is there a means of controlling the disproportionation reaction so that it is easy to separate the reduced portion of the product from the oxidized portion?

This dissertation will attempt to answer some of the questions described here. It will focus on those relevant to the reduction of non-volatile oxides, both refractory and non-refractory. While the reduction of volatile oxides is encountered incidentally in the course of the experimental work (via reduction of the silica reactor wall), an in-depth analysis of this process is outside the scope of this research.
CHAPTER 3

FUNDAMENTALS OF PLASMA PROCESSING

This chapter provides a brief summary of topics that are pertinent to the understanding of the physical phenomena occurring during the reduction of metal oxides by non-equilibrium hydrogen plasmas. The properties of plasma discharges are discussed, and the defining characteristics of both equilibrium and non-equilibrium plasmas are outlined. The importance of collisions within a plasma is described, including a discussion of both elastic and inelastic collisions. Sheath physics is also reviewed. While these phenomena are covered only briefly, the understanding gained by examining these properties from a fundamentals-oriented approach provides some context for unique properties of non-equilibrium plasmas.

3.1 Non-Equilibrium Plasmas

A plasma may be broadly defined as a gaseous phase which is ionized to an appreciable degree. More rigorously, one can follow Chen in defining a plasma as “a quasineutral gas of charged and neutral particles which exhibits collective behavior” (F. F. Chen 1984). Here, “quasineutral” refers to the absence of a net charge within a macroscopic volume in the plasma; while there may be local charge imbalances on the microscale, for volumes above a minimum cutoff value (where a sphere of that volume is denoted as the Debye sphere), there must be approximate equality between the contained amount of negative and positive charge. To provide a sense of scale, a hydrogen glow discharge at 10 Torr with a field strength of 100 volts per centimeter would have an electron density of about $3 \times 10^{10}$ electrons per cubic centimeter (Bell 1967); quasineutrality would require the ion density to be correspondingly $3 \times 10^{10}$ per cubic centimeter. This represents a degree of ionization of about $10^{-7}$ since the number density of hydrogen in the discharge is about $3 \times 10^{17}$ molecules per cubic centimeter.
The phrase “collective behavior” from Chen’s definition refers to the ability of distant portions of a plasma to influence other parts of the plasma. This property stems from ability of electromagnetic fields emitted from distant locations to affect charge carriers within other portions of the plasma. This is to be contrasted with the behavior of a traditional gas, which may be understood by considering solely short-range interactions between gas particles, such as intermolecular collisions.

Plasmas must be maintained by a requisite mechanism or energy source which can produce appreciable concentrations of ionized species. For the non-equilibrium plasmas under discussion in this work, an electric field is often the source of this energy: in the presence of an electric field, a charged particle will experience an acceleration in accordance with the equation (Griffiths 1999):

$$\frac{dv}{dt} = \left( \frac{q}{m} \right) \cdot (E + v \times B)$$

(3.1)

where $v$ is the velocity of the particle, $t$ is time, $q$ is the charge of the particle, $m$ is the mass of the particle, $E$ is the electric field, and $B$ is the magnetic field. From this equation, it is clear that less massive particles will experience a higher magnitude acceleration than more massive particles, *ceteris paribus*. Hence, for an electron of mass $m_e$ and a hydrogen ion (proton) of mass $\sim 1836 \, m_e$, the electron will experience a larger increase in velocity when exposed to an electric field for a given unit of time than the hydrogen ion.

The modifier “non-equilibrium” refers to the fact that in low-pressure plasmas, the temperature of the electrons can be much greater than the temperature of the other heavy species. This phenomenon (i.e., the non-equilibration of the electron and ion/neutral temperatures) will be discussed further in the subsequent text discussing collisions within a plasma.
3.2 Collisions and Cross Sections

The various species within a plasma (e.g., ions, electrons, radicals, and molecules) can interact with each other by means of collisions; i.e., when one particle of a given species impinges upon another, it may induce a reaction or excitation of one of the colliding particles, or it may result in a transfer of energy or momentum between the two particles. Per the discussion related to (3.1), the electrons within a plasma will in general be moving much faster than the other heavy species, such that the electrons may be considered to be the incident species in collisions with the heavy species (which can be approximated as being at rest). A mathematical development of the collision phenomena that can occur in a plasma follows, paralleling the treatment from [4] and [31].

Consider a rectangular volume of space of unit side area and thickness $\Delta x$. Within this volume, a number of target particles (e.g., ions, atoms, or molecules) are distributed randomly with number density (i.e., number of particles per unit volume) $n_T$. Initially, assume that the target particles are spheres such that the projection of each target particle onto the $x = 0$ plane produces a circle of area $\sigma$. Note that it is assumed that the target particles are at low number density and that $\Delta x$ is infinitesimal such that none of the projected circles overlap. This situation is depicted in Figure 3.1

If an incident point particle is directed at the $x = 0$ plane, then the (infinitesimal) probability that a collision event occurs within that (infinitesimal) volume is given by the ratio of the sum of the areas of the projected circles to the total area of the “front” side of the collision. This can be expressed mathematically as:

$$\Delta P_{\text{Collision}} = \frac{A_{\text{Targets}}}{A_{\text{Total}}} = \frac{n_T \sigma \Delta x}{1} = n_T \sigma \Delta x$$ (3.2)
Figure 3.1: A particle (e.g., an electron) is incident upon a rectangular volume with unit side area and thickness $\Delta x$. The probability that the electron collides with one of the target particles (e.g., hydrogen molecules) depends on the fraction of the area covered by the target particles.

If instead of a single particle being incident on the volume there is now a group of incident particles of number density $n_I$, the total number of collisions expected per unit volume is given by the product of the probability of collision for a single incident particle with the number of incident particles per unit volume. Assuming that an incident particle disappears once a collision occurs, the change in the number density of incident particles upon passing through the volume can be written as:

$$\Delta n_I = -n_I n_T \sigma \Delta x$$  \hspace{1cm} (3.3)

In the limit as $\Delta x \to 0$, equation (3.3) can be transformed into a differential equation which can be solved to yield an expression for the variation in number density in the $x$ direction:

$$n_I(x) = n_{I,x=0} e^{-n_T \sigma x}$$  \hspace{1cm} (3.4)

This allows one to define a quantity $\lambda_{\text{MFP}} \equiv (n_T \sigma)^{-1}$, the mean-free path of the incident particles, as the distance over which an incident stream of particles experiences a reduction in number density by a factor of $e$. Assuming that the incident particles have an average velocity of $\bar{v}$, the mean time between collisions can be defined as $\tau \equiv \lambda_{\text{MFP}} / \bar{v}$, while the collision frequency can be defined as $\nu \equiv \tau^{-1} = n_T \sigma \bar{v}$. 

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In general, the cross section for a given collision is not as simple as the projected area (discussed above) for the case of hard-sphere collisions. If the particles interact by means of another force that can exert its effects even when the particles are not in direct contact—such as the electrostatic Coulombic force—the collision cross section may be quite different. Significantly, the cross section may depend upon the relative velocity of the incident and target particles, as discussed in (Lieberman and Lichtenberg 2005). A table of some possible interaction potentials and their corresponding cross sections is presented in Table 3.1.

<table>
<thead>
<tr>
<th>Interaction Force</th>
<th>Potential, $U(r)$</th>
<th>Cross Section, $\sigma(v)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coulombic</td>
<td>$1/r$</td>
<td>$1/v^4$</td>
</tr>
<tr>
<td>Dipole</td>
<td>$1/r^2$</td>
<td>$1/v^2$</td>
</tr>
<tr>
<td>Induced Dipole</td>
<td>$1/r^4$</td>
<td>$1/v$</td>
</tr>
<tr>
<td>Hard Sphere</td>
<td>$1/r^i, i \to \infty$</td>
<td>const.</td>
</tr>
</tbody>
</table>

Given the dependence of cross sections on velocity, evaluating the total rate at which a process occurs within a plasma requires that one consider the velocity-weighted contributions of the participating species. Mathematically, one can express these weighted contributions to the overall collision frequency $\nu$ by writing:

$$\nu = \int_0^\infty n_T \sigma(v) \, v \, f(v) \, dv$$  \hspace{1cm} (3.5)

where $f(v)$ represents the distribution of incident particle velocities (e.g., Maxwellian); the target particles are assumed to be at rest relative to the incident particles.

### 3.3 Elastic Collisions and Energy Exchange

Using the mathematical framework for cross sections developed so far, this discussion will turn to consider the nature of energy exchange within a plasma. Collisions within a plasma
may be classified as elastic (in which the internal energies of the colliding particles do not change) and inelastic (in which the internal energies of one or more of the colliding particles do change via, e.g., ionization or electronic/vibrational/rotational excitation). Elastic collisions will be considered first.

In the simplified one-dimensional case, one may consider the elastic collision between an incident hard-sphere particle of mass \( m_1 \) and initial velocity of magnitude \( v_1 \) and a stationary hard-sphere particle of mass \( m_2 \). Subsequent to the collision, the particles have respective velocities \( v_1' \) and \( v_2' \). Conservation of energy requires that:

\[
\frac{1}{2}m_1 v_1^2 = \frac{1}{2}m_1 (v_1')^2 + \frac{1}{2}m_2 (v_2')^2
\]  
(3.6)

while conservation of momentum requires that:

\[
m_1 v_1 = m_1 v_1' + m_2 v_2'
\]  
(3.7)

Elimination of the variable \( v_1' \) allows one to combine these equations and to solve for the ratio of the post-collision kinetic energy of the target particle to the pre-collision kinetic energy of the incident particle as:

\[
\zeta_L \equiv \frac{1}{2} \frac{m_2 (v_2')^2}{m_1 v_1^2} = \frac{4\beta}{(1 + \beta)^2}
\]  
(3.8)

where \( \beta \equiv m_1/m_2 \). Hence, if the incident particle is an electron and the heavy target particle is a hydrogen atom or ion, then \( \beta \approx 1/1836 \) such that the fractional energy transfer from the electron to the heavy particle is of the order \( \zeta_L \approx 2 \times 10^{-3} \). Hence, it requires nearly \(~500\) collisions for an electron to transfer its energy to the heavy species within a plasma. In contrast, if \( \beta = 1 \), as for an electron-electron or atom-atom collision, then \( \zeta_L = 1 \) such that it requires only one collision to evenly distribute energy between species of comparable mass.
For the more general case of an elastic collision—in multiple dimensions, allowing for a non-hard-sphere collision cross section—it can be shown (see (Lieberman and Lichtenberg 2005) for a detailed derivation) that the fraction of energy transferred from an incident particle to a target particle via an elastic collision is given by:

\[
\langle \zeta_L \rangle_\theta = \frac{2\beta}{(1 + \beta)^2} \frac{\sigma_m}{\sigma_{\text{sc}}}
\]  

(3.9)

where \( \zeta_L \) is averaged over the scattering angle \( \Theta \) (in the center-of-mass frame), \( \sigma_m \) is the momentum transfer cross section and \( \sigma_{\text{sc}} \) is the total scattering cross section. The specific behavior of the cross-sections \( \sigma_{\text{sc}} \) and \( \sigma_m \) depends on the potential employed to model the interaction between the incident and target particles, as detailed in Table 3.1.

Using this expression for the fractional energy exchange that occurs within a single elastic collision, it is possible to construct a macroscopic energy balance within an electromagnetically-sustained non-equilibrium plasma as follows: the electromagnetic field accelerates the electrons in accordance with equation (3.1) while the ions are relatively unaffected by this field since they are so much more massive; the neutral species are totally unaffected since they bear no charge. The electrons then transfer energy to the ions and neutral species by means of collisions, such as those described by equation (3.9) (in addition to the inelastic collisions considered later). These heavy species then act to dissipate energy to the environment by means of, e.g., radiation, conduction, convection, and chemical reaction. This energy balance is depicted schematically in Figure 3.2.

Following (Boulos, Fauchais, and Pfender 1994) and (Fauchais, Boulos, and Pfender 1987), it is possible to express the energy balance of the electrons within the plasma by considering the steady-state situation in which the energy transferred to the electrons by the electromagnetic fields balances the energy transferred from the electrons by means of elastic
collisions. Note that this derivation from (Boulos, Fauchais, and Pfender 1994) and (Fauchais, Boulos, and Pfender 1987) ignores the energy transferred from electrons to heavy species by means of inelastic collisions, a point which disagrees with the analysis in (Fantz 2002), in which the author states that inelastic collisions dominate elastic collisions in low-temperature (non-equilibrium) plasmas. A precise resolution of this discrepancy requires a consideration of the respective cross sections for each of the elastic and inelastic collisions.

Figure 3.2: Energy balance within a plasma. Radiative excitation of ions and neutrals has been ignored (i.e., the plasma is assumed to be optically thin), as has electromagnetic excitation of all non-electron species, per the diminished acceleration of these massive/uncharged species specified by equation (3.1).

Nevertheless, under conditions when the energy transferred by means of inelastic collisions is small relative to the energy transferred by means of elastic collisions, it is possible to write the energy balance of the electrons (when the electric field is assumed to be time-invariant, or at least, when the frequency of modulation $\omega$ is much lower than the electron-heavy collision frequency $\nu_e$, that is, when $\omega \ll \nu_e$) as:

$$ E_{\text{In,EM}} = E_{\text{Out,Elas}} $$

The energy gained by an electron between collisions can be expressed by means of the expression:
\[ E_{\text{in,EM}} = q_e E_v \tau_e \]  

(3.11)

where \( q_e \) is the charge of the electron, \( E \) is the magnitude of the electric field, \( \tau_e \) is the average time between successive collisions, and \( v_d \) is the average drift velocity of the electron. The average drift velocity is defined by assuming that the electron is accelerated by the electric field in accordance with equation (3.1) (with no magnetic field) over a time period \( \tau_e \):

\[ v_d \equiv \frac{q_e}{m_e} E \tau_e \]  

(3.12)

Note that equation (3.11) is only valid for the situation in which the electric field is slowly varying compared to the collision frequency, i.e., \( \omega \ll \nu_e \). For situations in which \( \omega \sim \nu_e \), it is more appropriate (per [4] and [35]) to employ the expression

\[ E_{\text{in,EM}} = \frac{q_e^2 E_{\text{rms}}^2}{2m_e} \frac{1}{v_e^2 + \omega^2} \]  

(3.13)

with \( E_{\text{rms}} \) the root-mean-square electric field averaged over one period of electromagnetic oscillation. For the sake of simplicity, this argument will continue with the approximation that \( \ll \nu_e \). Taking the energy lost per collision by the electrons to be given by the difference in average energies of the electrons and the heavy species multiplied by the efficiency of energy exchange in a given collision, as provided by equation (3.9), it is possible to write the expression

\[ E_{\text{out,Elas}} = \langle \zeta_L \rangle \theta \times (\bar{E}_e - \bar{E}_h) \]  

(3.14)

where \( \bar{E}_e \) is the average energy of the electrons. This average energy can be quantified by assuming a Maxwellian distribution of velocities (an assumption which is not always valid in non-equilibrium plasmas, c.f. (Fridman 2008) and the discussion of Druyvesteyn and Margenau distributions) and may be defined in terms of the temperature of the electrons \( T_e \) by the equation

\[ \bar{E}_e \equiv \frac{3}{2} k_B T_e \]. \( \bar{E}_h \) is the average energy of the heavy species, defined similarly as \( \bar{E}_h \equiv \frac{3}{2} k_B T_h \).
For $\beta \ll 1$ (as in the case of an electron-heavy collision) and taking $\sigma_{sc} \approx \sigma_m$ as for the case of, e.g., hard-sphere collisions, $\langle \xi_e \rangle_e \approx 2\beta$ so that equation (3.14) may be simplified to yield

$$E_{\text{Out,Elas}} = 3\beta \times k_B (T_e - T_h) \quad (3.15)$$

Substituting equations (3.15) and (3.11) into equation (3.10) and using the definitions of $\tau_e$ and $v_d$, setting $\beta = m_e/m_h$ while employing the definition of the mean speed of a Maxwellian distribution $\bar{v}_e \equiv \sqrt{\frac{8k_B T_e}{\pi m_e}}$ (see (Reif 2009) for a derivation of this mean speed), one can arrive at the relationship:

$$\frac{(T_e - T_h)}{T_e} = \frac{\pi m_h}{24m_e} \left( \frac{\lambda_{\text{MFP}} q_e E}{k_B T_e} \right)^2 \quad (3.16)$$

Given that the mean free path of electrons can be defined in terms of the concentration of heavy species $n_h$ and the total scattering cross section $\sigma_{sc}$ as $\lambda_{\text{MFP}} \equiv 1/(n_h \sigma_{sc})$ as discussed previously, this expression can also be re-arranged to yield:

$$\frac{(T_e - T_h)}{T_e} = \frac{\pi m_h}{24m_e} \left( \frac{q_e}{\sigma_{sc} k_B T_e n_h} \right)^2 \quad (3.17)$$

This relationship is of the functional form:

$$\frac{\Delta T}{T_e} \sim \left( \frac{E}{n_h} \right)^2 \quad (3.18)$$

where $\Delta T$ represents the difference in temperature between the electrons and the heavy species. Hence, for a constant $T_e$, equation (3.18) shows the dependence of the equilibration between the temperature of the electron and heavy species on the so-called “reduced electric field” $E/n_h$. At low pressures (low number densities $n_h$), $\Delta T$ is predicted to be large such that the electrons are much hotter than the heavy species. In contrast, at high pressures (high concentrations $n_h$), $\Delta T$ is predicted to be small such that electron and heavy species are in thermal equilibrium. Thus, equation (3.18) reproduces the general behavior observable in Figure 3.3. This allows for an
understanding of the physical basis of the non-equilibrium behavior present in low pressure plasmas; i.e., how the electrons within a plasma discharge can be at such a high temperature relative to the temperature of the heavy species.

Figure 3.3: The influence of pressure on inter-species temperature equilibration within a plasma; adapted from (Julian Szekely 1984).

The preceding argument—following that presented by (Fauchais, Boulos, and Pfender 1987) and (Boulos, Fauchais, and Pfender 1994)—is not meant to provide a self-contained treatment of the equilibration of temperatures within non-equilibrium plasmas. Rather, it is intended to provide a high-level understanding of how this non-equilibrium behavior arises: electrons are excited by the electric field to a greater degree than heavy ions because of their lower mass. Because the exchange of energy between electrons and heavy species is relatively
inefficient due to the large difference in their masses, the electrons within a nonequilibrium plasma possess a higher temperature than do the heavy species. However, the heavy species and electrons approach thermal equilibrium at increased pressures and decreased electric field strengths. The fact that the electrons within a non-equilibrium plasma are at a high temperature relative to the heavy species within a plasma creates some of the novel properties of these plasma discharges: the high-temperature electrons within a plasma are capable of producing a high concentration of excited species such as atomic radicals or vibrationally excited molecules (via inelastic collisions, discussed below), thereby allowing for a high degree of chemical activity within the plasma.

Because the heavy species are at a relatively low temperature, thermal losses to the environment are minimized. This should be contrasted with the case of thermal (equilibrium) plasmas, where high chemical activity is achieved, but at the high thermal losses to the environment. In an industrial setting, a thermal plasma will often require extensive cooling to allow for extended reactor life and rapid quenching of the reaction products to prevent possible back-reactions. Since non-equilibrium plasmas do not experience these limitations to the same degree, they provide an attractive combination of high reactivity and high thermal efficiency.

3.4 Inelastic Collisions and Excited Species

Excited species within a plasma—e.g., ions, radicals, or vibrationally/rotationally excited molecules—are produced when electrons collide inelastically with lower-energy heavy species (i.e., ground state or metastable atoms, or molecules). As an example, the collision of an electron with a hydrogen molecule can produce two hydrogen atoms via the reaction:

\[ \text{e}^\text{fast} + \text{H}_2(\text{g}) = \text{e}^\text{slow} + 2\text{H}(\text{g}) \]
Here, the kinetic energy of the fast electron has been employed to dissociate the hydrogen molecule into the higher-energy state of two free hydrogen atoms. This reaction can be visualized as a collision between the incident electron and the target hydrogen molecule; the reaction possesses cross section like those discussed previously. In general, the cross section for inelastic collisions like this one depends on the relative velocity of the incident electron and the target reactant molecule, as discussed in relation to Table 3.1. This relative velocity, in turn, depends on the parameters of the plasma discharge—notably, the reduced electric field $E/n_h$ discussed in the context of equation (3.18).

Given that different types of inelastic collisions have distinct dependencies on the relative velocity of the incident particles (see (Fridman 2008) for an exhaustive, fine-details treatment of the cross sections for different collisions), different types of excited species will predominate under different plasma parameters. One may optimize the production of a particular excited species by tuning the plasma parameters to the desired range. A depiction of the relative prevalence of these different collisions (determined by the proportion of electron energy which is dissipated through each particular type of collision) in a hydrogen discharge is presented in Figure 3.4.

It is clear from Figure 3.4 that the choice of plasma operating parameters can have a significant impact on the energy efficiency of a particular process: moving from 20 to 100 V Torr$^{-1}$ cm$^{-1}$ changes the proportion of energy transferred from electrons to heavy species through elastic collisions by a factor of more than six. Figure 3.4 also provides an indication for how one can optimize the plasma parameters for producing a desired excited species. If, for example, one were interested in maximizing the efficiency of dissociation that would occur within a hydrogen
plasma (to produce atomic hydrogen), it would be optimal to operate in the regime of 30 to 50 V Torr$^{-1}$ cm$^{-1}$, given the contributions of the two contributing dissociation mechanisms.

Ionization—a specific case of an inelastic collision, in which an incident electron knocks free another electron from the target particle—is also the mechanism by which a plasma discharge is first formed: electrically accelerated electrons produce more electrons by ionizing neutral species. These daughter electrons are themselves accelerated until they can induce further ionization, and so on. This accelerating process (termed an “avalanche breakdown” (von Engel 1965)) results in the development of the appreciable degree of ionization that defines a plasma.

![Figure 3.4: Comparison of electron energy dissipation modes through radiation and different types of collisions in a hydrogen plasma; adapted from (Lunt and Meek 1936).](image-url)
3.5 Sheath Physics

As described in the context of equation (3.1) and equation (3.18), electrons have a higher average speed than do ions. Thus, a given (neutral) surface will experience a higher flux of electrons than of ions. This results in the development of a negative electrical potential on ungrounded solids placed within a plasma since there is a net flux of negative electric charge to solid. As this electrical potential becomes larger in magnitude, it acts to repel lower-energy electrons and attract ions, thereby resulting in a smaller magnitude negative current to the solid, thereby making the electrical potential of the solid closer to zero. This process eventually comes to equilibrium and a steady-state electrical potential develops. For an ungrounded solid, this potential is known as the floating potential; for a typical plasma, the floating potential may be lower than the potential of the bulk plasma by a quantity of 10 volts to 30 volts (Ruzic, Weed, and Society 1994). The floating potential transitions to the bulk plasma potential across a sheath, typically several Debye lengths in thickness (where the Debye length is the radius of the Debye sphere defined earlier).

A grounded solid or a solid biased at a potential different than the floating potential will attract a net current. Quantifying the magnitude of this collected current as a function of the biasing voltage using a device called a Langmuir probe allows one to determine a number of plasma parameters, including the electron temperature \( T_e \) and the concentration of ionized species within the plasma (Bellan 2008). Negative potentials may also be applied to solids with the intent of accelerating ions towards their surfaces. The resulting impacts of these highly accelerated ions on the surface of the solid can result in chemical reactions on the surface (the implications of the applied potential on the thermodynamic variables for a given reaction are
discussed in (Dembovsky 1984)), as well as in the dislodging of atoms from the surface a process called sputtering.

3.6 Summary

This chapter has outlined the basic phenomena responsible for some of the unique properties of non-equilibrium plasmas; salient points are reiterated here. Plasmas consist of partially ionized gases and are often sustained by an imposed electric field. This electric field acts to accelerate charged particles. Because of their lower mass, electrons are accelerated more strongly than ions. In a non-equilibrium plasma, electrons maintain a higher average velocity (and a higher temperature) due to the inefficient transfer of energy in collisions between particles of vastly different masses, though the temperature of these species comes to equilibrium in the limit of high pressures and low electric fields. Because the electrons have a much higher average energy than the ions, they are able to produce highly excited species such as ions and atomic radicals when they collide with heavy species inelastically. Some degree of specificity in the type of excited species produced within a plasma may be obtained by adjusting the ratio of the magnitude of the electric field to the discharge pressure. Solids in contact with a plasma can develop a potential due to the differing fluxes of electrons and ions from the plasma. This potential can accelerate ions into the solid with a great deal of energy, thereby precipitating chemical reactions or sputtering atoms from the surface of the solid. These properties of non-equilibrium plasmas—notably, the low-temperature production of excited species of high chemical potential—provide the basis for an investigation into the use of plasma discharges for achieving a desired reaction, such as the reduction of metal oxides.
CHAPTER 4
THEORETICAL CONSIDERATIONS

This chapter provides a theoretical analysis of the physico-chemical processes relevant to understanding the reduction of metal oxides in non-equilibrium hydrogen plasmas. The discussion begins with a description of actinometry, a spectroscopic method for evaluating the concentration of excited species within a plasma; actinometry was employed in this research to quantify the concentration of atomic hydrogen within the plasma. Equilibrium thermodynamic phase-stability analyses of the metal-oxygen-hydrogen systems are provided and an argument is made for the applicability of this approach to the metastable conditions that occur within the non-equilibrium plasma discharge. The equilibrium analysis is extended to a near-equilibrium situation to determine the maximum rate of reduction achievable in a plasma-discharge reactor. Finally, an analysis of the maximum depth of penetration of atomic hydrogen is considered by taking into account the diffusion of hydrogen atoms into the solid as well as the heterogeneous recombination of the atoms on the surface of the solid.

4.1 Population Balance Models and Actinometry

Actinometry, or more specifically, plasma emission actinometry, is a spectroscopic method for determining the concentration of an excited species within a plasma. It is conducted by flowing a known concentration of a tracer gas (argon, in this research) with similar excitation properties to the active species of interest. By examining the relative intensity of the emission lines of the tracer gas and of the species of interest, it is possible to quantify the concentration of the species of interest. Notably, this allows for an estimation of the extent of dissociation of atomic hydrogen, as well as an estimation of the partial pressure of atomic hydrogen within the plasma environment. While actinometry was first employed by (Coburn and Chen 1980) to
measure the concentration of fluorine atoms (using argon as an actinometer), it has also been
extended to the quantification of hydrogen atoms by (Geng et al. 2005). The subsequent
discussion follows the approach laid out by (Geng et al. 2005), appealing occasionally to
(Lieberman and Lichtenberg 2005) and (Fantz 2002).

When electrons change energetic states in an atom, characteristic line radiation can be
emitted; e.g., the hydrogen Balmer series occurs when electrons transition from \( p \) orbitals with
principal quantum numbers three or above to the \( 2s \) orbital (i.e., the \( H_\alpha \) line at 656.3 nanometers
results from the transition from \( 3p \) to \( 2s \), the \( H_\beta \) line at 486.1 nanometers results from the
transition from \( 4p \) to \( 2s \), the \( H_\gamma \) line at 434.0 nanometers results from the transition from \( 5p \) to
\( 2s \), etc.) (Atkins and de Paula 2014). The intensity of radiation detected at a characteristic line
wavelength is thus indicative of the frequency at which the corresponding electronic transition
occurs within the plasma volume. Significantly, this radiation intensity is proportional to the
concentration of species in the electronically-excited state. Mathematically, this can be expressed
by writing (for the particular case of hydrogen) (Geng et al. 2005):

\[
I(\lambda_{H,n,m}) = A_{H,n,m} [H_n] C(\lambda_{H,n,m}) E_{H,n,m}
\]

(4.1)

where \( \lambda_{H,n,m} \) is the wavelength of the characteristic radiation resulting from the transition of
electrons from the excited state \( n \) to lower-energy state \( m \), \( I(\lambda_{H,n,m}) \) is the flux of radiation
measured by the spectrometer (with dimensions of energy per area per time), \( A_{H,n,m} \) is the
spontaneous emission coefficient for the transition from state \( n \) to state \( m \) (the Einstein A
coefficient, with dimensions of inverse time (Griffiths 2005)), \( [H_n] \) is the concentration of
hydrogen atoms in the excited state \( n \) (with dimensions of inverse volume), \( C(\lambda_{H,n,m}) \) is a
correction factor accounting for the detection efficiency of the spectrometer (i.e., the volume of
plasma sample, losses and reflections in the fiber optic cable, and CCD detection efficiency;
dimensional analysis indicates that this correction factor must have dimensions of length), and $E_{H,n,m}$ is the characteristic energy of the transition from state $n$ to state $m$, defined by the relationship $E_{H,n,m} \equiv h \nu_{H,n,m} \equiv hc/\lambda_{H,n,m}$, with $h$ Planck’s constant, $c$ the speed of light, and $\nu_{H,n,m}$ the frequency of the radiation emitted by this transition. An expression analogous to equation (4.1) can be written for the tracer gas (here, argon):

$$I(\lambda_{Ar,p,q}) = A_{Ar,p,q} [Ar_p] C(\lambda_{Ar,p,q}) E_{Ar,p,q}$$

(4.2)

with $\lambda_{Ar,p,q}$ the wavelength of the characteristic radiation emitted during the transition of electrons from the excited state $p$ to the lower-energy state $q$, $I(\lambda_{Ar,p,q})$ the flux of radiation received by the spectrometer at this wavelength, $A_{Ar,p,q}$ the spontaneous emission coefficient for the $p$ to $q$ transition, $[Ar_p]$ the concentration of argon atoms in the excited state $p$, $C(\lambda_{Ar,p,q})$ the detection efficiency correction factor at this wavelength, and $E_{Ar,p,q} \equiv h \nu_{Ar,p,q} \equiv hc/\lambda_{Ar,p,q}$ the characteristic energy of radiation emitted during this transition.

In order to conduct a population-balance of these electronically-excited species, one must consider both decay mechanisms as well as excitation mechanisms. In the steady state (i.e., no temporal variations of the concentration of excited species), it is possible to write

$$r_{\text{excitation}} = r_{\text{decay}}$$

(4.3)

with $r_{\text{excitation}}$ the rate at which the electronically-excited species is generated and $r_{\text{decay}}$ the rate at which the electronically-excited species (in this discussion, state $n$ for hydrogen and state $p$ for argon) decays to lower-energy states. Note that this analysis ignores the loss of the excited species in question via excitation to even higher energy states, and also ignores the generation of the excited species as decay products of those higher energy states. For an optically-thin plasma, it is possible to ignore radiative excitation such that electronically-excited species can only be produced by inelastic collisions of low energy states with free electrons. If one is interested in
describing the creation of electronically-excited hydrogen atoms in state \( n \), it is important to consider the inelastic collisions of electrons both with lower-energy hydrogen atoms and with hydrogen molecules, as both of these collision events can result in the product of the electronically-excited state of interest. The former mechanism (the inelastic collision of electrons with hydrogen atoms) is termed the \textit{direct} excitation mechanism while the latter (the inelastic collision of electrons with hydrogen molecules) is termed the \textit{dissociative} excitation mechanism. Since argon does not form molecules, the production of electronically-excited argon atoms occurs only through the direct excitation mechanism. Mathematically, the overall rate of production of electronically-excited hydrogen and argon species can be expressed by writing:

\[
\begin{align*}
    r_{\text{excitation},H} &= k_{\text{dir},H}[H][e^-] + k_{\text{diss},H}[H_2][e^-] \\
    r_{\text{excitation},Ar} &= k_{\text{dir},Ar}[Ar][e^-]
\end{align*}
\]

Here, each of these contributing reactions is assumed to take place by a first-order reaction between the incident electrons and the ground state species of interest, per (Geng \textit{et al.} 2005). Note that this also implies that the excitation of meta-stable species to produce the excited species of interest is insignificant. The rate constants \( k_{\text{dir},H} \), \( k_{\text{diss},H} \), and \( k_{\text{dir},Ar} \) may be understood by considering the cross sections for these particular collision-reactions. As discussed in Chapter 3, the cross section for a given collision depends, in general, on the relative velocity of the participating species, such that the weighted contributions of different components of the electron velocity distribution must be considered. Analogous to equation (3.5), it is possible to write:

\[
k_{\text{reac}} = \int_0^\infty \sigma_{\text{reac}}(v) v f(v) \, dv
\]

with \( k_{\text{reac}} \) the rate constant for a reaction, \( \sigma_{\text{reac}}(v) \) the velocity-dependent cross section for that reaction, \( v \) the velocity of the electrons (given that the argon and hydrogen species are moving...
much more slowly than the electrons), and \( f(\nu) \) the electron velocity distribution (e.g., a Maxwellian distribution).

Per (Geng et al. 2005), the decay of electronically-excited species can occur both via radiative emissions and by “quenching” reactions in which collisions with other particles result in the loss of energy from the electronically-excited species. Given that the concentration of the tracer gas argon and the concentration of the dissociated and atomic species are small relative to the concentration of molecular hydrogen within the plasma, it is necessary only to consider quenching reactions with molecular hydrogen. It is thus possible to write:

\[
\begin{align*}
\dot{r}_{\text{decay},H} &= A_{H,n}[H_n] + k_{\text{quench},H}[H_n][H_2] \\
\dot{r}_{\text{decay},Ar} &= A_{Ar,p}[Ar_p] + k_{\text{quench},Ar}[Ar_p][H_2]
\end{align*}
\]

(4.7) (4.8)

with \( k_{\text{quench},H} \) and \( k_{\text{quench},Ar} \) the quenching coefficients for the electronically-excited hydrogen and argon species, respectively. Note that \( A_{H,n} \) and \( A_{Ar,p} \) are distinct from the spontaneous emission coefficients \( A_{H,n,m} \) and \( A_{Ar,p,q} \) defined previously: while the latter refer to the emission coefficients for the specific \( n \) to \( m \) and \( p \) to \( q \) transitions, the former refer to the total emission coefficients for all possible transitions from the \( n \) and \( p \) states. The other terms in equations (4.7) and (4.8) have been defined previously. Substituting equations (4.4), (4.5), (4.7), and (4.8) into equation (4.3), it is possible to obtain the steady-state population balance for the electronically-excited hydrogen and argon species:

\[
\begin{align*}
\dot{k}_{\text{dir},H}[H][e^-] + \dot{k}_{\text{diss},H}[H_2][e^-] &= A_{H,n}[H_n] + k_{\text{quench},H}[H_n][H_2] \\
\dot{k}_{\text{dir},Ar}[Ar][e^-] &= A_{Ar,p}[Ar_p] + k_{\text{quench},Ar}[Ar_p][H_2]
\end{align*}
\]

(4.9) (4.10)

Equations (4.9) and (4.10) can be re-arranged to yield expressions for the concentrations of ground-state atomic hydrogen and argon:
\begin{align*}
[H] &= \left( A_{H,n} + k_{\text{quench},H}[H_2] \right)[H_n] \\
&= \frac{k_{\text{dir},H}[e^-]}{k_{\text{dir},H}[H]} \left( 1 + \frac{k_{\text{diss},H}[H_2]}{k_{\text{dir},H}[H]} \right) \\
[Ar] &= \left( A_{Ar,p} + k_{\text{quench},Ar}[H_2] \right)[Ar_p] \\
&= \frac{k_{\text{dir},Ar}[e^-]}{k_{\text{dir},Ar}[e^-]}
\end{align*}
(4.11)

Similarly, equations (4.1) and (4.2) can be re-arranged to isolate expressions for the electronically-excited states of atomic hydrogen and argon:

\begin{align*}
[H_n] &= \frac{I(\lambda_{H,n,m})}{A_{H,n,m}C(\lambda_{H,n,m})E_{H,n,m}} \\
[Ar_p] &= \frac{I(\lambda_{Ar,p,q})}{A_{Ar,p,q}C(\lambda_{Ar,p,q})E_{Ar,p,q}}
\end{align*}
(4.13)

Substituting equations (4.13) and (4.14) into equations (4.11) and (4.12), taking the ratio of equations (4.11) and (4.12), and using the definition of the characteristic energies \( E_{Ar,p,q} = \frac{hc}{\lambda_{Ar,p,q}} \) and \( E_{H,n,m} = \frac{hc}{\lambda_{H,n,m}} \), an expression is achieved relating the concentration of atomic hydrogen to the concentration of argon and the relative intensity of the characteristic emission lines for the argon and hydrogen transitions:

\begin{align*}
\frac{[H]}{[Ar]} &= \left( \frac{A_{H,n} + k_{\text{quench},H}[H_2]}{A_{Ar,p} + k_{\text{quench},Ar}[H_2]} \right) \times \frac{k_{\text{dir},Ar}}{k_{\text{dir},H}} \left( 1 + \frac{k_{\text{diss},H}[H_2]}{k_{\text{dir},H}[H]} \right) \\
&= \frac{I(\lambda_{H,n,m})}{I(\lambda_{Ar,p,q})} \frac{A_{Ar,p,q}C(\lambda_{Ar,p,q})\lambda_{H,n,m}}{A_{H,n,m}C(\lambda_{H,n,m})\lambda_{Ar,p,q}}
\end{align*}
(4.15)

Equation (4.15) reproduces the result of (Geng et al. 2005), and provides the desired relationship between the concentration of atomic hydrogen within the reactor and the relative intensity of the hydrogen and argon emission lines. Note that a term containing the concentration of atomic hydrogen \([H]\) remains on the right-hand side equation (4.15). However, this term can be neglected provided that \( k_{\text{diss},H}[H_2]/k_{\text{dir},H}[H] \ll 1 \); this simplification is not, however,
always true, per (Fantz 2002). Of the terms in equation (4.15), $C(\lambda_{Ar,p,q})$ and $C(\lambda_{H,n,m})$ must be determined by calibrating the spectrometer with a light source of known spectral intensity. $I(\lambda_{H,n,m})$ and $I(\lambda_{Ar,p,q})$ are the measured radiation intensities of the emission peaks corresponding to the $n$ to $m$ and $p$ to $q$ transitions. The concentrations of $[Ar]$ and $[H_2]$ may be estimated using the flow rates of these two gases, the total pressure of the reactor, and the temperature of the gaseous species using an equation of state (e.g., the ideal gas law). The spectroscopic quantities $A_{H,n}, A_{Ar,p}, A_{H,n,m}, A_{Ar,p,q}, \lambda_{H,n,m},$ and $\lambda_{Ar,p,q}$ are well-known quantities and are presented in Table 4.1. Note that the 750.3 nanometer argon emission line is produced from a $4p$ to $4s$ transition, such that the principal quantum number of the transitioning electron does not change.

<table>
<thead>
<tr>
<th>Emission Line Designation</th>
<th>Quantum Numbers, n/m and p/q</th>
<th>$\lambda_{H,n,m}$ and $\lambda_{Ar,p,q}$, nm</th>
<th>$A_{H,n} \text{ and } A_{Ar,p}$, $10^7$ s$^{-1}$</th>
<th>$A_{H,n,m} \text{ and } A_{Ar,p,q}$, $10^7$ s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_\alpha$</td>
<td>3/2</td>
<td>656.3</td>
<td>9.98</td>
<td>4.41</td>
</tr>
<tr>
<td>$H_\beta$</td>
<td>4/2</td>
<td>486.1</td>
<td>3.02</td>
<td>0.842</td>
</tr>
<tr>
<td>$H_\gamma$</td>
<td>5/2</td>
<td>434.0</td>
<td>1.16</td>
<td>0.253</td>
</tr>
<tr>
<td>Ar-750.3 nm</td>
<td>4/4</td>
<td>750.4</td>
<td>4.47</td>
<td>4.45</td>
</tr>
</tbody>
</table>

Calculation of the collision rates $k_{\text{quench,H}}, k_{\text{quench,Ar}}, k_{\text{dir,H}}, k_{\text{dir,Ar}},$ and $k_{\text{diss,H}}$ requires a consideration of the appropriate cross-sections for these reactions as well as the velocity distributions of the electron and heavy species, using equation (4.6). The collision rates recommended by (Geng et al. 2005) for the excitation of the argon-$4p$ state and the hydrogen $n = 3$ state (i.e., the excited state whose radiative decay produces the $H_\alpha$ line) are presented in Table 4.2.
Table 4.2: Collision rates for the production of the $n = 3$ electronically-excited hydrogen state and the argon 4$p$ electronically-excited state; adapted from (Geng et al. 2005), using an assumed Maxwellian temperature distribution of the electrons at the specified temperatures.

<table>
<thead>
<tr>
<th>Electron Temperature, eV</th>
<th>$k_{dir,H}$, cm$^3$/s</th>
<th>$k_{dir,Ar}$, cm$^3$/s</th>
<th>$k_{diss,H}$, cm$^3$/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>$2.64 \times 10^{-14}$</td>
<td>$1.56 \times 10^{-15}$</td>
<td>$1.33 \times 10^{-17}$</td>
</tr>
<tr>
<td>2.0</td>
<td>$1.23 \times 10^{-11}$</td>
<td>$1.43 \times 10^{-12}$</td>
<td>$6.81 \times 10^{-14}$</td>
</tr>
<tr>
<td>2.5</td>
<td>$4.14 \times 10^{-11}$</td>
<td>$5.44 \times 10^{-12}$</td>
<td>$3.78 \times 10^{-13}$</td>
</tr>
</tbody>
</table>

Note that, in order to use the collision rates provided in Table 4.2, it is necessary to know the temperature of the electrons within the plasma, so as to choose the appropriate rates. The electron temperature may be estimated per (Geng et al. 2005): (1) by evaluating the relative intensity of the hydrogen Balmer lines, with higher electron temperatures corresponding to a higher intensity of the shorter wavelength emission lines relative to the intensity of the longer wavelength emission lines; computational details are specified in (Kirsch, Hanamura, and Wineford 1984) and in (Patel, Heithmar, and Winefordner 1987); (2) by estimating the microwave power density (MWPD) of the plasma and employing correlations established between the MWPD and the electron temperature such as those provided by (C.-K. Chen et al. 1999); or (3) by measuring the electron temperature via, e.g., a Langmuir probe. If the electron temperatures estimated by these methods are not close to those provided in Table 4.2, it will be necessary to tabulate the collision rates manually by conducting the integration using equation (4.6) and velocity-dependent cross-sections, such as those specified by (Lavrov and Pipa 2002).

The equation used for estimating the electron temperature in this work is given by:

$$T_e \approx T_{H-Exc}^{\alpha-\beta} = \frac{E_3 - E_4}{k_B \log \left( \frac{I(\lambda_{H,A,2}) \lambda_{H,A,2}/(C(\lambda_{H,A,2})g_4A_{42})}{I(\lambda_{H,3,2}) \lambda_{H,3,2}/(C(\lambda_{H,3,2})g_3A_{32})} \right)} \quad (4.15b)$$

where $E_n$ is the energy of the respective excited state $n$, $k_B$ is Boltzmann’s constant, $g_n$ is the multiplicity of state $n$; the other terms have been described previously. Note that this analysis
essentially treats the distribution of electronic states of hydrogen as being in thermodynamic
equilibrium. This is clearly not true for the non-equilibrium plasma in question. However, $T_{H-Exc}^{\alpha-\beta}$
may be used as a lower bound for the electron temperature, per (Geng et al. 2005).

The remaining terms in equation (4.15), $k_{\text{quench},H}$ and $k_{\text{quench},Ar}$, may be calculated by
means of equation (4.6), using the velocity distribution of the heavy species within the plasma.
(Geng et al. 2005) use the cross-section data provided by (Bittner et al. 1988) and (Gicquel et al.
1998) to estimate $\tilde{\sigma}_{\text{quench},Ar} \approx 65 \times 10^{-16}$ cm$^2$ and $\tilde{\sigma}_{\text{quench},H} \approx 61.5 \times 10^{-16}$ cm$^2$. Note that the
authors appear to treat these cross-sections as independent of the relative velocity of the colliding
particles: i.e., they approximate equation (4.6) by writing $k_{\text{quench},H} \approx \tilde{\sigma}_{\text{quench}} \tilde{v}$. It is not clear if
this treatment of the quenching cross-sections as constants is accurate, as the experiments used to
derive these results did not conduct a controlled investigation of the dependence of the cross
sections on the temperature of the gas.

The method of actinometry in this section allows for an evaluation of the proportion of
molecular hydrogen which has been dissociated to form atomic hydrogen by observing the
relative intensity of spectral emission lines. This technique, while not as accurate as laser-
induced fluorescence (LIF) or electron-spin resonance (ESR) techniques, is much simpler to
employ. When used to process spectroscopic data collected from a hydrogen plasma, plasma
emission actinometry allows for an estimation of the partial pressure of the atomic hydrogen
within the reactor, information which is essential for evaluating the reduction behavior of metal
oxides within the reactor.

### 4.2 Thermodynamic Analysis of the Metastable Configuration

This section of the dissertation provides a thermodynamic analysis of the non-equilibrium
plasma environment within the reactor. This analysis is conducted by means of equilibrium
phase-stability diagrams generated with the aid of HSC Chemistry 5.1 (Roine 2002). These diagrams predict the predominant phase within a given system at a specified temperature based on the partial pressures of two (independently-variable) gaseous species at equilibrium with the system. It is worth noting that these equilibrium phase-stability diagrams do not directly correspond to the configuration existing within the reactor due to the non-equilibrium nature of the plasma environment. This can be understood by examining a representative phase-stability diagram with isobars of molecular hydrogen superimposed on the diagram, presented in Figure 4.1.

In Figure 4.1, the approximate reactor operating conditions are depicted based on a partial pressure of atomic hydrogen of about $10^{-3}$ atmospheres and a partial pressure of water vapor of about $10^{-8}$ atmospheres (these are estimated values; measurements and calculations pertinent to their estimation are presented in Chapter 6). Under these conditions, the equilibrium partial pressure of molecular hydrogen can be calculated by means of the reaction:

$$2\text{H(g)} = \text{H}_2\text(g)$$

with equilibrium constant $K_{eq,600^\circ C} = 4.473 \times 10^{20}$ (Roine 2002). Using this equation, it is possible to calculate the equilibrium partial pressure of molecular hydrogen at each point in the phase-stability diagram; selected isobars are drawn in Figure 4.1 to provide some perspective of the partial pressures involved. Clearly, the equilibrium partial pressures of molecular hydrogen are much larger than those within the actual reactor: with a nominal atomic hydrogen partial pressure of $10^{-3}$ atmospheres, the equilibrium partial pressure of molecular hydrogen is $4.473 \times 10^{14}$ atmospheres. Given that the total pressure within the reactor is on the order of $10^{-2}$ atmospheres, the equilibrium partial pressure of molecular hydrogen is clearly unphysical. The
discrepancy between the equilibrium and actual partial pressures of molecular hydrogen may be understood by considering the non-equilibrium environment with the plasma discharge: for a given partial pressure of atomic hydrogen (as quantified via actinometry), the actual pressure of molecular hydrogen is much lower than would be expected in an equilibrium configuration.

Equivalently, it may be said that the partial pressure of atomic hydrogen within the plasma discharge is much higher than the equilibrium partial pressure of atomic hydrogen predicted for the partial pressure of molecular hydrogen within the reactor. This above-equilibrium concentration of atomic hydrogen describes the nature of the metastable environment within the plasma discharge.

Figure 4.1: Phase-stability diagram for titanium-oxygen-hydrogen system at 600 degrees Celsius, calculated using (Roine 2002). Of the intermediate Magneli oxides, only TiO has been considered in this diagram. The isobars for molecular hydrogen are indicated by the dotted lines. The approximate reactor operating conditions are indicated by the area contained within the red rectangle.
Clearly, the environment within the plasma is not accurately described by equilibrium thermodynamics, at least in consideration of the speciation of the gaseous components; this point has eluded some previous researchers (Gaskell 1996; Robino 1996) but was acknowledged by others (Jacob, Chandran, and Mallya 2000). Hence, it is not entirely clear if the equilibrium thermodynamic analysis required to construct Figure 4.1 is justified. Thus, one of the hypotheses of this work—to be evaluated empirically—is that equilibrium phase-stability diagrams of the type presented in Figure 4.1 may be used to predict the steady-state configuration of solid metal/oxide systems placed within the metastable plasma environment, provided that both the equilibrium system and the metastable system have the same concentrations of atomic hydrogen and water vapor, and are maintained at the same temperature. Thus, while the equilibrium system is clearly not directly representative of the metastable plasma environment, based on the shared concentrations of atomic hydrogen and water vapor, both systems are expected to have the same speciation. It is worth reemphasizing that this is ultimately an empirical question, as the metastable plasma environment is not amenable to equilibrium thermodynamic arguments except by analogy. It is possible that a detailed kinetic model could be constructed which incorporated both excitation/recombination phenomena as well as reduction and oxidation of the solid phases. This would provide information regarding the net reduction or oxidation of a solid phase within the gaseous environment; a limited kinetic treatment is presented in section 4.3.

Figures 4.2 through 4.5 provide similar phase-stability analyses of the other metal-oxygen-hydrogen systems considered in this work. For the nominal reactor conditions of $10^{-3}$ atmospheres of atomic hydrogen and $10^{-8}$ atmospheres of water vapor, these phase-stability diagrams predict that a reduced state (the metallic state for copper and molybdenum and the hydride state for cerium and neodymium) will be the stable solid phase. Thus, based on this
Figure 4.2: Phase-stability diagram for copper-oxygen-hydrogen system at 600 degrees Celsius, calculated using (Roine 2002). The approximate reactor operating conditions are indicated by the area contained within the red rectangle.

Figure 4.3: Phase-stability diagram for molybdenum-oxygen-hydrogen system at 600 degrees Celsius, calculated using (Roine 2002). The approximate reactor operating conditions are indicated by the area contained within the red rectangle.
analysis, even the most stable metal oxides considered within the scope of this work should be able to be converted to these reduced forms (metals and metal hydrides) by the plasma.

Figure 4.4: Phase-stability diagram for neodymium-oxygen-hydrogen system at 600 degrees Celsius, calculated using (Roine 2002). The approximate reactor operating conditions are indicated by the area contained within the red rectangle.

A consideration of the temperature dependence of the thermodynamically stable phases in the plasma environment is presented in Figures 4.6 through 4.10. These phase-stability diagrams are constructed for the nominal reactor condition of $p_H = 10^{-3}$ atmospheres; the approximate reactor conditions of 500 to 700 degrees Celsius and $p_{H_2O} \approx 10^{-8}$ atmospheres are denoted by the red rectangles drawn in each figure. Clearly, for these metal/oxide systems the equilibrium phase under these conditions is a reduced phase (the metal for the copper and molybdenum systems and the hydride for the titanium, cerium and neodymium phases). This stable phase is fairly invariant over the temperature ranges considered: for the copper, molybdenum, and titanium systems, the stable phase is unchanged across the entire range of
parameters considered ($p_{H_2O}$ ranging from $10^{-20}$ atmospheres to $10^9$ atmospheres and temperature ranging from 0 to 1000 degrees Celsius), provided that the partial pressure of atomic hydrogen is maintained at $p_H = 10^{-3}$ atmospheres. For the neodymium and cerium systems, a more oxidized phase becomes thermodynamically stable at the upper range of temperatures and water partial pressures considered. Given the stability of the reduced metal/hydride phases under the reactor conditions, it is expected that oxides of these metals will be reduced when exposed to the plasma environment. It is worth reiterating that these predictions are strictly applicable only to the equilibrium configuration, which the metastable plasma environment does not satisfy. It is only by arguing that the metastable configuration is analogous to the equilibrium configuration because both configurations have the same partial pressure of water, the same partial pressure of atomic hydrogen, and the same temperature; the two configurations have vastly different partial pressures of molecular hydrogen.

The considerations discussed in this section provide a justification for the ability of atomic hydrogen to reduce even very stable oxides: based on the phase-stability diagrams presented here, it is expected that reduced phases such as metals and metal hydrides will be the stable species within the reactor environment. This is true for a wide range of temperatures, atomic hydrogen partial pressures, and water partial pressures. However, the conclusions from this section—based as they are upon equilibrium thermodynamic calculations—are not conclusively applicable to the metastable configuration that exists within the reactor. The validity of these predictions rests upon the suitability of the equilibrium systems discussed here as proxies for the metastable plasma environment.
Figure 4.5: Phase-stability diagram for titanium-oxygen-hydrogen system with $p_H = 10^{-3}$ atmospheres, calculated using (Roine 2002). The approximate reactor operating conditions are indicated by the area contained within the red rectangle.

Figure 4.6: Phase-stability diagram for copper-oxygen-hydrogen system with $p_H = 10^{-3}$ atmospheres, calculated using (Roine 2002). The approximate reactor operating conditions are indicated by the area contained within the red rectangle.
Figure 4.7: Phase-stability diagram for molybdenum-oxygen-hydrogen system with $p_H = 10^{-3}$ atmospheres, calculated using (Roine 2002). The approximate reactor operating conditions are indicated by the area contained within the red rectangle.

Figure 4.8: Phase-stability diagram for neodymium-oxygen-hydrogen system with $p_H = 10^{-3}$ atmospheres, calculated using (Roine 2002). The approximate reactor operating conditions are indicated by the area contained within the red rectangle.
4.3 Rate of Conversion in a Pseudo-Homogeneous Near-Equilibrium Reactor

This section of the thesis discusses a model for predicting the rate of conversion achievable in a pseudo-homogeneous reactor operating under near-equilibrium conditions. This kinetic analysis provides a means of evaluating the contributions of reduction, recombination, and reoxidation, and the implications of the relative magnitude of these rates on the maximum achievable production of reduced material in a given reactor system. The model discussed here is applicable for conditions in which the rate of reaction can be expressed as a first-order, irreversible reaction of the form:

\[ R_{\text{reduction}} = k_{\text{reduction}}(p_H - p_{H,\text{eq,red}}) \]  

(4.16)

In equation (4.16), \( R_{\text{reduction}} \) is the rate of reduction (with dimensions of number per time per volume), \( k_{\text{reduction}} \) is the reduction rate constant (with dimensions of number per time per volume per pressure), \( p_H \) is the partial pressure of atomic hydrogen within the reactor, and \( p_{H,\text{eq,red}} \) is the equilibrium partial pressure of atomic hydrogen, where that equilibrium partial pressure is determined by the reaction:

\[ \text{MeO}_m + n \text{ H(g)} = \text{MeH}_q + m \text{ H}_2\text{O(g)} \]

where \( n = 2m + q \), with equilibrium constant \( K_{\text{eq,red}} = (p_{H_2O}/p^o)^m/(p_{H,\text{eq,red}}/p^o)^n \) (i.e., assuming the solid phases to have unit activity) and \( p_{H_2O} \) is the partial pressure of water vapor within the reactor. This discussion does not consider the case of intermediate suboxide reaction products. The restriction described by equation (4.16) effectively reduces the applicability of the model to situations in which mass transport does not limit the rate of reaction, e.g., in the limit of small particles distributed homogeneously within a well-mixed, isothermal, and isobaric continuous-flow reactor (such as might occur within a spouted or fluidized bed). Thus, while the reaction between the solids and the gaseous environment is necessarily heterogeneous, in the
limit of small particles distributed throughout the well-mixed gaseous phase, it is reasonable to
treat this system in a pseudo-homogeneous fashion.

An analogous rate expression can be written for the recombination of atomic hydrogen to
form molecular hydrogen:

\[ R_{\text{recombination}} = k_{\text{recombination}} (p_H - p_{H,eq,\text{recomb}}) \]  \hspace{1cm} (4.17)

where \( R_{\text{recombination}} \) is the rate of recombination (with dimensions of number per time per
volume), and \( k_{\text{recombination}} \) is the recombination rate constant (with dimensions of number per
time per volume per pressure), and \( p_{H,eq,\text{recomb}} \) is the equilibrium partial pressure for the
recombination reaction:

\[ 2H(g) = H_2(g) \]

with equilibrium constant \( K_{eq,\text{recomb}} = (p_{H_2}/p^o)/(p_{H,eq,\text{recomb}}/p^o)^2 \), and \( p_{H_2} \) the partial
pressure of molecular hydrogen within the reactor. Note that by neglecting surface areas within
the reactor configuration, equation (4.17) essentially treats the recombination reaction as
homogeneous recombination. In general, homogeneous recombination of atomic hydrogen is
much slower than heterogeneous recombination, but the conceptualization of this model (with a
small, homogeneously distributed solid phase) allows for the treatment of this heterogeneous
reaction in a homogeneous fashion. Equation (4.17) also specifies first-order recombination
kinetics, a reasonable restriction for heterogeneous recombination per (Wise and Wood 1968;
Mozetič et al. 1994).

The re-oxidation of the reduced metal/hydride species by water vapor is expressed by the
reaction:

\[ R_{\text{reoxidation}} = k_{\text{reoxidation}} (p_{H_2O} - p_{H_2O,eq,\text{reox}}) \]  \hspace{1cm} (4.18)
where $R_{\text{reoxidation}}$ represents the rate of re-oxidation (with dimensions of number per time per volume), $k_{\text{reoxidation}}$ the reoxidation rate constant (with dimensions of number per time per volume per pressure), and $p_{H_2O,eq,\text{reox}}$ the equilibrium partial pressure of water vapor for the reoxidation reaction:

$$\text{MeH}_q + m \text{H}_2\text{O}(g) = \text{MeO}_m + \frac{n}{2} \text{H}_2(g)$$

with equilibrium constant $K_{eq,\text{reox}} = \left(\frac{p_{H_2}}{p^o}\right)^{n/2}/\left(\frac{p_{H_2O,eq,\text{reox}}}{p^o}\right)^m$.

An overall steady-state population balance for the species within the reactor can be constructed by writing:

$$M_{H,in} = M_{H,out} + V[R_{\text{reduction}} + R_{\text{recombination}}] \quad (4.19)$$

$$M_{H_2,in} + V \left[\left(\frac{1}{2}\right)R_{\text{recombination}} + \left(\frac{n}{2m}\right)R_{\text{reoxidation}}\right] = M_{H_2,out} \quad (4.20)$$

$$M_{H_2O,in} + V \left[\left(\frac{m}{n}\right)R_{\text{reduction}}\right] = M_{H_2O,out} + V[R_{\text{reoxidation}}] \quad (4.21)$$

where $M_{j,in}$ and $M_{j,out}$ represent the rate at which species $j$ enters and exits (respectively) the reaction volume; these quantities have dimensions of number per time. Note that this population balance does not consider the dissociation of species within the reactor to produce atomic hydrogen; i.e., the reactor volume is placed “downstream” of the atomic hydrogen generation location. By substituting equations (4.16) through (4.18) into equations (4.19) through (4.21), the following population balances can be constructed:

$$M_{H,in} = M_{H,out} + V \left[[k_{\text{reduction}}(p_H - p_{H,eq,\text{red}})] + \{k_{\text{recombination}}(p_H - p_{H,eq,\text{comb}})\}\right] \quad (4.22)$$
\[ M_{H_2,\text{in}} + V \left[ \left( \frac{1}{2} \right) k_{\text{recombination}}(p_H - p_{H,eq,\text{recomb}}) \right] + \left( \frac{n}{2m} \right) \left[ k_{\text{reoxidation}}(p_{H_2O} - p_{H_2O,eq,\text{reox}}) \right] = M_{H_2,\text{out}} \] (4.23)

\[ M_{H_2O,\text{in}} + V \left[ \left( \frac{m}{n} \right) k_{\text{reduction}}(p_H - p_{H,eq,\text{red}}) \right] = M_{H_2O,\text{out}} + V \left[ k_{\text{reoxidation}}(p_{H_2O} - p_{H_2O,eq,\text{reox}}) \right] \] (4.24)

By appealing to the well-mixed nature of the reactor, it is possible to express the rate of outflow of species \( j \) as \( M_{j,\text{out}} = p_j Q / (RT) \) with \( p_j \) the partial pressure of species \( j \) within the reactor, \( Q \) the volumetric flow rate of gas from the reactor, \( R \) the ideal gas constant, and \( T \) the temperature of the reactor/gas stream; this expression is applicable only if ideal-gas behavior accurately describes the gaseous species. Substituting these expressions into equations (4.22) through (4.24), it is possible to write:

\[ M_{H,\text{in}} = p_H Q / (RT) + V \left[ k_{\text{reduction}}(p_H - p_{H,eq,\text{red}}) \right] + \left[ k_{\text{recombination}}(p_H - p_{H,eq,\text{recomb}}) \right] \] (4.25)

\[ M_{H_2,\text{in}} + V \left[ \left( \frac{1}{2} \right) k_{\text{recombination}}(p_H - p_{H,eq,\text{recomb}}) \right] + \left( \frac{n}{2m} \right) \left[ k_{\text{reoxidation}}(p_{H_2O} - p_{H_2O,eq,\text{reox}}) \right] = p_{H_2} Q / (RT) \] (4.26)

\[ M_{H_2O,\text{in}} + V \left[ \left( \frac{m}{n} \right) k_{\text{reduction}}(p_H - p_{H,eq,\text{red}}) \right] = p_{H_2O} Q / (RT) + V \left[ k_{\text{reoxidation}}(p_{H_2O} - p_{H_2O,eq,\text{reox}}) \right] \] (4.27)

The quantities \( M_{j,\text{in}} \) could be determined by quantifying the composition of the gas feed stream and by measuring the extent of dissociation of atomic hydrogen. \( Q, R, T, \) and \( V \) are all known characteristics of the reactor system. The rate constants \( k_{\text{reduction}}, k_{\text{recombination}}, \) and \( k_{\text{reoxidation}} \) could be (hypothetically) quantified by kinetic experiments; e.g. catalytic probe measurements similar to those conducted by (Mozetič et al. 1994) could be used to measure the
rate of recombination, and thermogravimetric experiments (in which a water-vapor bearing stream is passed over a reduced solid) could be conducted to evaluate the rate of oxidation. Once the rates of reoxidation and recombination were quantified separately, it would be possible to account for these effects during reduction experiments. In practice, it might be difficult to arrange for situations in which the effects of each reaction could be completely isolated. The quantities \( p_{H,eq,\text{red}} \), \( p_{H,eq,\text{recomb}} \), and \( p_{H_2O,eq,\text{reox}} \) are (nonlinear) functions of the respective equilibrium constants for these reactions and of \( p_{H_2} \) and \( p_{H_2O} \), as specified by the equilibrium constant expressions for each reaction. Substituting the expressions for \( p_{H,eq,\text{red}} \), \( p_{H,eq,\text{recomb}} \), and \( p_{H_2O,eq,\text{reox}} \) into equations (4.25), (4.26), and (4.27), the following relationships are obtained:

\[
M_{H,in} = \frac{p_H \cdot Q}{(RT)} + V \left\{ k_{\text{reduction}} \left( p_H - p^o \left[ \frac{(p_{H_2O}/p^o)^{m/n}}{(K_{eq,\text{red}})^{1/n}} \right] \right) \right. \\
\left. + k_{\text{recombination}} \left( p_H - p^o \left[ \frac{(p_{H_2}/p^o)^{1/2}}{(K_{eq,\text{recomb}})^{1/2}} \right] \right) \right\} \quad (4.28)
\]

\[
M_{H_2,in} + V \left[ \left( \frac{1}{2} \right) k_{\text{recombination}} \left( p_H - p^o \left[ \frac{(p_{H_2}/p^o)^{1/2}}{(K_{eq,\text{recomb}})^{1/2}} \right] \right) \right. + \\
\left. \left( \frac{n}{2m} \right) k_{\text{reoxidation}} \left( p_{H_2O} - p^o \left[ \frac{(p_{H_2}/p^o)^{n/2m}}{(K_{eq,\text{reox}})^{1/m}} \right] \right) \right] = \frac{p_{H_2} \cdot Q}{(RT)} \quad (4.29)
\]

\[
M_{H_2O,in} + V \left[ \left( \frac{m}{n} \right) k_{\text{reduction}} \left( p_H - p^o \left[ \frac{(p_{H_2O}/p^o)^{m/n}}{(K_{eq,\text{red}})^{1/n}} \right] \right) \right] \\
= \frac{p_{H_2O} \cdot Q}{(RT)} + V \left[ k_{\text{reoxidation}} \left( p_{H_2O} - p^o \left[ \frac{(p_{H_2}/p^o)^{n/2m}}{(K_{eq,\text{reox}})^{1/m}} \right] \right) \right] \quad (4.30)
\]

Thus, the system of equations (4.28) through (4.30) consists of three equations in the three unknowns \( p_H, p_{H_2}, \) and \( p_{H_2O} \). This system of equations can be, in principle, solved to
provide information about the steady-state reactor operating conditions (specified by the partial pressures of each gaseous component). By substituting the steady-state values of $p_H$ and $p_{H_2O}$ into equations (4.16) and (4.18) and by using the stoichiometry of the reduction and oxidation reactions, it is possible to quantify the net rate of reduction achievable within the reactor. In practice, this system of equations is untenable until numerical values for the various constants are provided. This discussion will continue with the optimal case (in terms of maximizing reduction within the reactor) in which $k_{\text{reduction}} \gg k_{\text{recombination}}$ and $k_{\text{reduction}} \gg k_{\text{reoxidation}}$. This reduces the system of equations (4.28) through (4.30) to the more tractable set:

$$M_{H,in} = p_H Q / (RT) + V k_{\text{reduction}} \left( p_H - p^o \left[ \frac{(p_{H_2O}/p^o)^{m/n}}{(K_{eq,\text{red}})^{1/n}} \right] \right)$$ (4.31)

$$M_{H_2,in} = p_{H_2} Q / (RT)$$ (4.32)

$$M_{H_2O,in} + V \left[ \frac{m}{n} \right] \left[ k_{\text{reduction}} \left( p_H - p^o \left[ \frac{(p_{H_2O}/p^o)^{m/n}}{(K_{eq,\text{red}})^{1/n}} \right] \right) \right] = p_{H_2O} Q / (RT)$$ (4.33)

Under these conditions, the partial pressure of molecular hydrogen no longer needs to be considered (it does not change within the reactor and it does not influence the other variables) such that equation (4.32) will be neglected going forward. Once numerical values characterizing the system are provided, it will be possible to solve equations (4.31) and (4.33) for the steady-state values of $p_H$ and $p_{H_2O}$ within the reactor. Using these values and substituting them into equation (4.16), an expression will be obtained for the rate of reduction achievable within the reactor. This value, derived under conditions in which recombination and reoxidation are negligible, will constitute a “best-case” estimate of the productivity of the reactor, and could be used as an upper bound for the throughput achievable in the device. This could prove useful for, e.g., preliminary economic analyses of the feasibility of a reduction reactor employing atomic hydrogen.
This section has described a method for analyzing the steady-state composition of the gaseous environment within a continuous-flow, pseudo-homogeneous gas-solid reactor (such as might be achieved within a fluidized bed). By providing an analysis of the dependence of the gas composition on the reactor parameters, this method has enabled the analysis of the maximum rates of reduction achievable within a given reactor. While admittedly of limited practical use until more data is available (notably, the rate constants $k_{\text{reduction}}$, $k_{\text{recombination}}$, and $k_{\text{reoxidation}}$), this model still provides a means of understanding the capabilities of such a reactor.

### 4.4 Moving-Boundary Analysis for Reduction by Atomic Hydrogen

This section considers a mathematical model for the temporal evolution of the product layer in a metal oxide exposed to atomic hydrogen. The goal of this model is to provide an explanation for some of the qualitative features evident during the reduction of metal oxides by atomic hydrogen (such as the existence of a finite penetration-depth of reduction), as well as to provide an analysis of the dependence of the reduction behavior upon the characteristics of the reacting system. The effects of the chemical reaction at the product-oxide interface are considered, as are diffusion and recombination of atomic hydrogen within the product layer. Note that the reoxidation of the reduced product layer by water vapor is not consider in this model; indeed, water vapor is not treated at all within the scope of this discussion. A schematic depiction of the system is presented in Figure 4.9.

In this diagram, the $z$-axis represents the displacement within the solid sample from the solid-plasma interface (located at $z = 0$). The interface between the product layer (here, considered to be a metal, though it might also be a metal hydride, depending on the particular system in question) and the unreacted metal oxide occurs at $z = Z(t)$. As the reaction proceeds, this interface moves deeper within the metal oxide; both the reduction reaction and the
recombination reaction are taken to be first-order and irreversible, while the possible re-
oxidation of the reduced layer by water vapor is neglected. This model considers a one-
dimensional metal oxide exposed to a plasma containing atomic hydrogen, corresponding to the
situation of large, flat particles such as the thin-film samples investigated experimentally in this
research. The model could be adapted to situations involving spherical or cylindrical geometries,
but such an analysis is not conducted here.

![Diagram of mass-balance](image)

**Figure 4.9:** Diagram representing evolution of product layer (here, a metal) in a metal oxide
exposed to atomic hydrogen.

Consider a mass-balance of the atomic hydrogen species within a rectangular shell of the
metal region defined by planes at locations $z$ and $z + dz$. It is possible to write:
\[ \text{AN}_{\text{Hz}}|_z - \text{AN}_{\text{Hz}}|_{z+dz} - k_{\text{recomb}} C_{\text{total}} X_{\text{H}}|_z \sigma \, dz \, A = \frac{\partial}{\partial t} (C_{\text{total}} X_{\text{H}}|_z \, dz \, A) \] (4.34)

where \( A \) is the cross-sectional area under consideration, \( \text{N}_{\text{Hz}}|_z \) is the molar flux of atomic hydrogen in the positive \( z \) direction (at location \( z \)), \( \text{N}_{\text{Hz}}|_{z+dz} \) is the molar flux of atomic hydrogen in the positive \( z \) direction (at location \( z + dz \)), \( k_{\text{recomb}} \) is the rate constant of the recombination reaction (with dimensions of length per time), \( C_{\text{total}} \) is the molar concentration of the gaseous species (i.e., atomic hydrogen and molecular hydrogen), \( X_{\text{H}}|_z \) is the mole fraction of atomic hydrogen (the ratio of the moles of atomic hydrogen at location \( z \) to the total moles of gaseous species at this location), \( \sigma \) is the specific surface area of the metal product layer (with dimensions of area per unit volume), \( dz \) is the thickness of the rectangular shell, and \( t \) is time. Substituting Fick’s law \( \text{N}_{\text{Hz}} = -D_H \frac{\partial}{\partial z} (C_{\text{total}} X_{\text{H}}) \) for the flux expression (with \( D_H \) the effective diffusivity of atomic hydrogen within the product layer), it is possible to write:

\[ -AD_H \frac{\partial}{\partial z} (C_{\text{total}} X_{\text{H}})|_z + AD_H \frac{\partial}{\partial z} (C_{\text{total}} X_{\text{H}})|_{z+dz} - k_{\text{recomb}} C_{\text{total}} X_{\text{H}}|_z \sigma \, dz \, A = \frac{\partial}{\partial t} (C_{\text{total}} X_{\text{H}}|_z \, dz \, A) \] (4.35)

It is important to note that this implementation ignores both the contributions of diffusion due to bulk flow as well as the interactions of the diffusing species with water vapor. Neglecting bulk flow is not entirely accurate because this system involves non-equimolar fluxes due to the stoichiometry of the recombination reaction; see (J. Szekely 1967) for a discussion of the steady-state behavior of a similar system incorporating bulk flow effects. Furthermore, the general treatment of the diffusion behavior all three of the gaseous species—i.e., considering the interactions of \( \text{H(g)} \) and \( \text{H}_2(g) \) with \( \text{H}_2\text{O(g)} \)—would require the utilization of the general Maxwell-Stefan theory. This following discussion considers neither of these sophistications.
Taking $C_{\text{total}}$ to be independent of position (the isobaric assumption), dividing by $C_{\text{total}}$ and $A$, and collecting terms, it is possible to write:

$$
D_H \left( \frac{\partial}{\partial z} (X_H)|_{z+dz} - \frac{\partial}{\partial z} (X_H)|_z \right) \frac{d z}{d z} - k_{\text{recomb}} \sigma X_H|_z = \frac{\partial}{\partial t} (X_H|_z)
$$

(4.36)

In the limit as $dz$ approaches zero, this equation can be simplified using the definition of the derivative to yield:

$$
D_H \frac{\partial^2 X_H}{\partial z^2} - (k_{\text{recomb}} \sigma) X_H = \frac{\partial X_H}{\partial t}
$$

(4.37)

Equation (4.37) is essentially the standard diffusion equation with an added term representing the loss of atomic hydrogen via surface recombination. The boundary conditions for this differential equation are taken to be $X_H|_{z=0} = X_{H,0}$ and $-D_H \frac{\partial}{\partial z} (C_{\text{total}} X_H) A = k_{\text{reac}} C_{\text{total}} (X_H - X_{H,\text{min}}) A$, or equivalently, $rac{\partial X_H}{\partial z}|_{z=Z(t)} = \frac{-k_{\text{reac}}}{D_H} (X_H|_{z=Z(t)} - X_{H,\text{min}})$ where $X_{H,0}$ is the mole fraction of atomic hydrogen at the plasma-metal interface, $X_{H,\text{min}}$ is the minimum mole fraction of atomic hydrogen necessary for the reaction to proceed, and $k_{\text{reac}}$ is the reaction rate constant for the transformation of the metal oxide into the metal (with dimensions of length per time). Physically, these boundary conditions describe the situation in which a constant mole fraction of the reagent is imposed at the metal-plasma interface and a first-order chemical reaction is taking place at the metal/metal-oxide interface. The initial conditions for this boundary-value problem are given by $X_H(z, t = 0) = 0$; i.e., that there is initially no atomic hydrogen within the solid.

The complementary equation which must be solved to describe the evolution of this system is the equation-of-motion for the metal/metal-oxide interface, $Z(t)$. This may be
calculated by considering the stoichiometric relationship between the flux of atomic hydrogen to the interface with the moles of metal oxide converted to metal:

\[-D_H \frac{\partial}{\partial z} (C_{total}X_H) \bigg|_{z=Z(t)} A \frac{1}{n} = (1 - p) \rho A \frac{dZ(t)}{dt} \]  \hspace{1cm} (4.38)

where \( n \) is a stoichiometric constant relating the number of moles of hydrogen necessary to reduce one mole of oxide to the metal or metal hydride (via the representative reaction, e.g., \( \text{MeO}_m + n \text{ H(g)} = \text{MeH}_q + m \text{ H}_2\text{O(g)} \)), \( p \) is the porosity of the product layer, and \( \rho \) is the molar density of the product (with dimensions of moles per volume). Note that this analysis is applicable to conditions in which the reactant layer is non-porous while the product layer is porous. The equation-of-motion has the initial condition \( Z(t = 0) = 0 \); i.e., that initially the solid is entirely unreacted.

Solving the coupled system defined by equations (4.37) and (4.38) to yield \( X_H(z, t) \) and \( Z(t) \) for all time \( t > 0 \) and for all space \( z > 0 \) will describe the evolution of the reduction of the metal oxide by atomic hydrogen. First, it is useful (especially for subsequent numerical simulation) to conduct a change of variables which will allow the moving boundary \( Z(t) \) to be brought to rest. This is conducted by defining a new variable \( \xi = z / Z(t) \), similar to the transformation conducted by (Landau 1950). Application of the chain rule then recasts equation (4.37) as:

\[ D_H \frac{\partial^2 X_H}{\partial \xi^2} \left( \frac{1}{[Z(t)]^2} \right) = \left( k_{\text{recomb}} \sigma \right) X_H = \frac{\partial X_H}{\partial t} + \frac{\partial X_H}{\partial \xi} \frac{-\xi}{Z(t)} \frac{dZ(t)}{dt} \]  \hspace{1cm} (4.39)

with boundary conditions \( X_H|_{\xi=0} = X_{H,0} \) and \( \frac{\partial X_H}{\partial \xi} \bigg|_{\xi=1} = -Z(t) \frac{k_{\text{reac}}}{D_H} \left( X_H \big|_{\xi=1} - X_{H,\text{min}} \right) \) and initial condition \( X_H(\xi, t = 0) = 0 \). Equation (4.38) is recast in the new coordinate system as:

\[ \frac{dZ(t)}{dt} = - \frac{D_H C_{\text{total}}}{(1 - p) \rho n Z(t)} \frac{\partial X_H}{\partial \xi} \bigg|_{\xi=1} \]  \hspace{1cm} (4.40)
with initial condition $Z(t = 0) = 0$. At this point, it is convenient to convert equations (4.39) and (4.40) into dimensionless form. This can be accomplished by defining the dimensionless variables $\chi \equiv X_H / X_{H,0}$, $\Xi \equiv X_{H,\text{min}} / X_{H,0}$, $\tau \equiv t D_H / L^2$ (the Fourier number), $z^* \equiv z / L$ and $\zeta(t) \equiv Z(t) / L$, with $L$ a characteristic length scale for the reduction phenomenon. Using these new variables, equation (4.39) is transformed (after rearrangement) to yield:

$$\zeta^2 \frac{\partial \chi}{\partial \tau} + \lambda_1 \chi \zeta^2 = \frac{\partial^2 \chi}{\partial \xi^2} + \xi \frac{\partial \chi}{\partial \xi} \frac{d\zeta}{d\tau}$$  \hspace{1cm} (4.41)

with $\lambda_1 \equiv k_{\text{recomb}} \sigma L^2 / D_H$, analogous to the second Damköhler number $Da_{\text{II}}$ for the recombination reaction. Equation (4.41) has boundary conditions given by $\chi|_{\xi=0} = 1$ and by $\frac{\partial \chi}{\partial \xi}|_{\xi=1} = -\lambda_2 \zeta (\chi|_{\xi=1} - \Xi)$ with $\lambda_2 \equiv L k_{\text{reac}} / D_H$ the second Damköhler number (sometimes alternatively referred to as the Thiele modulus) for the reduction reaction. The initial condition for equation (4.41) is given by $\chi(\xi, \tau = 0) = 0$. Similarly, equation (4.39) can be converted to these dimensionless coordinates with the following result:

$$\zeta \frac{d\zeta}{d\tau} = -\gamma_1 \frac{\partial \chi}{\partial \xi}|_{\xi=1}$$  \hspace{1cm} (4.42)

with $\gamma_1 \equiv X_{H,0} C_{\text{total}} / ((1 - p) \rho n)$. Equation (4.42) has the initial condition $\zeta(\tau = 0) = 0$.

Solving the system defined by equations (4.41) and (4.42) with the appropriate initial and boundary equations will thus provide a description of the reduction behavior observed in this system; consideration of the dimensionless numbers $\lambda_1, \lambda_2, \gamma_1, \text{and } \Xi$ will provide an analysis of the effect of changing the relative rates and magnitudes of the relevant physical parameters (i.e., the relative rates of diffusion, recombination, and reaction, and the relative molar concentrations of the solid and gaseous species).

Per (P. R. Taylor, De Matos, and Martins 1983), provided that $\gamma_1 < 0.1$, it is reasonable to make the quasi-steady state approximation such that the terms in equation (4.41) incorporating
time derivatives may be ignored. This is tantamount to proceeding under the condition in which “the rate of accumulation of the gaseous species...is negligibly small compared to the diffusive fluxes” (Julian Szekely, Evans, and Sohn 1976). Note that neither of these authors were considering situations in which loss of the gaseous reagent could occur in any manner except by reaction at the interface. Thus, employing the quasi-steady state approximation for the system currently under consideration involves the additional condition that the accumulation of gaseous species is negligibly small relative to the loss of the gaseous species by recombination. It seems unlikely that this is an accurate restriction for the general situation: if the recombination reaction is rapid relative to the reduction reaction, then the loss of atomic hydrogen within a local region could be large relative to the diffusive fluxes moving through the local region. In this case, it is not reasonable to neglect the (de-)accumulation terms since they may be of approximately the same order as the recombination term and may be even larger than the diffusive flux term. Thus, this discussion will proceed with the general system described by equations (4.41) and (4.42) and will not employ the quasi-steady state approximation.

A numerical solution of the system defined by equations (4.41) and (4.42) was constructed using a finite-difference method; computational details of this solution are presented in Appendix B. Figure 4.10 depicts the concentration profiles from this numerical solution at various times during the course of a reaction. The concentration profiles are similar to those of a decaying-exponential function. The location of the reaction interface \( \zeta(\tau) \) at each time \( \tau \) occurs at the normalized displacement \( z^* \) where \( \left. \frac{\partial x}{\partial z^*} \right|_{z^*=\zeta(\tau)} \approx 0 \). As the reaction time increases, the incremental reduction per unit time becomes smaller and smaller. This can be understood heuristically in terms of an asymptotic approach towards a maximum “penetration depth”: past a certain limiting depth, no further reduction can be achieved since all of the atomic hydrogen has
been lost via recombination before it has reached this depth.

Figure 4.10: Numerically-calculated concentration profiles at various times during the course of the reduction reaction. Parameter values employed were $\lambda_1 = 10, \lambda_2 = 100, \gamma_1 = 0.1,$ and $\xi = 0.0001$; the reaction domain was discretized with $n = 1000$ nodes.

The movement of the reaction interface is presented in Figure 4.11 for various values of $\lambda_2$. Increasing $\lambda_2$ while the other parameters are held constant increases the rate of the reduction reaction. This results in a more rapid approach of the reaction interface towards the maximum penetration depth. However, changing $\lambda_2$ does not change the asymptotic limit of the maximum penetration depth. It is unclear if the “blip” in the reaction interface trace for $\lambda_2 = 100$ visible at $\tau \approx 0.2$ is an accurate depiction of a reaction feature or if it represents a failure of the numerical discretization scheme at this extreme value of $\lambda_2$. 
Figure 4.11: Numerically-calculated reaction-interface traces during the course of the reduction reaction. Parameter values employed were $\lambda_1 = 10$, $\lambda_2$ as specified, $\gamma_1 = 0.1$, and $\zeta = 0.0001$; the reaction domain was discretized with $n = 1000$ nodes.

The maximum penetration depth $\delta \equiv \lim_{\tau \to \infty} \zeta(\tau)$ can be modified by changing $\lambda_1$ since this parameter affects the relative rate of diffusion and of the recombination reaction. If the diffusion of atomic hydrogen is rapid relative to the recombination reaction ($\lambda_1$ small), then $\delta$ will be relatively large since the active species will be able to travel to the reaction interface and reduce the metal oxide before they have recombined. If the diffusion of atomic hydrogen is slow relative to the recombination reaction ($\lambda_1$ large), then $\delta$ will be relatively small since the active species will recombine before they are able to travel to the reaction interface and reduce the metal oxide. This behavior is depicted in Figure 4.12.
Figure 4.12: Numerically-calculated reaction-interface traces during the course of the reduction reaction. Parameter values employed were $\lambda_1$ as specified, $\lambda_2 = 10$, $\gamma_1 = 0.1$, and $\zeta = 0.0001$; the reaction domain was discretized with $n = 1000$ nodes.

It is possible to develop an analytical expression for the steady-state penetration depth $\delta$. This is accomplished by considering the time-invariant behavior of equations (4.41) and (4.42). Replacing the time-derivatives in these two equations with zero and replacing $\zeta$ with $\delta$ in this limit, the steady-state system of equations can be reduced to:

$$\lambda_1 \chi_{SS} \delta^2 = \frac{\partial^2 \chi_{SS}}{\partial \xi^2} \tag{4.43}$$

with boundary conditions $\chi_{SS}|_{\xi=0} = 1$ and $\frac{\partial \chi_{SS}}{\partial \xi}|_{\xi=1} = 0$, with the additional restriction that $\chi_{SS}|_{\xi=1} = \zeta$. Equation (4.43) has solutions of the form:
\begin{equation}
\chi_{SS}(\xi) = c_1 \cosh(\delta\sqrt{\lambda_1\xi}) + c_2 \sinh(\delta\sqrt{\lambda_1\xi})
\end{equation}

where \( \cosh(x) \) represents the hyperbolic cosine of \( x \) and \( \sinh(x) \) represents the hyperbolic sine of \( x \). Using the boundary conditions and the formula \( c_1 \cosh(x) + c_2 \sinh(x) = \sqrt{c_1^2 - c_2^2} \cosh(x + \tanh^{-1}(c_2/c_1)) \) for \( |c_2/c_1| < 1 \) (with \( \tanh^{-1}(x) \) the inverse hyperbolic tangent of \( x \)), it is possible to write to solution to equation (4.43) as:

\begin{equation}
\chi_{SS}(\xi) = \frac{\cosh(\delta\sqrt{\lambda_1}(1 - \xi))}{\cosh(\delta\sqrt{\lambda_1})}
\end{equation}

Employing the restriction \( \chi_{SS}\xi=1 = \Xi \), equation (4.45) can be rearranged to yield:

\begin{equation}
\delta = \frac{1}{\sqrt{\lambda_1}} \cosh^{-1}\left(\frac{1}{\Xi}\right)
\end{equation}

with \( \cosh^{-1}(x) \) the inverse hyperbolic cosine of \( x \). There is good agreement between the steady-state penetration depth predictions from the analytical results of (4.46) with the predictions obtained using the numerical model; a comparison for several values of \( \lambda_1 \) and \( \Xi \) is presented in Tables 4.3 and 4.4.

<table>
<thead>
<tr>
<th>( \lambda_1 )</th>
<th>( \delta_{\text{Analytical}} )</th>
<th>( \delta_{\text{Numerical}} )</th>
<th>( \delta_{\text{Analytical}}/\delta_{\text{Numerical}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 10^1 )</td>
<td>3.13</td>
<td>3.13</td>
<td>0.999</td>
</tr>
<tr>
<td>( 10^2 )</td>
<td>0.990</td>
<td>0.991</td>
<td>0.999</td>
</tr>
<tr>
<td>( 10^3 )</td>
<td>0.313</td>
<td>0.313</td>
<td>0.999</td>
</tr>
<tr>
<td>( 10^4 )</td>
<td>0.0990</td>
<td>0.0991</td>
<td>0.999</td>
</tr>
</tbody>
</table>

The ratio between the analytical value and numerical estimates of the penetration depth appears to be independent of the choice of \( \lambda_1 \), at least within rounding errors, as can be seen by examining Table 4.3. However, the difference between the analytical value and the numerical
estimates does change as \( \Xi \) decreases, with the numerical estimate transitioning from an underprediction of the analytical value for \( \Xi \leq 10^{-4} \) to an overprediction for \( \Xi = 10^{-5} \). A detailed study of the source of this error was not conducted.

Table 4.4: Comparison of analytical and numerical estimates of maximum penetration depth. Numerical values were obtained using \( \lambda_1 = 10, \lambda_2 = 10, \gamma_1 = 0.1 \), and \( \Xi \) as specified; the reaction domain was discretized with \( n = 1000 \) nodes.

<table>
<thead>
<tr>
<th>( \Xi )</th>
<th>Analytical</th>
<th>Numerical</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 10^{-5} )</td>
<td>3.86</td>
<td>3.85</td>
</tr>
<tr>
<td>( 10^{-4} )</td>
<td>3.13</td>
<td>3.13</td>
</tr>
<tr>
<td>( 10^{-3} )</td>
<td>2.40</td>
<td>2.40</td>
</tr>
<tr>
<td>( 10^{-2} )</td>
<td>1.68</td>
<td>1.68</td>
</tr>
</tbody>
</table>

Clearly, the quantitative predictions of the steady-state penetration depth obtained from the numerical model are accurate, given their fidelity to the analytical results. The numerical model is also useful for gaining an understanding (both qualitative and quantitative) of the propagation of the reaction interface and of the changing shapes of the concentration profiles; further examination of the effect the parameters \( \gamma_1 \) and \( \Xi \) on the numerical model follows.

The effect of adjusting \( \gamma_1 \) on the movement of the reaction interface is presented in Figure 4.13. Comparison of Figures 4.13 and 4.15 indicates that adjusting \( \gamma_1 \) and \( \lambda_2 \) has an identical effect on the movement of the reaction interface. This is to be expected from an examination of equations (4.41) and (4.42): in considering the equation-of-motion for the reaction interface, it is possible to write \( \zeta \frac{dK}{d\tau} = -\gamma_1 \lambda_2 \zeta (\chi|_{\zeta=1} - \Xi) \). This makes it clear that multiplying \( \gamma_1 \) or \( \lambda_2 \) by the same factor modifies the propagation of the reaction interface in an identical manner. The same feature remarked upon in Figure 4.13 is visible in Figure 4.15 in the reaction-interface trace for \( \gamma_1 = 10^0 \) at \( \tau \approx 0.2 \); it is unclear if this is a feature of the reacting system or merely an artifact of the discretization scheme at this extreme parameter value.
Figure 4.13: Numerically-calculated reaction-interface traces during the course of the reduction reaction. Parameter values employed were $\lambda_1 = 10$, $\lambda_2 = 10$, $\gamma_1$ as specified, and $\Sigma = 0.0001$; the reaction domain was discretized with $n = 1000$ nodes.

The effects of adjusting the parameter $\Sigma$ on the propagation of the reaction interface are presented in Figure 4.14. $\Sigma$ controls the minimum concentration of the active species which is capable of inducing the reduction reaction; i.e., $\Sigma$ would be smaller for the oxides of more noble metals and would be larger for highly stable oxides, since a larger concentration of atomic hydrogen is required to reduce the more stable oxides (in accordance with the equilibrium constant expression for the reduction reaction). Lowering $\Sigma$ allows for a larger steady state penetration depth $\delta$. However, this effect is not as large as the effect gained by decreasing $\lambda_1$, as can be seen by contrasting Figure 4.12 and Figure 4.16: a ten-fold decrease in $\Sigma$ increases $\delta$ by
about 40%, whereas a ten-fold decrease in $\lambda_1$ increases $\delta$ by about 220% (for the parameter ranges considered in these figures).

![Numerical reaction-interface traces](image)

Figure 4.14: Numerically-calculated reaction-interface traces during the course of the reduction reaction. Parameter values employed were $\lambda_1 = 10$, $\lambda_2 = 10$, $\gamma_1 = 0.1$, and $\Xi$ as specified; the reaction domain was discretized with $n = 1000$ nodes.

This section has discussed a mathematical model and its numerical implementation for understanding the reduction behavior of metal oxides reacting with atomic hydrogen. Through the development of this model, a finite depth-of-reduction (the so-called penetration depth $\delta$) has been predicted, corroborating experimental reports of this penetration depth. This is a novel feature not found in traditional gas-solid reaction systems. It occurs because of the loss of the active species (atomic hydrogen) via recombination within the reduced product layer. The
existence of this penetration depth has the important ramification that no matter how long a solid
is exposed to the plasma, the extent of reaction will be limited to an exterior shell of thickness $\delta$.

4.5 Summary

This chapter has provided several theoretical developments which are useful for
understanding the reduction of metal oxides by atomic hydrogen. The discussion of actinometry
in section 4.1 provides a derivation of the analytical techniques employed in this research to
obtain useful information (viz., the partial pressure of atomic hydrogen) from the raw
spectroscopic data. The partial pressure of atomic hydrogen within the reactor, the partial
pressure of water vapor within the reactor, and the reactor temperature form the essential
characteristics for describing the ability of a non-equilibrium hydrogen plasma to reduce metal
oxides.

The thermodynamic analysis based on these parameters ($p_H$, $p_{H_2O}$, and $T$) from section
4.2 creates a framework for determining the stable phase under a given set of conditions, thereby
allowing for prediction of which metal oxides can be reduced within the plasma reactor; the
nominal conditions employed for describing the reactor used in this research suggest that even
oxides as stable as those of the rare-earth metals can be reduced.

The kinetic model in section 4.3 enables an analysis of the maximum rates of reduction
achievable by atomic hydrogen under the conditions in which mass transport is not a limiting
factor; the rate-balance considered therein also provides a potential means of resolving the
conundrum involved in analyzing the metastable plasma environment in terms of equilibrium
thermodynamic arguments. However, more information concerning the rate constants $k_{\text{reduction}}$,
$k_{\text{recombination}}$, and $k_{\text{reoxidation}}$ is required for this kinetic model to be practically useful.
The moving boundary model covered in section 4.4 provides a credible explanation for one of the most distinctive effects observed in previous studies of the reduction of metal oxides by atomic hydrogen: the finite penetration depth of reduction. Knowing the penetration depth $\delta$ and its dependence on the plasma parameters is critical for designing an effective reactor system: by ensuring that the metal-oxide feed particles possess a minimum dimension no larger than $\delta$, it will be possible to achieve the complete reduction of these feed particles by the application of atomic hydrogen. The pseudo-homogeneous reaction described in section 4.3 should thus be constrained to consider solid particles which are approximately of size $\delta$ or smaller.
CHAPTER 5
EXPERIMENTAL METHODS

This chapter outlines the methodology and equipment employed to conduct this research. A brief discussion of surface-excited plasma discharges is provided, as is a description and a visual depiction of the experimental apparatus. The techniques employed to investigate the experiments as they progressed are detailed, as are the post-reaction sample characterization methods. Sample preparation is described, and the procedures employed to carry out each type of experiment are specified.

5.1 Surface-Excited Discharges

As discussed in Chapter 3, non-equilibrium plasmas are often maintained by an electric field which provides the energy necessary to produce ionization. In one such type of discharge configuration, known as a surface-excited discharge, the sustaining electric field is propagated by means of a travelling wave along the bounding surface of the plasma, where this bounding surface is composed of a dielectric material such as quartz. Surface-excited discharges were first studied by (Trivelpiece and Gould 1959) and have been investigated both experimentally and theoretically since then, with an especially thorough treatment by (Moisan and Pelletier 1999).

In order to provide a fundamental understanding of these surface-excited discharges, a brief discussion of the underlying phenomena follows, paralleling the discussion in (Lieberman and Lichtenberg 2005) and (Bellan 2008). The goal of this derivation is to develop an expression for the spatial distribution of electric and magnetic fields within a surface-excited discharge. Once these fields are known, it will be possible to solve for the spatial distribution of species-excitation within a plasma reactor employing this type of discharge. The derivation begins with considering Faraday’s law and Ampere’s law from Maxwell’s equations:
\[ \nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t} \tag{5.1} \]
\[ \nabla \times \mathbf{B} = \mu_0 \mathbf{J} + \epsilon_0 \mu_0 \frac{\partial \mathbf{E}}{\partial t} \tag{5.2} \]

where \( \mathbf{E} \) is the electric field, \( \mathbf{B} \) is the magnetic field, \( t \) is time, \( \mathbf{J} \) is the (free) current density, \( \epsilon_0 \) is the permittivity of free-space, and \( \mu_0 \) is the permeability of free space. Given temporal perturbations of a single frequency \( \omega \) (such as one induced by an imposed electromagnetic field from, in the case of this investigation, a microwave generator)—i.e., when all variables \( \mathbf{F}(\mathbf{r}, t) \) exhibit temporal dependence of the form \( \mathbf{F}(\mathbf{r}, t) = \mathbf{F}_0(\mathbf{r}) \Re\{e^{i(\omega t + \phi)}\} \)—it is possible to express these equations as

\[ \nabla \times \mathbf{E} = -i\omega \mathbf{B} \tag{5.3} \]
\[ \nabla \times \mathbf{B} = \mu_0 \mathbf{J} + \epsilon_0 \mu_0 i\omega \mathbf{E} \tag{5.4} \]

Given that ion velocities are small relative to electron velocities, as discussed in section 3.1, the contribution to the current density should be given purely by the flux of electrons: \( \mathbf{J} = q_e n_e \mathbf{v}_e \), with \( q_e \) the electron charge, \( n_e \) the number density of electrons, and \( \mathbf{v}_e \) the velocity of electrons. Using equation (3.1) in the case of electron velocities small relative to the speed of light, the electron velocity can be expressed in terms of the electric field by writing \( \frac{d\mathbf{v}_e}{dt} = \left(\frac{q_e}{m_e}\right)\mathbf{E} \). Using the same sinusoidal temporal dependence of frequency \( \omega \) employed earlier, this expression simplifies to \( \mathbf{v}_e = \left(\frac{q_e}{i\omega m_e}\right)\mathbf{E} \). Thus, the current density can be expressed by writing \( \mathbf{J} = \left(n_e q_e^2 / i\omega m_e\right)\mathbf{E} \). With \( \omega_{pe} \equiv \left(n_e q_e^2 / \epsilon_0 m_e\right)^{1/2} \) (where \( \omega_{pe} \) is the plasma electron frequency, the frequency of free oscillations of electrons within the plasma), the current density can be re-expressed as \( \mathbf{J} = \epsilon_0 (\omega_{pe}^2 / i\omega)\mathbf{E} \). This leads to a natural definition of the electrical conductivity of the plasma \( \sigma \) as \( \sigma \equiv \omega_{pe}^2 / i\omega \). Note that this expression is only strictly true for a
collisionless plasmas (where the collision frequency \( \nu \) is much smaller than the frequency \( \omega, \nu \ll \omega \)). For the general case of a collisional plasma (discussed later), the conductivity can be expressed as \( \sigma \equiv \omega_{pe}^2 / (\nu + i \omega) \) per (Moisan and Pelletier 1999), as can be derived through a Langevin-equation approach (Reif 2009). Substituting the expression for the current density into equation (5.2), it is possible to write

\[
\mathbf{V} \times \mathbf{B} = \mu_0 \varepsilon_0 \sigma \mathbf{E} + \varepsilon_0 \mu_0 i \omega \mathbf{E}
\]  

(5.5)

Since \(\mu_0 \varepsilon_0 \equiv 1/c^2\) with \(c\) the speed of light, this expression can be simplified to yield

\[
\mathbf{V} \times \mathbf{B} = \frac{i \omega}{c^2} P \mathbf{E}
\]  

(5.6)

where \(P\) is the dielectric function for an unmagnetized plasma \(P \equiv 1 - \omega_{pe}^2 / \omega^2\). It is now convenient to restrict this discussion to a situation of cylindrical symmetry (the geometry of the surface-excited discharge employed in this research). Following (Bellan 2008), this allows equations (5.3) and (5.6) to be broken up into their transverse and axial components:

\[
(\mathbf{V}_t + \hat{z} \frac{\partial}{\partial z}) \times (\mathbf{E}_t + E_z \hat{z}) = -i \omega (\mathbf{B}_t + B_z \hat{z})
\]  

(5.7)

\[
(\mathbf{V}_t + \hat{z} \frac{\partial}{\partial z}) \times (\mathbf{B}_t + B_z \hat{z}) = i \omega \frac{1}{c^2} P (\mathbf{E}_t + E_z \hat{z})
\]  

(5.8)

where \(\mathbf{V}_t \equiv \hat{r} \partial / \partial r + \hat{\theta} (1/r) \partial / \partial \theta\), \(\mathbf{B}_t = \hat{r} B_r + \hat{\theta} B_\theta\), and \(\mathbf{E}_t = \hat{r} E_r + \hat{\theta} E_\theta\), with \(\hat{z}\) the axial direction, \(\hat{\theta}\) the azimuthal direction, \(\hat{r}\) the radial direction, and \(r\) the radial displacement. Since the curl of a transverse vector lies in the axial direction, the curl of an axial vector must lie in the transverse direction, and since the cross product of two axial vectors is necessarily a zero vector, this differential operator can be distributed so that equations (5.7) and (5.8) can be broken up component-wise to yield the set of equations:

\[
(\mathbf{V}_t \times \mathbf{E}_t) \cdot \hat{z} = -i \omega B_z
\]  

(5.9)
\[
(\nabla_t \times E_z \hat{z}) + \hat{z} \times \frac{\partial E_t}{\partial z} = -i\omega B_t
\]  \quad (5.10)

\[
(\nabla_t \times B_t) \cdot \hat{z} = \frac{i\omega}{c^2} P E_z
\]  \quad (5.11)

\[
(\nabla_t \times B_z \hat{z}) + \hat{z} \times \frac{\partial B_t}{\partial z} = \frac{i\omega}{c^2} P E_t
\]  \quad (5.12)

At this point, it is convenient to restrict the discussion to considering a spatial
dependence of all variables to be of the form \( F(r, \theta, z) = F_0(r, \theta) \Re\{e^{i(kz+\phi)}\} \). This is
equivalent to restricting the solution to be a sinusoidal travelling wave propagating in the \( \hat{z} \)
direction, and is essentially a “shortcut for spatial Fourier analysis” per (Bellan 2008). Note that
\( P \) is also assumed to be constant with respect to variations in \( z \). This means that the travelling
wave solution propagates in an axially homogeneous medium extending to infinity in this
direction. This is unphysical for a situation in which the plasma density decreases in the axial
direction, as occurs within the reactor employed in this research. Nevertheless, per (Moisan and
Pelletier 1999), results obtained using the assumption of axial homogeneity are still valid for
describing the local properties of an axially non-homogeneous plasma column provided that the
condition \( \frac{1}{n_e} \frac{\partial n_e}{\partial z} \ll k \) is valid, i.e., that the functions are slowly varying in the axial direction
(analogous to the conditions of validity for the Wentzel-Kramers-Brillouin (WKB)
approximation for solving differential equations with slowly varying coefficients). Proceeding
under this condition, it is possible—using the sinusoidal dependence of variables in the axial
direction, employing the fact that \( \nabla_t \times F_z \hat{z} = \nabla_t F_z \hat{z} \), and using the vector identity \( A \times (B \times C) = B(A \cdot C) - C(A \cdot B) \)—to substitute equations (5.10) and (5.11) into one another to write:

\[
B_t = \left( \frac{\omega^2}{c^2} P - k^2 \right)^{-1} \left[ ik\nabla_t(B_z) + \frac{i\omega}{c^2} P \nabla_t(E_z) \times \hat{z} \right]
\]  \quad (5.13)
\[ E_t = \left( \frac{\omega^2}{c^2} P - k^2 \right)^{-1} \left[ \imath k \mathbf{v}_t(E_z) - \imath \omega \mathbf{v}_t(B_z) \times \mathbf{z} \right] \] (5.14)

By substituting equations (5.13) and (5.14) into equations (5.9) and (5.11) and appealing to the condition of cylindrical symmetry, it is possible to decouple these equations to write using the same vector identity \( A \times (B \times C) = B(A \cdot C) - C(A \cdot B) \) employed above:

\[ \mathbf{v}_t \cdot \left\{ \frac{P}{P - k^2 c^2 / \omega^2} \mathbf{v}_t(E_z) \right\} + \frac{\omega^2}{c^2} \mathbf{P} E_z = 0 \] (5.15)

\[ \mathbf{v}_t \cdot \left\{ \frac{1}{P - k^2 c^2 / \omega^2} \mathbf{v}_t(B_z) \right\} + \frac{\omega^2}{c^2} B_z = 0 \] (5.16)

These equations (5.15) and (5.16) thus describe the axial electric and magnetic fields for a travelling wave of temporal frequency \( \omega \) and wavelength \( k \) moving in the axial direction of a collisionless plasma with cylindrical symmetry. Since the transverse electric and magnetic fields are determined entirely by the axial fields as shown by equations (5.13) and (5.14), solving equations (5.15) and (5.16) with the appropriate boundary conditions will describe the distribution of fields in a surface-excited discharge, thereby allowing for a calculation of the excitation of species throughout such a discharge. Restricting the discussion to situations in which there is no axial magnetic field (i.e., \( B_z = 0 \), the so-called “transverse-magnetic” or TM mode (Griffiths 1999) as is relevant for the surface discharge employed in this research, it is possible to expand equation (5.15) using the definition of \( \mathbf{v}_t \) and the condition of cylindrical symmetry to write (employing the formula for the divergence of a vector field in curvilinear coordinates specified in (Haberman 2004))

\[ \frac{1}{r} \frac{\partial}{\partial r} \left( \frac{r P}{P - k^2 c^2 / \omega^2} \frac{\partial E_z}{\partial r} \right) + \frac{\omega^2}{c^2} \mathbf{P} E_z = 0 \] (5.17)

which can be simplified to yield

\[ r^2 \frac{\partial^2 E_z}{\partial r^2} + r \frac{\partial E_z}{\partial r} + r^2 \left( \frac{\omega^2}{c^2} P - k^2 \right) E_z = 0 \] (5.18)
If the quantity \( \left( \frac{\omega^2}{c^2} P - k^2 \right) < 0 \) (as is this case for these surface waves, per (Lieberman and Lichtenberg 2005)), then the solutions of equation (5.17) can be recognized as modified Bessel functions of the first and second kind of order zero, \( I_0(\kappa r) \) and \( K_0(\kappa r) \) per (Arfken, Weber, and Harris 2013) with \( \kappa \equiv (k^2 - \frac{\omega^2}{c^2} P)^{1/2} \). The surface-discharge consists of a plasma for \( r < R \) and a dielectric for \( r > R \). For simplicity, this dielectric is assumed to be vacuum, such that \( P \equiv 1 \) there; more involved calculations such as those in (Ramo, Whinnery, and Van Duzer 1994) and in (Moisan and Pelletier 1999) take into account the presence of multiple dielectrics of varying permittivity (such as a quartz tube surrounded by air, as in the case of the experimental apparatus employed in this research) or conducting boundaries. Given that the electric field is a physical quantity and must be finite at all points, the solution \( K_0 \) may be rejected for \( r < R \) while the solution \( I_0 \) may be rejected for \( r > R \). A final physical boundary condition is imposed by considering the fact that the parallel component of the electric field must be continuous across the interface (as shown in (Mateev, Zhelyazkov, and Atanassov 1983)). This fact allows one to equate the solutions within the plasma and vacuum regions to yield

For \( r < R \):

\[
E_z(r, \theta, z, t) = E_{z0} \frac{I_0(\kappa_p r)}{I_0(\kappa_p R)} \Re\{e^{i(kz+\omega t+\phi)}\} \tag{5.19}
\]

For \( r > R \):

\[
E_z(r, \theta, z, t) = E_{z0} \frac{K_0(\kappa_d r)}{K_0(\kappa_d R)} \Re\{e^{i(kz+\omega t+\phi)}\} \tag{5.20}
\]

where \( \kappa_p \) and \( \kappa_d \) are the values of \( \kappa \equiv (k^2 - \frac{\omega^2}{c^2} P)^{1/2} \) for the plasma and dielectric region, respectively. Hence, equations (5.19) and (5.20) specify the distribution of the axial electric field in a surface-excited discharge for the conditions specified; expressions for the other components of the electric and magnetic field are completely determined by means of equations (5.13) and (5.14). Thus, these equations specify the distribution of fields within this discharge, thereby
providing a means for calculating the creation of excited species within the discharge (as specified by the collision mechanisms discussed in section 3.4). Heuristically, the locations with the strongest electric fields will also possess the highest concentrations of excited species (ignoring the loss of those excited species via diffusion to the reactor walls and recombination there), such that equations (5.19) and (5.20) are important for analyzing reactions that depend on these excited species. A depiction of time-averaged axial electric fields for a more realistic case involving the presence of an intermediate dielectric wall between the plasma and the surrounding air is presented in Figure 5.1. The intensity of the electric field depicted in Figure 5.1 gradually decreases as one moves from the discharge wall towards the center of the reactor. Hence, the largest density of excited species should be, to first approximation, near the reactor walls.

Figure 5.1: Calculated electric field intensity for a surface-excited discharge. Excitation frequency is 600 MHz, $\omega / \omega_{pe} = 0.2$, and $\epsilon_{wall}/\epsilon_0 = 3.8$; adapted from (Mateev, Zhelyazkov, and Atanassov 1983).
An additional restriction on the possible field distributions is imposed by considering the continuity of the azimuthal magnetic field across the interface when no free currents are allowed there (per (Lieberman and Lichtenberg 2005)). This condition results in the dispersion relation (per (Mateev, Zhelyazkov, and Atanassov 1983))

\[
\frac{P I'_0(\kappa_p R)}{\kappa_p I_0(\kappa_p R)} = \frac{1}{\kappa_d} \frac{K'_0(\kappa_d R)}{K_0(\kappa_d R)} \tag{5.21}
\]

where the prime symbol denotes the derivative. Since \(\kappa_p, \kappa_d,\) and \(P\) depend both on \(\omega\) and on \(k\), equation (5.21) provides an implicit relationship between \(\omega\) and \(k\) for a given \(R\). For the case of a given surface-excited discharge with radius \(R\) and frequency \(\omega\) (set by the microwave generator, in the experimental apparatus employed in this research), this relationship specifies the wavenumber of the surface mode \(k\).

Determining the distribution of fields in the general case involves considering the loss of surface-mode energy via collisions within the plasma. This results in a gradual decay in electric field strength (and, correspondingly, in excited-species density) as one proceeds in the axial direction away from the surface-wave “launcher.” This general case is treated both by (Mateev, Zhelyazkov, and Atanassov 1983) and by (Moisan and Pelletier 1999). A depiction of the axial dependence of the electron number density and the axial electric field is presented in Figure 5.2 and in Figure 5.3; the former for the case of low pressures (where the loss of charged particles is dominated by wall-recombination) and the latter for the case of high pressures (where the loss of charged particles is dominated by homogeneous recombination within the plasma).

Figures 5.2 and 5.3 depict an approximately linear decline in electron number density \(n_e\) (normalized with respect to the electron density \(n_{e,cr} \equiv m_e \omega^2 e_0 q_e^{-2}\), i.e., the critical electron
density below which the local electron plasma frequency $\omega_{pe}$ becomes smaller than the applied frequency $\omega$) as one moves further away from the surface-wave launcher.

In Figure 5.2 and in Figure 5.3, $\zeta \equiv \delta z/R$, with $\delta$ the ratio of the collision frequency to the applied frequency $\delta \equiv v/\omega$, $z$ is the displacement from the wave launcher in the axial direction, and $R$ is the radius of the surface-wave discharge.
This section has described the radial and axial distribution of the electric field and electron density in surface-excited discharges. As described in Chapter 3, these quantities are important because the electric field acts to accelerate electrons which produce excited species by means of inelastic collisions.

![Graph showing the axial dependence of electron density and electric field in a surface-excited discharge operating at high pressures; adapted from (Mateev, Zhelyazkov, and Atanassov 1983).](image)

Figure 5.3: Axial dependence of electron density and electric field in a surface-excited discharge operating at high pressures; adapted from (Mateev, Zhelyazkov, and Atanassov 1983).

Thus, the analysis presented here provides first-order description of the spatial distribution of excited species within the reactor employed in this research: the highest production of excited species production is expected to be close to the wave-launcher in the axial direction and close to the walls in the radial direction. The production of excited species should decrease approximately linearly as one moves away from the wave launcher in the axial direction.
(as depicted in Figure 5.2 and Figure 5.3) and should decrease towards to center of the reactor like a zeroth-order modified Bessel function of the first kind (as depicted in Figure 5.1). A major caveat to the analysis presented here is that it does not consider the loss of these excited species, but only their generation. While the electric field and electron density may be highest near the walls of the surface-excited discharge, diffusion of excited species towards those walls could lower the concentration of excited species there relative to the concentration at the center of the discharge. This effect (the loss of excited species by diffusion to the walls and heterogenous recombination there) could explain some of the results reported by (Moisan and Pelletier 1999) which indicate that the highest concentration of excited species occurs in the center of the discharge, not near the walls.

5.2 Experimental Equipment

Reduction experiments were carried out in two reactors. The first (employed for the investigation of the reduction of bulk metal oxides) incorporated real-time thermogravimetric analysis to enable measurements of the reaction kinetics. The second reactor (employed for investigating the reduction of metal oxide thin films) was able to maintain a higher-quality vacuum (i.e., a lower leak-rate of atmosphere into the chamber) by forgoing thermogravimetric analysis. Both reactors employed the same microwave-frequency surface-excited discharge to sustain a plasma. The reactor incorporating thermogravimetric analysis will be described first; this experimental setup is depicted schematically in Figure 5.4 and a photograph of the complete apparatus is provided in Figure 5.5.

The plasma discharge was produced by applying microwave-frequency electromagnetic waves to a fused silica tube. These microwaves were produced by a Cober Electronics Model S2.5/3709 Variable Power Source, operating at 2.45 GHz. This power source was capable of
supplying up to 2.5 kW of continuous power through an integral WR-284 waveguide. The amount of power applied could be increased in increments of approximately 2.5 W by adjusting a 10-turn potentiometer; a digital voltmeter (an Omega Engineering HM93 Omegaette Multimeter with 1 millivolt resolution) measured this applied power. The amount of power reflected by the microwave discharge was also measured by means of an antenna located within the waveguide, though this reflected power was generally below the limits of detection.

The WR-284 waveguide was coupled to a Gerling Applied Electronics Surface Wave Plasma Applicator Model GAE 913575-1. This applicator featured a tapered profile in which the height of the waveguide gradually decreased. This resulted in an increase in the magnitude of the electric field within the tapered section. At the thinnest portion of the applicator, a circular cut-out permitted a 50-millimeter diameter tube to be inserted through the applicator. This functioned as the launching point for the surface-wave, as the large-magnitude electric field
within the tapered section acted to excite a travelling wave along the tube interface, as described in section 5.1. A drawing of the surface-wave plasma applicator is presented in Figure 5.6.

The reactor chamber itself consisted of a 50-millimeter outer-diameter, 46 millimeter inner-diameter fused silica tube obtained from Allen Scientific Glass, Incorporated, Boulder, Colorado. The tube was sealed on both ends with a double O-ring sealing flange configuration. These sealing flanges were water-cooled to prevent overheating. This tube was approximately 24 inches long and passed co-axially through the waveguide applicator and an electrically-heated tubular resistance furnace. The resistance furnace, a Model MTI-OTF-1200X-S-VT produced by MTI Corporation, incorporated a single-stage nichrome heating element and was capable of
maintaining temperatures of up to 1100 degrees Celsius within its constant-temperature zone.

The incorporation of this furnace allowed for the comparison of conventional radiative heating with heating delivered via the surface-wave discharge, thereby allowing for direct discrimination between the effects of atomic hydrogen and molecular hydrogen on the reduction of metal oxides. The reaction chamber and furnace/wave-launcher assembly are depicted in Figure 5.7.

The gases employed in these experiments were ultra-high purity (99.999% pure) argon and hydrogen, obtained from General Air. The flowrate of these gases was controlled by means of mass flow controllers obtained from Unit Instruments, Inc.; the hydrogen gas was controlled by a Model 7361 mass flow controller with a maximum throughput of 1000 standard cubic centimeters of hydrogen per minute and a resolution of +/- 1 standard cubic centimeter per
Figure 5.7: Thermogravimetric analysis reaction chamber with furnace and wave-launcher assembly. The bell-jar chamber at the top of the image is connected with the reaction chamber and contains the analytical balance and feedthroughs for thermogravimetric and thermocouple data. Note that the fused-silica reaction chamber is hidden from view: it is covered by the furnace in the bottom portion of the image and by the microwave-shielding tube above the surface-wave launcher.

minute, while the argon gas was controlled by a Model 8160 mass flow controller with a maximum throughput of 100 standard cubic centimeters of argon per minute with a resolution of +/- 0.1 standard cubic centimeters per minute. These mass flow controllers were both controlled with a Unit Instruments URS-40 Flow Controller. Downstream of the mass flow controllers, the gas streams were merged and passed through a Matheson 64-1000 Series Oxygen Remover and a packed bed of five angstrom molecular sieve. The oxygen remover acted to catalyze the reaction between oxygen and hydrogen to form water molecules which were subsequently adsorbed onto the molecular sieve. The gas control and purification systems are pictured in Figure 5.8 on the next page.
The vacuum pump employed in this research was a Sargent Welch DirectTorr rotary vane mechanical pump. The off-gas from this vacuum pump was diluted with air introduced via an effusion mixer to eliminate the possibility of explosion from the presence of unreacted hydrogen. A Model HIC 821 hydrogen sensor from Industrial Test Equipment Company monitored for the presence of any hydrogen leaks. A Holaday Industries Model 1501 Microwave Survey Meter was also employed to verify that microwave radiation emanating from the reaction system was within safe levels.

![Image of gas control and purification equipment]

Figure 5.8: Photograph of gas control and purification equipment. The EdgeTech DPS-1 Dew Point Monitor pictured in the upper left of the image was used to verify that the gases employed had dew points below -50 degrees Celsius. This was a one-time verification; it was not used to measure the continuously-flowing gas streams.
The low-leak reactor employed the same microwave production, gas handling, electrical heating, and vacuum systems as those discussed previously. Instead of using the bell-jar/fused-silica tube arrangement described earlier, the low-leak reactor used a fused silica chamber with integral KF-25 vacuum flanges attached by glass-to-metal seals; this reaction chamber was also fabricated by Allen Scientific Glass. The low-leak reaction chamber is shown Figure 5.9.

![Figure 5.9: Reaction chamber for low-leak reactor; KF-25 flanges at ends joined by glass-to-metal seals.](image)

This low-leak reactor arrangement (i.e., employing glass-to-metal seals without the bell-jar chamber) was necessary to reduce the rate at which atmosphere leaked into the reactor; as described in Chapter 6, it was determined that the bell-jar chamber was responsible for the majority of the leaks into the entire reaction system. A photograph of the experimental set-up using the low-leak reactor is presented in Figure 5.10 while a schematic is shown in Figure 5.11.
Figure 5.10: Assembled low-leak reactor apparatus. Note that in this configuration there is no connection between the reaction chamber and the bell-jar chamber. The partially-coiled red cable on the lower left portion of the screen is the fiber optic cable employed for spectroscopic measurements.
5.3 Analytical Techniques

Several *in situ* techniques were employed for characterizing the conditions within the reactor and for measuring the extent of the reduction reaction. These techniques included thermogravimetric analysis, optical emission spectroscopy, contact temperature measurement of both the sample and the chamber walls, and measurement of the reaction chamber pressure. This section will briefly describe the implementation of these methods.

Thermogravimetric analysis was conducted by measuring the weight change of the sample throughout the course of the reaction. This was accomplished by suspending the sample from an analytical balance, an Ohaus Model STX 123 with 1 milligram resolution. The balance was located in a bell jar above the reaction chamber; an alumina tube connected to the underhook of the balance passed through an adapter port (visible in Figure 5.12) at the bottom of the bell jar.
chamber into the top portion of the reaction chamber. The sample was attached to the bottom of this alumina tube by means of a basket woven from platinum wire of thickness 0.010”. Data from the balance was collected at a frequency of one measurement per second.

Optical emission spectroscopy was employed to characterize the radiation emitted from the plasma. By employing a technique called actinometry (described in Chapter 4), this spectroscopic data could be used to measure the concentration of atomic hydrogen within the plasma, thereby enabling an evaluation of the efficacy of the surface-excited discharge at dissociating molecular hydrogen to produce the active species of interest. The instrument employed for this purpose was an Avantes Model 3648 UV/VIS/NIR spectrometer with a 25-micrometer entrance slit. The relative intensity of radiation in the range 200 nanometers to 1100 nanometers could be quantified, with a nominal resolution of 1.3 nanometers. Light was conveyed from the plasma to the spectrometer by a collimating lens and a fiber-optic cable; the collimating lens could be threaded into a series of taps in the microwave-shielding tube (visible in Figure 5.10); this allowed an estimation of the axial variation of the excited species concentration within the reactor. During some experiments, sequential spectra were captured every 15 seconds, thereby allowing for an estimation of the temporal variation of the excited species concentration throughout the course of the reaction.

The sample temperature was measured during the course of the experiments with a shielded, ungrounded, type K thermocouple. Shielded, ungrounded thermocouples were necessary for maintaining the signal integrity in the presence of the intense microwave radiation: unshielded thermocouples or shielded, grounded thermocouples gave erroneous readings. Note that this is in contrast to the reports from (Daniel Edward Bullard 1993) in which it was described that shielded, grounded thermocouples were able to measure temperatures within a
microwave plasma. For the experiments conducted with the thermogravimetric apparatus, the thermocouple was a 0.010” diameter stainless-steel sheathed thermocouple obtained from Omega Engineering. The thermocouple was threaded through the alumina sample-support tube and was inserted into the center of the samples. In order to prevent interference (i.e., vibrations and time-varying forces) between the thermocouple leads and the gravimetric measurements of the analytical balance, fine nichrome wires (0.003” in diameter) were employed to make an electrical connection between the support rod and a fixed thermocouple extension wire; this arrangement is pictured in Figure 5.12. For the experiments conducted with the low-leak reactor, the thermocouple employed was a 1/16” diameter stainless-steel sheathed thermocouple obtained from Omega Engineering. An additional 0.010” diameter stainless-steel sheathed thermocouple was also employed to measure the temperature of the exterior of the reactor wall in the vicinity of the sample. Data from the thermocouples were collected using an Omega Engineering HH509R Digital Thermometer, with a resolution of 0.1 degrees Celsius; data points were collected at a rate of one measurement per second throughout the course of the reaction.

The pressure within the reactor was monitored throughout the course of the reaction by means of an Inficon PCG-554 digital vacuum gauge. This device employs both a capacitance diaphragm gauge and a Pirani gauge to allow for pressure measurements in the medium vacuum to atmospheric pressure range (3.8 \times 10^{-5} \text{Torr to 1125 Torr}) with a repeatability of approximately +/- 2% of the reading. For the thermogravimetric analysis reactor, the pressure gauge was located at the bottom of the reaction chamber (pictured in Figure 5.7), while for the low-leak reactor, the pressure gauge was located at the top of the reaction chamber (visible in Figure 5.10). During the course of the reaction, measurements of the pressure within the chamber were collected at a rate of one measurement per second.
Several techniques were employed to characterize the samples post-reaction. These *ex situ* techniques included X-ray diffraction, optical microscopy, and scanning electron microscopy with energy dispersive spectroscopy. Bulk X-ray diffraction was conducted using a Panalytical X’Pert-Pro Materials Research Diffractometer. Diffraction measurements were taken using an Empyrean Copper X-ray tube with an acceleration voltage of 45 kilovolts and a current of 40 milliamps. Grazing-incidence X-ray diffraction was conducted using a Panalytical Empyrean Diffractometer. Diffraction patterns were compared to references obtained from the International Centre for Diffraction Data’s PDF-4+ 2018 RDB database and from the Inorganic Crystal Structure Database Version 3.7.0. Microscopy was conducting by sectioning samples (as appropriate), polishing the exposed surface with increasingly fine silicon carbide (finishing with a 6-micron diamond suspension polish), and examining the samples using a reflection microscope. Electron microscopy was conducted with a FEI Quanta 600i Environmental SEM.
with an EDAX Element Silicon Drift Detector. X-ray photoelectron spectroscopy was conducted on a Physical Electronics PHI 4800 ESCA system.

5.4 Sample Preparation

This section will describe the techniques employed to prepare the samples used in this research. In general, the samples may be categorized into three distinct groups: those consisting of bulk metal oxide powders pressed into a pellet or packed into a boat, those consisting of metal coupons with a thin, thermally-grown metal oxide film on the surface, and those consisting of a thin metal oxide film deposited on an underlying substrate by means of a sol-gel technique. This discussion will first review the techniques employed for preparing the bulk metal oxide samples.

Bulk metal oxide samples were prepared from cupric oxide and from molybdenum dioxide. The cupric oxide samples were porous spheres while the molybdenum dioxide samples were porous cylinders and powder-filled boats. The cupric oxide samples were prepared using \( \geq 99.0\% \) CuO obtained from Alfa Aesar, lot R13A019. The molybdenum dioxide samples were prepared using \( \text{MoO}_2 \) obtained from H.C. Starck, lot XMP 6886/Climax 5507X. The porous spheres and cylinders used ammonium bicarbonate as a volatile filler material. This ammonium bicarbonate was prepared using Reagent Plus 99.0\%+ \( \text{NH}_4\text{HCO}_3 \) obtained from Sigma Aldrich, lot BCBR0615. The particle size distribution for the copper oxide is presented in Figure 5.13. This plot indicates an average diameter of about 10 microns with a narrow distribution of sizes (about 90\% of the particles have diameters between 1 micron and 20 microns).

The cupric oxide samples were prepared via a four-step process: mixing, pressing, sintering, and shaping. Mixing was conducted by adding 5.603 grams of CuO (as-received) and 0.473 grams of \( \text{NH}_4\text{HCO}_3 \) (sized to -150 mesh, +270 mesh) to an agate mortar and pestle and grinding until the mixture was homogeneous to (unmagnified) visual inspection; this took about
ten minutes. The mixture was then poured into a 0.5” diameter cylindrical steel die. After levelling the surface, 30 drops of ethanol were added to the mixture with an eyedropper. The die was then compressed with 6000 pounds of force for ten minutes. Following removal from the die, the resulting cylindrical pellet was allowed to dry (i.e., exposed to atmosphere with the intent of allowing residual ethanol to evaporate) for a period of four hours.

The samples were then heated in an electric furnace with air-circulation to 800 degrees Celsius. The ramp rate for heating was one degree Celsius per minute; temperature “soaks” were conducted at 50 °C for two hours, 120 °C for one hour, 150 °C for one hour, 180 °C for one hour, 210 °C for one hour, 250 °C for one hour, and 800 °C for eight hours, following cooling at a rate of one degree Celsius per minute to room temperature. This gradual heating profile was employed to ensure the structural integrity of the resulting samples: rapid heating rates resulted
in the formation of cracks, whereas the gradual heating described here produced samples with satisfactory strength and structure.

Following removal from the furnace, the cylinders were shaped into their final spherical form. This was accomplished by beveling the edges of the cylinders using 240 grit sand paper and subsequently turning the cylinders end-over-end in a die made from a 12.00-millimeter hole drilled in a steel plate of thickness 0.200". The resulting spheres were placed in a hemispherical fixture and a hole was drilled to the center of the spheres with a No. 60 drill bit; this hole was designed to accommodate the insertion of the 0.010" diameter thermocouple into the center of the sample.

The molybdenum dioxide cylinder samples were prepared by combining 4.000 grams of molybdenum dioxide (sized to +150 mesh) with 1.000 gram of ammonium bicarbonate (sized to -150 mesh, +270 mesh), loosely mixing these powders with a spatula, and then pouring the mixture into the 0.5” diameter cylindrical steel die. 30 drops of ethanol were added to this mixture and the resulting pellet was pressed with 1000 pounds of force for ten minutes. After drying for four hours, the cylinders were heated at 75 degrees Celsius for several hours to drive off the ammonium bicarbonate. Finally, 20 drops of a 1% ammonium hydroxide solution were dripped onto the cylinders. This ammonium hydroxide solution acted to provide the samples with sufficient green strength, possibly by forming an ammonium dimolybdate phase which acted to join adjacent grains. Note that it was not possible to provide structural integrity to these samples by sintering in a furnace exposed to the ambient atmosphere because molybdenum dioxide converted to molybdenum trioxide under oxidizing conditions. The molybdenum dioxide packed-bed samples were prepared by loosely packing the powder (screened to +150 mesh) into alumina boats with a spatula.
The method of preparation employed for the metal coupon samples will now be detailed. These samples consisted of neodymium and titanium metal coupons approximately one centimeter by one centimeter in size. The neodymium sheet (≥99% total rare earth metals by mass, ≥99.9% of which rare earth metals was neodymium, obtained from Edgetech Industries LLC) was two millimeters thick, while the titanium sheet (grade 2 commercially-pure titanium, McMaster-Carr) was 0.02” thick. The metal coupons were cut to the appropriate size using a sheet-metal shear; they were subsequently ground with 1200 grit sand paper until the surface exhibited a metallic luster (thereby indicating that the passivating oxide layer had been removed). A cross-hole for mounting was then drilled with a No. 52 drill. Following deburring of the hole and filing of the coupon corners, the samples were rinsed with ethanol. Some samples were introduced into the reactor in this state. Other samples were exposed to localized heating via a butane torch. This localized heating produced a thin oxide film on the surface, detectable by means of the resulting interference fringes (analogous to those discussed by (Sakamoto and Ishibe 1980)).

An alternative method of preparing thin oxide films was accomplished by means of a sol-gel technique. The precursor solution (following the general recipe from (Ozer, Demiryont, and Simmons 1991)) was obtained by mixing 100 milliliters of isopropanol (Aldrich) with 5 milliliters of titanium tetra-isopropoxide (97% pure, Aldrich) in a nitrogen-purged glovebox. Upon removal from the glovebox, 20 microliters of glacial acetic acid were added to the solution, following which the solution was mixed for several minutes and bottled. A variety of substrates were used for these thin films: soda-glass microscope slides, copper coupons (McMaster-Carr), and alumina sheets (MTI Corporation). These substrates were cleaned according to the following procedure: mechanical cleaning with liquid soap and tap water,
ultrasonic cleaning in deionized water for 180 seconds, sequential rinsing with acetone/methanol/isopropanol, and heating at 60 degrees Celsius for 30 minutes.

Once this cleaning procedure was completed, thin-films of amorphous titanium dioxide were deposited on the substrates by means of a spin-coating process using a G3-P Spin Coater (Specialty Coating Systems). 20 drops of the precursor solution were deposited onto the substrate while it was spinning at 2000 rotations per minute; the drops were deposited at a rate of approximately one drop per second. Following 30 seconds of further spinning past the deposition of the final drop, the substrate was brought to rest and removed from the spin coater. Final drying of the deposited film was accomplished by 30 minutes of heating at 85 degrees Celsius. Some samples underwent multiple spin-coating depositions to increase the film thickness; these samples were heated for the same 30 minutes at 85 degrees Celsius between sequential depositions.

5.5 Procedures Employed for Experiments

This section will describe the procedures employed to conduct each experiment, beginning with a discussion of a representative thermogravimetric experiment. First, the sample was removed from the dessicator in which it was kept and loose dust was removed by directing a stream of compressed air at the sample. The sample was weighed, measured with calipers, and photographed. It was subsequently placed in the reactor and attached to the alumina support rod via the platinum wire basket; the thermocouple was inserted into the sample. This arrangement is pictured in Figure 5.14.

Next, the reactor was assembled by inserting the fused silica tube into the surface-wave launcher, tightening the end-cap flanges, and inserting the pressure gauge, vacuum pump line, and bell-jar adapter into their respective locations. The external wall thermocouple was installed.
If the experiment was to be conducted with external heating provided by the electric furnace, a temperature ramp of three degrees Celsius per minute would be initiated at this time.

The system was subsequently pumped down to a pressure of 200 millitorrs to 300 millitorrs over a period of approximately 10 minutes. At this time, the flow of cooling water was initiated, the effusion-mixing air flow was commenced, and the microwave generator was turned on to its standby state. Next, argon gas was continuously flowed through the system (at the flow rate employed for the particular experiment) for 10 minutes. Following this, the hydrogen gas flow was initiated at the appropriate flow rate whilst maintaining the argon flow rate. After 10 minutes, the pressure was adjusted to the desired value by throttling the vacuum pump with a valve. At this time, the analytical balance was tared (via commands sent through the data-acquisition software) and all data collection systems (analytical balance, thermocouples, pressure gauge, and spectrometer) were initiated. The power applied by the microwave generator
was then increased to the appropriate value; the time at which this occurred was defined as the initiation time for the experiment.

Once the reaction was judged to have been completed (based on the measured mass change, the sample temperature, and other data), the microwave power (and/or the electrical furnace power) was turned off, along with all data collection systems. The system was cooled while maintaining the same argon and hydrogen flowrates until all thermocouples registered temperatures below 100 degrees Celsius. At this point the hydrogen flow was turned off. The system continued to be purged by argon for approximately 10 minutes. The argon flow and the vacuum pump were then turned off, and the system was brought up to atmospheric pressure by allowing air to enter the chamber. The water flow and effusion-mixing air flow were turned off, the reactor was disassembled (the fused silica tube, flanges, pressure gauge, bell-jar adapter, and vacuum pump hose were removed), and the sample was removed from the reaction chamber. The sample was weighed, measured, and photographed. Some samples were also sectioned and prepared for further analysis.

The experimental procedure employed with the low-leak reactor was very similar to that described above, with a few exceptions. First, the sample was introduced by attaching it to the mounting device (either the alumina-tube/thermocouple arrangement or a platinum wire) outside of the reaction chamber, at which point the mounting flange-sample assembly was re-inserted into the chamber and the KF-25 flange was sealed. The low-leak reactor experiments were also pumped down to a lower ultimate pressure (in the range of 100 millitorr) than that employed in the thermogravimetric experiments. Finally, rather than shutting off the applied microwave power instantaneously (as was performed with the thermogravimetric experiments), in the low-leak reactor experiments the power was decreased at a rate of 2.5 watts per minute once the desired
reaction time had elapsed. This rate of decrease was maintained until a plasma discharge was no longer evident within the reactor, at which point the applied power was turned off entirely.

5.6 Summary

This concludes the discussion of the experimental procedures employed in the course of this research, and the overview of the methodology employed. In summary, a surface-excited discharge was employed to create a non-equilibrium hydrogen plasma within two reactor designs: one incorporating thermogravimetric analysis and another designed to minimize the leak rate into the reactor. These reactors were controlled environments in which several experimental parameters could be varied (applied microwave power, gas flow rates, pressure, and external heating) and multivariate data could be collected in real-time (including temperature measurements, mass changes, emission spectra, and pressure variations). The samples employed in these experiments included both bulk metal oxide samples as well as thin films of metal oxides prepared both by thermal oxidation and by a sol-gel technique. The next chapters will discuss the results obtained from these experimental investigations.
CHAPTER 6

PLASMA REACTOR CHARACTERIZATION: RESULTS AND DISCUSSION

This chapter presents the experimental results characterizing the plasma environment within the reactor. These results include a discussion of the leak-rate of atmosphere into the reactor, a study of the heating capabilities of the plasma (and the steady-state temperatures attained by solid objects immersed within the plasma), as well as a presentation of the results from the spectroscopic studies of hydrogen dissociation within the reactor. These results provide a description of the salient variables (i.e., the partial pressure of water vapor, the partial pressure of atomic hydrogen, as well as the local temperature) necessary for understanding the efficacy of the plasma reactor as a reducing environment.

6.1 Pressure Measurements: Vacuum System Leak Testing

In order to establish the rate at which atmospheric gases leaked into the various reactors, a series of experiments were conducted. These experiments involved pumping the reactor down to the lowest-attainable pressure (with no feed gas flowing) and subsequently closing the valve to the vacuum pump. Over time, the pressure within the reactor gradually increased due to gas flow from the atmosphere into the reactor via, e.g., leaky O-rings. The resulting pressure versus time curves could be used (along with the volume of the reactors) to calculate the flow rate of atmosphere into the reactor. Together with the flow rate of the feed gas (along with the compositions of these two gas streams), sufficient information is available to characterize the partial pressures of water vapor and hydrogen within the reactor.

Figure 6.1-6.3 present pressure-time traces obtained during the leak-testing of the various reactors. Figure 6.1 depicts the pressure-time trace for the thermo-gravimetric reactor. Figures 6.2 and 6.3 depict the pressure-time traces for the low-leak reactor, with and without the
Figure 6.1: Pressure-time trace during leak test of the thermogravimetric analysis reactor. The reactor volume was contiguous with the down-stream portion of the feed gas train during this experiment.

Figure 6.2: Pressure-time trace during leak test of low-leak reactor. The reactor was isolated from the inlet gas train during this test. The cross-hatched symbols and dotted lines represent individual data points and interpolated data, respectively; the solid line represents continuously-acquired data.
Figure 6.3: Pressure-time trace during leak test of low-leak reactor with thermocouple feedthrough. The reactor volume was contiguous with the down-stream portion of the inlet gas stream during this test. The cross-hatched symbol represents an individual data point while the dotted line represents interpolated data; the solid line represents continuously acquired data.

thermocouple-feedthrough, respectively. In all reactor configurations, the pressure-time traces appear roughly linear in the pressure range above about 7 Torr.

In order to calculate the volumetric flow-rate at which external atmosphere leaks into a reactor from a pressure-time trace, it is necessary to estimate the volume of the reactor. Then, using an equation of state, it will be possible to determine the leak rate. The ideal gas law is employed as an equation of state for the gas within the reactors:

\[ PV = nRT \]  \hspace{1cm} (6.1)

with \( P \) the pressure within the reactor, \( V \) the volume of the reactor, \( n \) the number of moles of gas within the reactor, \( R \) the ideal gas constant, and \( T \) the absolute temperature. Taking the time derivative of both sides under isochoric and isothermal conditions and rearranging yields the relationship:
\[ \frac{dn}{dt} = \frac{V}{RT} \frac{dP}{dt} \]  

(6.2)

with \( t \) time. The quantity \( dP/dt \) can be determined by estimating the slope of the pressure-time trace under the appropriate conditions, i.e., at the temperature and pressure at which the experiments are conducted. Given that the slope of the pressure-time curves is approximately linear in the region of pressures (approximately 7 Torr and above) employed for the experiments, it is reasonable to use the slope of a linear fit to these curves (specifically, to the portion of the curves at 7 Torr and above) as an estimate of the quantity \( dP/dt \). Given the differing volumes of the thermo-gravimetric reactor and the low-leak reactor, it is necessary to correct for these different volumes in order to determine the quantity \( dn/dt \).

The reactors can be decomposed into a series of geometric shapes in order to estimate their volumes. The thermo-gravimetric reactor is approximated to consist of the bell jar (decomposable into a cylinder of inner diameter 12 inches and height 6 inches and a hemisphere of inner diameter 12 inches) and the reactor tube (a cylinder of inner diameter 46 millimeters and length 25 inches). The low-leak reactor is approximated to consist only of the reactor tube (a cylinder of inner diameter 46 millimeters and length 25 inches). The volume displaced by adaptors or other portions of the reaction systems is considered to be negligible relative to the aforementioned volumes. Using these reactor volumes, an ambient temperature of 20 degrees Celsius, and equation (6.2), a comparison plot of the leak rate experiments is presented in Figure 6.4.

Using the slope of the fit lines presented in Figure 6.4, a summary of the leak testing of the various reactors is presented in Table 6.1. The thermo-gravimetric reactor has a leak rate approximately two orders of magnitude larger than that of the low-leak reactor without the thermocouple feedthrough. Implementation of the thermocouple feedthrough in the low-leak
reactor increased the leak rate by a factor of about 2.5, though it is still much smaller (by a factor of about 60) than the leak rate observed in the thermo-gravimetric reactor. Clearly, the larger gasket areas employed with the thermo-gravimetric reactor increase the rate of leakage into the system.

Table 6.1: Summary of Leak Test Experiments. The linear fits employed here are depicted in Figure 6.4.

<table>
<thead>
<tr>
<th>Reactor Type</th>
<th>Reactor Volume, cm$^3$</th>
<th>Pressures for Fit, Torr</th>
<th>$R^2$ for Fit</th>
<th>Leak Rate: Slope of Fit, moles hr$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TGA Reactor</td>
<td>$1.59 \times 10^4$</td>
<td>6 to 51</td>
<td>0.9997</td>
<td>$5.21 \times 10^{-4}$</td>
</tr>
<tr>
<td>Low-Leak Reactor with TC</td>
<td>$1.06 \times 10^3$</td>
<td>5 to 24</td>
<td>0.9944</td>
<td>$9.06 \times 10^{-6}$</td>
</tr>
<tr>
<td>Low-Leak Reactor without TC</td>
<td>$1.06 \times 10^3$</td>
<td>4 to 28</td>
<td>0.9983</td>
<td>$3.67 \times 10^{-6}$</td>
</tr>
</tbody>
</table>
In order to estimate the total amount of water vapor entering the reactor system, it is necessary to account not only for oxygen entering the reactor via leaks but also for oxygen entering via the feed gas stream. The feed gas stream is composed of a mixture of UHP (99.999% pure) argon and hydrogen gas, as detailed in Chapter 5. The manufacturer’s specifications detail a maximum water content of 1 part per million and a maximum oxygen content of 1 part per million (“Typical Certificate of Analysis: Argon Grade 5,” n.d., “Typical Certificate of Analysis: Hydrogen UHP Grade 5,” n.d.). These parts per million specifications are assumed to be provided on a mass/mass basis (versus, e.g., a volume/volume basis), although this distinction was not specified in the certificate of analysis. Taking the total water content of the feed-gas stream to be as stated by the manufacturer and assuming that all of the oxygen entering the reactor is converted to water by reaction with hydrogen, it is possible to write an expression for the partial pressure of water vapor within the reactor as:

$$p_{H_2O} = \left(\frac{M_{H_2O,\text{leak}} + M_{H_2O,\text{feed}}}{M_{\text{total}}}\right)p_{\text{total}}$$  \hspace{1cm} (6.3)

with $p_{H_2O}$ the partial pressure of water within the reactor, $M_{H_2O,\text{leak}}$ the moles of water entering via atmospheric leaks per unit time, $M_{H_2O,\text{feed}}$ the moles of water entering via the feed gas per unit time, $M_{\text{total}}$ the rate at which all gases are entering the reactor, and $p_{\text{total}}$ the total pressure within the reactor. Consideration of the various stoichiometries involved allows a final formula for the partial pressure of water vapor within the reactor to be written as:

$$p_{H_2O} = \left(0.21M_{\text{all,leak}} + (1.19 \times 10^{-8} \text{ moles hr}^{-1} \text{ SCCM}^{-1})Q_{Ar} + (6.01 \times 10^{-10} \text{ moles hr}^{-1} \text{ SCCM}^{-1})Q_{H_2}\right) \frac{p_{\text{total}}}{(2.68 \times 10^{-3} \text{ moles hr}^{-1} \text{ SCCM}^{-1})(Q_{Ar} + Q_{H_2}) + M_{\text{all,leak}}}$$  \hspace{1cm} (6.4)
where $M_{\text{all, leak}}$ is the moles of all gases entering via atmospheric leaks per unit time, $Q_{Ar}$ is the volumetric flow rate of feed argon entering the reactor, and $Q_{H_2}$ is the volumetric flow rate of feed hydrogen entering the reactor. Using equation (6.4), the leak rates calculated in Table 6.1, and the extreme values of the gas flow rates and total pressures employed in the experiments, a summary of the range of water partial pressures achievable within the reactors is presented in Table 6.2.

Table 6.2: Extremal values of water partial pressures $p_{H_2O}$ (in atmospheres) achievable using various reactor configurations; water content of feed gases taken to be as specified by manufacturer’s certificate of analysis, i.e., 1 ppm oxygen and 1 ppm water vapor.

<table>
<thead>
<tr>
<th></th>
<th>Low Feed Gas Flow-rates: $Q_{H_2} = 210$ SCCM, $Q_{Ar} = 10$ SCCM</th>
<th>High Feed Gas Flow-rates: $Q_{H_2} = 1000$ SCCM, $Q_{Ar} = 100$ SCCM</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Total Pressure</strong></td>
<td>$p_{\text{total}}$</td>
<td>$p_{\text{total}}$</td>
</tr>
<tr>
<td>Low Total Pressure, $p_{\text{total}} = 6$ Torr</td>
<td>$1.47 \times 10^{-6}$</td>
<td>$1.47 \times 10^{-5}$</td>
</tr>
<tr>
<td>High Total Pressure, $p_{\text{total}} = 60$ Torr</td>
<td>$1.19 \times 10^{-6}$</td>
<td>$2.98 \times 10^{-6}$</td>
</tr>
<tr>
<td><strong>TGA Reactor</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Low-Leak Reactor with TC</td>
<td>$2.88 \times 10^{-8}$</td>
<td>$2.88 \times 10^{-7}$</td>
</tr>
<tr>
<td>Low-Leak Reactor without TC</td>
<td>$1.36 \times 10^{-8}$</td>
<td>$1.36 \times 10^{-7}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Medium Total Pressure, $p_{\text{total}} = 24$ Torr</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>High-Leak Reactor with TC</td>
<td>$3.96 \times 10^{-8}$</td>
<td>$9.89 \times 10^{-8}$</td>
</tr>
<tr>
<td>High-Leak Reactor without TC</td>
<td>$2.74 \times 10^{-8}$</td>
<td>$6.86 \times 10^{-8}$</td>
</tr>
</tbody>
</table>

Table 6.2 presents a selection of water vapor partial pressures achievable under various reactor configurations. The low-leak reactor is capable of attaining water vapor partial pressures of as low as about $10^{-8}$ atmospheres. This agrees with the values employed for the thermodynamic calculations in Chapter 4. Introduction of the thermocouple feedthrough into the low-leak reactor marginally increases the partial-pressure of water vapor within this configuration. The thermogravimetric reactor is capable of achieving water vapor pressures of as
low as about $10^{-6}$ atmospheres, two orders of magnitude higher than the minimum water-vapor partial pressure attainable in the low-leak reactor configuration.

Increasing the flow-rate serves to reduce the partial pressure of water vapor in the reactors by diluting the effect of the atmospheric leaks (at a constant pressure). However, limitations on the pumping speed of the vacuum pump mean that increasing the flow-rate increases the (lowest achievable) total pressure within the reactor. This increases the partial pressure of water vapor within the reactor. Thus, the minimum achievable water vapor partial pressures are attained under conditions of low total pressures and low gas flow rates. Note that this analysis assumes that the leak rates measured during leak testing correspond to the leak rates observed during the actual experiments. This may not be the case if, e.g., heating of the gaskets and reactor vessel results in an increased leak rate.

Furthermore, the water composition of the feed gas stream could be higher than that specified by the typical certificates of analysis provided by the manufacturer. The feed gas stream was characterized with a hygrometer as detailed in chapter 5, and the water content of the gas streams at atmospheric pressure was below the limits of detection, with a dew/frost point below -50 degrees Celsius. This dew point corresponds to a water partial pressure below $6.45 \times 10^{-5}$ atmospheres, as calculated using (Roine 2002), and a total water content below 576 parts per million for the hydrogen gas and below 29.1 parts per million for the argon gas. The analytical equipment used to characterize the feed gas stream was thus unable to verify that the gases were as pure as stated by the manufacturer. Using the “worst-case” scenario in which the water content of the feed gases was 576 parts per million for the hydrogen gas and 29.1 parts per million for the argon gas, the expression for the water partial pressure within the reactor is given by:


\[
p_{\text{H}_2\text{O}} = \left(0.21 M_{\text{all,leak}} + \left(3.42 \times 10^{-6} \text{ moles hr}^{-1} \text{ SCCM}^{-1}\right) Q_{\text{Ar}}
+ \left(1.73 \times 10^{-7} \text{ moles hr}^{-1} \text{ SCCM}^{-1}\right) Q_{\text{H}_2}\right)
\times \frac{1}{p_{\text{total}}}
\left(2.68 \times 10^{-3} \text{ moles hr}^{-1} \text{ SCCM}^{-1}\right)\left(Q_{\text{Ar}} + Q_{\text{H}_2}\right) + M_{\text{all,leak}}
\] (6.5)

Using equation (6.5), a new summary of the maximum partial pressures of water vapor which could exist within the reactor are presented in Table 6.3. Clearly, these partial pressures are considerably higher than those calculated using the manufacturer’s typical water-content values.

Table 6.3: Extremal values of water partial pressures \( p_{\text{H}_2\text{O}} \) (in atmospheres) achievable using various reactor configurations; water content of feed gases taken to be as high as the detection limit for the hygrometer, 576 ppm for the hydrogen and 29.1 ppm for the argon.

<table>
<thead>
<tr>
<th></th>
<th>Low Feed Gas Flow-rates: ( Q_{\text{H}<em>2} = 210 \text{ SCCM}, Q</em>{\text{Ar}} = 10 \text{ SCCM} )</th>
<th>High Feed Gas Flow-rates: ( Q_{\text{H}<em>2} = 1000 \text{ SCCM}, Q</em>{\text{Ar}} = 100 \text{ SCCM} )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Low Total Pressure, ( p_{\text{total}} = 6 \text{ Torr} )</td>
<td>High Total Pressure, ( p_{\text{total}} = 60 \text{ Torr} )</td>
</tr>
<tr>
<td>TGA Reactor</td>
<td>( 2.41 \times 10^{-6} )</td>
<td>( 2.41 \times 10^{-5} )</td>
</tr>
<tr>
<td></td>
<td>( 6.69 \times 10^{-6} )</td>
<td>( 1.67 \times 10^{-5} )</td>
</tr>
<tr>
<td>Low-Leak Reactor with TC</td>
<td>( 9.70 \times 10^{-7} )</td>
<td>( 9.70 \times 10^{-6} )</td>
</tr>
<tr>
<td></td>
<td>( 5.54 \times 10^{-6} )</td>
<td>( 1.38 \times 10^{-5} )</td>
</tr>
<tr>
<td>Low-Leak Reactor without TC</td>
<td>( 9.55 \times 10^{-7} )</td>
<td>( 9.55 \times 10^{-6} )</td>
</tr>
<tr>
<td></td>
<td>( 5.52 \times 10^{-6} )</td>
<td>( 1.38 \times 10^{-5} )</td>
</tr>
</tbody>
</table>

Using the higher estimates of the water content of the feed gases reduces the relative effect of the different leak rates in the separate reactor configurations because a larger portion of the water vapor within the reactor originates from the feed gas stream. The minimum achievable water vapor partial pressure in this configuration is on the order of \( 10^{-6} \) atmospheres and is comparable across the various reactor configurations. Increased flow rates reduce the water partial pressure within the thermogravimetric reactor but marginally increase the water partial pressure.
pressure within the low-leak reactor. Increased total pressures increase the water-vapor partial pressure within the reactor.

In summary, the minimum achievable partial pressure of water vapor in the low-leak reactor is estimated to be on the order of $10^{-8}$ atmospheres if the manufacturer’s purity measurements are accurate. At worst, the minimum achievable partial pressure of water within the low-leak reactor is on the order of $10^{-6}$ atmospheres. The minimum partial pressure of water vapor achievable within the thermogravimetric reactor is estimated to be on the order of $10^{-6}$ atmospheres, using either the manufacturer’s purity estimates or the independent purity quantification performed during this research.

6.2 Temperature Measurements: Heating in Non-Equilibrium Plasmas

This section discusses the effect of the adjustable experimental parameters (applied microwave power, total reactor pressure, and gas flow rate) on the steady-state temperature achievable within the plasma. These results were collected via two types of experiments. The first set of experiments measured the temperature within the plasma at the [radial] center of the waveguide and were conducted using a bare thermocouple exposed directly to the plasma. The second set of experiments measured the temperature within the plasma at the [radial] center of the top portion of the furnace, a location 7-centimeters below the center of the waveguide and were conducted concurrently with the copper oxide reduction experiments and measured the steady-state temperature attained at the interior of the resulting copper pellets, as measured by the embedded thermocouple.

The temperature attained by solid particles immersed within the plasma is a function of the heat balance of those particles. The heat balance takes into account the heat entering the particle and the heat leaving the particle; in the steady state, these two heat fluxes balance such
that a time-invariant temperature is attained. A schematic depiction of the heat balance of a solid particle in the plasma is presented in Figure 6.5. In general, the relative efficiency of each of these energy-transfer-modes is a function of the temperature of the solid (as well as a function of the other plasma parameters), such that changing the experimental parameters and the contribution of any given mode can result in a different steady-state temperature.

![Schematic representation of the heat-balance of a solid particle immersed within a plasma](image)

Figure 6.5: Schematic representation of the heat-balance of a solid particle immersed within a plasma; adapted from (Daniel Edward Bullard 1993)

The heat flux from the plasma into a solid particle may be considered to consist of inelastic collisions, elastic collisions, exothermic chemical reactions, and radiation adsorption, per (Daniel Edward Bullard 1993). Inelastic collisions and elastic collisions refer to the transfer of energy from incident plasma particles to the solid. These collisions can include the traditional mechanisms by which gases and solids exchange heat, as well as the transfer of energy from vibrationally-excited molecules to the solid. Exothermic chemical reactions between the gas and
the solid or between adsorbed molecules on the solid can also release energy to the solid. (Daniel Edward Bullard 1993) asserts that the “energy input [to a solid within the plasma] by chemical reactions is small.” However, this is an inaccurate assessment. As discussed in Chapter 2, the recombination of atomic hydrogen is highly exothermic, with an enthalpy change of -435.68 kilojoules per mole at 298 Kelvin. If the recombination rate on the solid is appreciable, this recombination reaction can lead to significant local heating at the surface of the solid. Indeed, the contribution of the recombination reaction to the heating of solids has even been used as a means of quantifying the concentration of atomic hydrogen within the plasma, as has been presented by (Mozetič et al. 1994). The transfer of energy to the solid by radiation is considered to be small relative to the other modes by (Daniel Edward Bullard 1993) provided that the sample does not directly couple with the electromagnetic fields within the plasma. The energy loss modes from the solid include the traditional mechanisms of conduction, convection, and radiation, as well as the loss of energy from the solid via, e.g., volatilization. At temperatures of several hundred degrees Celsius and above, infrared radiation from the sample to the reactor walls will dominate, while at lower temperatures conduction and convection may be more significant.

Figure 6.6 presents the effect of adjusting the microwave power on the temperature within the plasma. Clearly, increasing the applied power increases the temperature of solids within the plasma in a roughly linear fashion. Heuristically, this makes sense, as an increased energy input into the plasma (and an increased heat flux from the plasma to the solid particle) requires a higher steady-state temperature to produce an equivalently increased heat loss from the particle. The temperature at the waveguide center is consistently higher (by over a hundred degrees Celsius) than the temperature at the furnace center for the same experimental conditions.
This is likely due to the finite extent of the plasma: the discharge is localized near the waveguide and decreases in intensity as one moves away from the waveguide in the axial direction. This agrees with the model discussed for surface-excited discharges in Chapter 5.

Figure 6.6: Effect of applied microwave power on the steady-state temperature at two locations within the reactor. Experiments conducted at total pressures of 5.8 Torr, with hydrogen flow rates of 210 SCCM and argon flow rates of 10 SCCM.

Figure 6.7 presents the pressure dependence of the steady-state temperature within the plasma. There is a weak trend of decreasing temperature with increasing pressure at both locations within the reactor. Once again, the temperatures obtained in the furnace (7 centimeters below the waveguide center) are cooler than those obtained in the waveguide center by over one hundred degrees Celsius. This is true even though the measurements obtained at the furnace center were gathered for a higher applied power than those gathered at the waveguide center (600 watts as opposed to 200 watts).
Figure 6.7: Effect of reactor pressure on the steady-state temperature within the plasma. Measurements taken at the locations and powers specified, with a hydrogen flow rate of 210 SCCM and an argon flow rate of 10 SCCM.

However, the trend presented in Figure 6.7 is not consistent with the qualitative evidence of the pressure dependence of the reactor temperature. Notably, at the highest pressures investigated within this research (in the range of 60 Torr), there was evidence of volatilization and softening of the quartz reactor tube, as shown in Figure 6.8. This agrees with the results reported by (Daniel Edward Bullard 1993) and (McTaggart 1964) with regard to the reduction of silica in nonequilibrium hydrogen plasmas. This phenomenon is discussed further in Chapters 9 and 10, but is pertinent to the current discussion: per (Daniel Edward Bullard 1993), the softening of fused silica becomes significant near the Einsink temperature, in the range of 1220 degrees Celsius. Hence, the deformation of the tube wall during the high-pressure experiments (an event that did not occur during the low-pressure experiments) indicates that the local wall
temperature was actually higher during the high-pressure experiments than during the low-pressure experiments.

Figure 6.8: Quartz reactor tube following a high-pressure experiment. Experiment conducted with an applied power of 600 watts at a total pressure of 60 Torr, with flow rates of 210 SCCM of hydrogen and 10 SCCM of argon.

The discrepancy between the trend presented in Figure 6.7 and the qualitative evidence shown in Figure 6.8 may be understood in the context of the effect of the reactor pressure on the spatial extent of the plasma discharge. As discussed in Chapter 3, the reduced electric field strength (the ratio of the electric field to the number density of molecules within the plasma) controls the excitation of the plasma. Per the models of surface-excited discharges presented in Chapter 5, the discharge ceases to propagate at an axial location where the reduced electric field falls below a critical intensity necessary to maintain ionization within the plasma. Hence, at higher pressures, the reduced electric field becomes correspondingly smaller, such that the critical reduced electric field necessary for propagation of the discharge occurs at smaller axial
distances from the discharge center. This causes the discharge to become smaller at higher pressures. This effect is presented in Figure 6.9. The method of estimating the plasma volume was crude, as the plasma was approximated to consist of a rectangular parallelepiped with dimensions determined by comparison with a ruler next to the reactor. However, a trend of decreasing plasma volume with increasing pressure is apparent. This echoes the results of (Daniel Edward Bullard 1993).

![Figure 6.9: Effect of reactor pressure on the plasma volume and on the average microwave power density within the plasma. Experiments conducted with an applied power of 200 watts and flow rates of 210 SCCM hydrogen and 10 SCCM argon, at the pressures specified.](image)

As discussed by (Hassouni et al. 1999), the average microwave power density (MWPD) is one of the most important parameters controlling the behavior of the plasma discharge. To first order, increased MWPD results in higher temperatures within the plasma volume. Hence, in agreement with Figure 6.9, higher pressures result in higher microwave power densities (and
therefore higher temperatures) within the plasma volume. This agrees with the qualitative
evidence of higher reactor wall temperatures achieved at higher pressures, as presented in Figure 6.8.

The trend observed in Figure 6.7 of decreasing temperature with increasing pressure may
be understood by the contraction of the discharge volume with increasing pressure. Both sets of
measurements in Figure 6.7 were taken at the center of the quartz reactor tube. However, the
plasma discharge is concentrated towards one side of the waveguide, as shown in Figure 6.10.
Note that this is in contrast with the predictions of the surface-excited discharge model presented
in Chapter 5, which predicted azimuthal symmetry of the discharge within the reactor tube. Thus,
as the plasma discharge becomes smaller at higher pressures, the distance between the
thermocouples and the discharge (the primary heat source) becomes larger. This is proposed to

Figure 6.10: Photograph of the plasma discharge. This image was taken while 200 watts of
microwave power were applied to the plasma at a pressure of 20 Torr, with flow rates of 210
SCCM of hydrogen and 10 SCCM of argon.
account for the trend of decreasing apparent temperature with increasing pressure in Figure 6.7.

Figure 6.11 presents the effect of gas flow rate on the temperature of solid particles immersed within the plasma discharge. There is a weak trend of decreasing temperature with increasing flow rate for measurements taken at both locations within the plasma. This may be understood by considering the effects of increasing convective heat loss from the solid particles within increasing flow rates. For constant heat inputs (with the other variables, e.g., power input, being held constant) a lower steady-state temperature is attained when the heat loss from the solid is increased. However, given the gradual nature of the temperature-flow rate trend, it appears that the convective heat loss is not a significant contributor to the heat balance of the solid. Once again, Figure 6.11 corroborates the decrease in temperature as one moves away from

![Figure 6.11: Effect of gas flow rate on the steady-state temperature within the plasma. Measurements taken at the locations, powers, and pressures specified, with a hydrogen to argon flow-rate-ratio of 21:1.](image)
the region of highest plasma intensity (i.e., the temperatures measured in the furnace are approximately 200 degrees Celsius cooler than those measured in the center of the waveguide, despite the higher applied powers employed for the former measurements).

In summary, the applied microwave power had the strongest effect on the temperature of solids immersed in the plasma, while pressure and gas flow rate had weaker effects. The effect of applied power and flow rate on temperatures within the plasma have clear explanations in terms of the heat balance of solids in the discharge. However, understanding the effect of pressure on temperature requires a more-involved consideration of the interaction between the reactor pressure, the plasma volume, and the average microwave power density within the plasma. Furthermore, the axial inhomogeneity within the reactor results in large variations (on the order of a few hundred degrees Celsius) for measurements taken at locations as little as 7 centimeters apart. Clearly, the relative position of the discharge and a metal oxide sample within the reactor can have a large impact on the reduction of that metal oxide, inasmuch as the reduction behavior is related to the local temperature.

6.3 Actinometry: Quantification of Hydrogen Dissociation by Spectroscopy

This section presents the results obtained from the spectroscopic measurements of the plasma. Only the summary results are presented here; the unprocessed spectra are presented in Appendix B. Following the methodology described in Chapter 4 and using the spectra from Appendix B, it is possible to construct a series of summary plots describing the dependence of the atomic hydrogen partial pressure on the experimental parameters (total pressure, flow rate, and applied microwave power). These summary plots are presented in Figure 6.12 through Figure 6.14.
Figure 6.12 presents the effect of applied microwave power on the hydrogen partial pressure and hydrogen-excitation temperature within the plasma. Increasing the applied power increases the partial pressure of hydrogen within the reactor almost linearly (or perhaps slightly sub-linearly), increasing from about $10^{-4}$ atmospheres to about $5 \times 10^{-4}$ atmospheres as the applied power increases from 100 watts to 800 watts. The trend for the hydrogen-excitation temperature is not as clear: there is a sharp decrease in this temperature (from about 0.8 eV to about 0.5 eV) as the applied power increases from 100 watts to 200 watts, with a gradual increase as the applied power is increased from 200 watts to 800 watts. The sharpness of the initial decrease contrasted with the convincing trend of the other points lends some uncertainty to

![Graph showing the effect of applied microwave power on hydrogen partial pressure and excitation temperature.](image)

Figure 6.12: Effect of applied microwave power on the partial pressure of atomic hydrogen within the plasma and on the hydrogen-excitation temperature (as quantified using the relative intensity of the hydrogen $\alpha$ and $\beta$ lines). Measurements taken at a pressure of 5.8 Torr, with a hydrogen flow rate of 210 SCCM and an argon flow rate of 10 SCCM. These measurements were taken from the first spectrometer port.
the validity of the initial measurement.

Figure 6.13 presents the effect of total reactor pressure on the partial pressure of atomic hydrogen and on the hydrogen-excitation temperature. Increasing the total reactor pressure increases the partial pressure of atomic hydrogen in a sub-linear (i.e., concave down) fashion, levelling off at about $6 \times 10^{-4}$ atmospheres as the pressure reaches the upper end of the investigated region (between 40 and 60 Torr). The hydrogen-excitation temperature exhibits a generally decreasing trend as the total reactor pressure increases.

Figure 6.13: Effect of total pressure on the partial pressure of atomic hydrogen within the plasma and on the hydrogen-excitation temperature (as quantified using the relative intensity of the hydrogen $\alpha$ and $\beta$ lines). Measurements taken at the pressures specified, with an applied power of 200 Watts, a hydrogen flow rate of 210 SCCM, an argon flow rate of 10 SCCM. These measurements were taken from the opened door of the furnace (aiming at the point of highest plasma-intensity).
Figure 6.14 presents the effect of flow rate on the partial pressure of atomic hydrogen and on the hydrogen-excitation temperature. Increasing the flow rate decreases the partial pressure of atomic hydrogen, levelling off at around $3 \times 10^{-4}$ atmospheres as the flow rate increases above 400 SCCM. This is a somewhat surprising effect, as the mechanism by which the flow rate affects the dissociation of hydrogen is not immediately clear. Perhaps increased gas velocities (corresponding to increased flow rates within the reactor) distribute the hydrogen atoms across a larger volume of space, thereby reducing their concentration at the measurement location (the point of maximum intensity at the center of the waveguide). Increasing the gas flow rate has a
very slight effect on the hydrogen-excitation temperature within this set of experiments, with the
temperature staying in the range of 0.5 eV.

It is worth noting that the hydrogen-excitation temperatures measured in these
experiments were outside of the range of temperatures used for calculating the excitation rate
coefficients described in Chapter 4 (i.e., the lowest temperature available for the rate coefficients
was only 1.0 eV). Hence, it has been necessary to extrapolate these rate coefficients outside of
their originally intended range. Given that argon has a fairly similar electronic excitation profile
to that of hydrogen (i.e., the dependence of their respective cross-sections on electron velocities
are fairly similar—this is the reason argon is used as an actinometer for hydrogen dissociation),
this may be a reasonable extrapolation. Furthermore, per (Geng et al. 2005), the hydrogen
excitation temperature underestimates the electron temperature, such that the actual electron-
temperature value is likely closer to the value employed for these calculations (1.0 eV).
However, rigorous verification of this extrapolation will require more in-depth calculations of
the excitation rate coefficients at these lower electron temperatures.

In summary, the actinometric measurements have quantified the dependence of the partial
pressure of atomic hydrogen within the reactor on the experimental parameters: the partial
pressure of atomic hydrogen under these conditions stays within the range of about 1 x 10^{-4}
atmospheres and 7 x 10^{-4} atmospheres. This corresponds fairly well to the partial-pressure regime
employed for the calculations in Chapter 4 (i.e., 10^{-4} atmospheres to 10^{-2} atmospheres). The
hydrogen excitation temperatures measured in these experiments range between 0.5 eV and 0.8
eV, lower than those temperatures found by (Geng et al. 2005).
6.4 Discussion and Summary

This chapter has presented results relevant to the characterization of the experimental apparatus employed in this research. The leak tests have enabled the quantification of the partial pressure of water vapor within the reactor, while the actinometry measurements have allowed for the quantification of the partial pressure of atomic hydrogen within the reactor. Together with the temperature measurements presented in this chapter, these parameters provide sufficient information to employ the phase-stability diagram analysis (presented in Chapter 4) for predicting the tendency of a given metal oxide to be reduced within the reactor. The results presented in this chapter agree with the conditions used in Chapter 4, thereby validating that those conditions are realistically achievable within the reactor system.
CHAPTER 7

PROCESSING OF COPPER OXIDE: RESULTS AND DISCUSSION

This chapter presents the results obtained from the experiments investigating the reduction of porous spheres of cupric oxide in a non-equilibrium hydrogen plasma. An overview of the most conspicuous features of the reduction process are presented, followed by an analysis of the dependence of the reaction kinetics on the experimental parameters of applied power, total reactor pressure, and gas flow-rate. A brief discussion of sintering phenomena and structural changes within the pellets follows, along with the development of a coupled heat- and mass-transfer model which reproduces some features of the reduction kinetics. The chapter closes with a discussion of the implications of these results and a summary of the important findings.

7.1 Overview

An image of a pre-reaction copper oxide sphere and a post-reaction copper sphere are presented in Figure 7.1. The pre-reaction samples are black in color and are relatively friable. Post-reaction, the resulting spheres are a pale orange color and are resistant to abrasion.

Figure 7.1: Representative pre-reaction copper oxide sphere (left) and post-reaction copper sphere (right).
Using the gravimetric data from the analytical balance and the temperature data from the thermocouple embedded inside the copper oxide samples, it was possible to construct extent-of-reaction and temperature traces for the various experiments. A representative plot is presented in Figure 7.2; the entire collection of plots obtained from the copper oxide reduction experiments are presented in Appendix C. On these plots, the times for 95% reaction and 99% reaction have been denoted on the upper-horizontal axis, while the temperature at 99% reaction (used as a proxy for the temperature attained by the pellets under steady-state conditions in the plasma) has been denoted on the right-hand vertical axis. Note that the mass data have been normalized to display the total extent of reaction for each sample and the temperature data have been normalized to display a temperature:

\[ \theta = \frac{T_P - T_L}{T_H - T_L} \]  

(7.1)

with \( \theta \) the normalized pellet temperature, \( T_P \) the pellet temperature in degrees Celsius, \( T_L \) a semi-arbitrary “low” reference temperature of 100 degrees Celsius, and \( T_H \) a semi-arbitrary “high” reference temperature of 750 degrees Celsius. Several salient features can be observed from these plots. First, the extent-of-reaction curves generally exhibit sigmoidal behavior: i.e., their slope begins small, gradually increases, and then decreases to an asymptotic zero slope. Second, the temperature traces exhibit a generally increasing trend with a maximum temperature occurring near the time of maximum reaction rate.

As will be discussed later in this chapter, it is proposed that these two features (the sigmoidal shape of the extent-of-reaction curve and the simultaneous occurrence of the period of accelerating reaction rate with the time at which the pellet attains maximum temperatures) are related by the exothermic nature of the reduction reactions:
CuO + H₂(g) = Cu + H₂O(g) \hspace{1cm} \Delta H_{600^\circ C} = -22.8 \text{ kcal/mol}

CuO + 2H(g) = Cu + H₂O(g), \hspace{1cm} \Delta H_{600^\circ C} = -128.7 \text{ kcal/mol}

These exothermic chemical reactions increase the local temperature as the reaction proceeds, thereby increasing the rate at which the relevant phenomena (e.g., diffusion and chemical reaction) occur. This in turn increases the rate of reaction, further increasing the local temperature. This coupling between the heat and mass transport phenomena is thus proposed to produce a feedback mechanism which results in the period of accelerating rates observable in the extent-of-reaction curves. Note, however, that the sigmoidal behavior of the extent of

Figure 7.2: Representative extent-of-reaction and temperature traces for cupric oxide sample processed with 300 watts of applied microwave power at a total pressure of 5.8 Torr, with flow rates of 210 SCCM hydrogen gas and 10 SCCM of argon gas.
reaction curves becomes less apparent at higher applied powers, as depicted in Figure 7.3. Heuristically, this is proposed to occur because the heating from the exothermic reaction becomes less significant (relative to the heating delivered directly from the plasma) at higher applied powers, thereby reducing the feedback effect during the course of the reaction; a quantitative description of this behavior is presented later in this chapter.

![Figure 7.3: Extent-of-reaction versus time (normalized to the time for 95% reaction for each sample): qualitative comparison of reaction traces. Experiments conducted at total pressure of 5.7-6 Torr, hydrogen flow rate of 210 SCCM, and argon flow rate of 10 SCCM.](image)

Note that there are two transient phenomena observable in the temperature traces of these reactions: the first results from the heating of the entire reactor/pellet configuration due to the ignition of the plasma at the beginning of the experiment (i.e., the reactor and pellet are transitioning from their initial room-temperature state into thermal equilibrium with the plasma) while the second results from the exothermic nature of the chemical reaction. These two features are distinguishable by comparing the temperature traces obtained at two different thermocouples.
The first thermocouple, located on the reactor wall, experiences only the heating effect from the plasma since no exothermic reduction reaction takes place there. The second thermocouple, located within the pellet, experiences heating due both to the plasma as well as to the exothermic reduction reaction. These two features can be seen in Figure 7.4.

The pellet temperature follows the same general trend as the wall temperature with an additional peak (resulting from the chemical reaction) superimposed on it. Thus, the heating contribution due to the exothermic reduction reaction may be evaluated independently by subtracting the temperature trace from the thermocouple at the wall from the temperature trace...
from the thermocouple within the pellet in Figure 7.4. It might even be possible to correlate the extent-of-reaction by using the temperature trace of the pellet.

Figure 7.5 through Figure 7.7 present micrographs of a partially reacted copper oxide sample at increasing levels of magnification. In Figure 7.5, the entirety of the cross-section of the sample can be seen. At this length scale, the reaction interface appears relatively sharp: the exterior region of the sample appears to be metallic and copper-colored, while the interior of the pellet appears to be dark-colored, much like the unreacted copper oxide pellet. Figure 7.6 presents a magnified image of the reaction-interface region. At this length scale, it appears that the interfacial region (i.e., the transitional region between the exterior, entirely copper region and the interior, entirely cupric oxide region) is approximately 400 micrometers thick.

Figure 7.5: Optical micrograph of a sectioned partially-reacted copper/copper oxide sample. The sample was processed with an applied microwave power of 600 W, a total pressure of 5.8 Torr, a hydrogen flow rate of 210 SCCM, and an argon flow rate of 10 SCCM.
Figure 7.6: Overlaid optical micrographs of the reaction-interface region within the partially-reacted copper/copper oxide sample. The sample was processed with an applied microwave power of 600 W, a total pressure of 5.8 Torr, a hydrogen flow rate of 210 SCCM, and an argon flow rate of 10 SCCM.
Figure 7.7 shows a magnified view of individual grains within the partially-reacted pellet, near the reaction-interface zone. It is clear in this image that the reaction interface is not perfectly sharp: the exterior regions of the grains have been reduced to copper while the interior regions remain as unreacted cupric oxide. This situation is thus most accurately represented by the grain model developed in (J. Szekely and Evans 1970, 1971, Sohn and Szekely 1972, 1973; J. Szekely, Lin, and Sohn 1973) in which the porous pellet is considered to consist of multiple grains each reacting via the shrinking-core model of (Yagi and Kunii 1955).

Figure 7.7: Optical micrograph of individual grains within the partially-reacted copper/copper oxide sample. The sample was processed with an applied microwave power of 600 W, a total pressure of 5.8 Torr, a hydrogen flow rate of 210 SCCM, and an argon flow rate of 10 SCCM.

However, given that the thickness of the partially-reacted interfacial region is less than one-tenth the radius of the pellet (approximately 5500 micrometers), it is reasonable to
approximate the reaction interface as a sharp interface. This amounts to considering the multi-
particle grain model in the limit in which the pellet may be treated as a single homogeneous
particle reacting via shrinking-core behavior. As discussed in (Julian Szekely, Evans, and Sohn
1976), this limit is tantamount to the situation in which diffusion within the pores of the pellet is
the rate-limiting step for the overall heterogeneous reaction. Thus, the micrographs presented in
Figure 7.5 through Figure 7.7 support the choice of modelling the overall reaction of the pellet as
a pore-diffusion controlled process of the shrinking unreacted-core type. This information will be
used to construct the model presented later in this chapter.

7.2 Dependence of Reaction Kinetics on Experimental Parameters

Figure 7.8 through Figure 7.11 present summary plots of the influence of the plasma
processing parameters (applied microwave power, total pressure, and gas flow rates) on the
reduction reaction. These plots use the time for 95% reaction and the pellet temperature at 99%
reaction (as called out in Figure 7.2 and in figures in Appendix C) as proxies for the total
reaction time and steady-state temperature, respectively. Thus, parameter changes which increase
the reaction time may be interpreted as slowing down the overall rate of reduction, while
parameter changes which increase the steady-state temperature may be interpreted as resulting in
a larger heat flux from the plasma to the pellet. Error bars are presented for each of the data
points in these plots. These are constructed using the standard deviation of the time for 95%
reaction and the temperature at 99% reaction for a set of three trials performed under identical
conditions, presented in Appendix C (600 watts of applied power, 6 Torr total pressure,
hydrogen flow rate of 210 SCCM, and argon flow rate of 10 SCCM).

Figure 7.8 presents the effect of adjusting the applied microwave power on the reaction
time and the steady-state pellet temperature. Clearly, increasing the applied microwave power
has a strong effect on both of these variables, reducing the time for total reaction and increasing the steady-state pellet temperature. The increase in temperature with applied power appears to be fairly linear, while the decrease in reaction times with increase applied power is asymptotic.

Figure 7.8: Effect of applied microwave power on reaction time and steady-state temperature. Experiments conducted at total pressures of 5.7-6 Torr, hydrogen flow rates of 210 SCCM, and argon flow rates of 10 SCCM.

The sharp decrease in the reaction time observed in Figure 7.8 in the transition from 200 watts of applied power to 300 watts may be exaggerated by the choice of reaction time as starting from the moment at which the microwave power is initially applied. At very low applied powers, the pellet heats from room temperature very slowly. This means that a large proportion of the reaction time occurs when the pellet is at low temperatures. At these low temperatures, it may be impossible for the solid-state reduction reaction to occur at a measurable rate due to kinetic limitations. Thus, it might be superior to determine the minimum temperature at which
the reaction proceeds at an appreciable rate and then define the reaction time as the time elapsed since the pellet achieved that temperature. Alternatively, these experiments could be conducted such that the pellets are pre-heated to their steady-state temperature by radiative heating via the furnace or by an argon (non-reducing) plasma.

It is worth noting at this point that the copper-oxide samples were suspended outside the region of highest intensity within the plasma: the support rod by which they were suspended ended at a location approximately equidistant between the waveguide and the top of the resistance furnace. This position (shown in Figure 5.14) was chosen to allow for independent heating of the samples via either the action of the plasma or by the furnace. However, this location is not ideal in that the sample is not located at a symmetric location with respect to the plasma: the region of highest electric field strength (and the highest concentration of excited species) is located at the waveguide, with a gradual decrease in the magnitude of these variables as one moves further from the waveguide in the axial direction (as discussed in section 5.1). Given that the size of the plasma can change as the relevant plasma parameters are varied (generally, the discharge volume increases with increasing applied power and decreasing pressure), it is possible that the location of the sample relative to the plasma discharge changed under different conditions. That is to say, at high powers and low pressures, the discharge may fill a relatively large volume such that the pellet is exposed to a spatially-invariant surrounding environment. At low powers and high pressures, however, the plasma may be concentrated near the waveguide, such that the sample is exposed only to the “afterglow” of the discharge.

Figure 7.9 presents the effect of adjusting the total reactor pressure on the time for 95% reaction and on the steady-state pellet temperature. The effect of adjusting the total pressure is not as strong as the effect of adjusting the applied power described previously: the steady-state
temperature is relatively unaffected by changes in the total reactor pressure, while the reaction
time exhibits a relatively small decrease (from about 18 minutes to about 12 minutes) upon
increasing the pressure from 10 Torr to 50 Torr.

Figure 7.9: Effect of total reactor pressure on reaction time and steady-state temperature.
Experiments conducted with 600 watts of applied power, hydrogen flow rates of 210 SCCM,
and argon flow rates of 10 SCCM.

It is worth noting, however, that at increased pressures the temperature of the reactor wall
appears to have increased significantly. This is evidenced by partial deformation of the quartz
reactor wall and evidence for the volatilization of silicon monoxide, as mentioned in Chapter 6.
Heuristically, the presence of higher concentrations of the reacting species (atomic and
molecular hydrogen) at higher pressures allows for a higher rate of reduction. This
generalization, however, does not take into account the impact of the pressure on the microwave
power density (MWPD), a variable proposed by (Hassouni et al. 2006) to be one of the most important parameters for influencing the behavior of the plasma discharge.

Figure 7.10 presents the influence of the gas flow rate on the reaction time and steady-state pellet temperature; the argon to hydrogen partial pressure (and flow rate) ratio was maintained at a constant ratio of 1:21 throughout these experiments. The steady state pellet temperature is relatively unaffected by adjusting the gas flow rate. This indicates that, within the parameter regime considered, convective cooling does not play a significant role in the overall heat balance of the pellet; this is discussed further in the context of the coupled heat-and mass-transfer model developed later in this chapter. The flow rate influences the time for 95% reaction via an inverse asymptotic relationship: at very low flow rates, the pellet takes a long time to

![Figure 7.10: Effect of gas flow rate on reaction time and steady-state temperature. Experiments conducted with 600 watts of applied power, total pressure of 23-24 Torr, and a hydrogen to argon partial pressure ratio of 21:1.](image)
react, while increasing the flow rate reduces the reaction time to an asymptotic value. This may be understood by considering the fact that at very low flow rates the reaction is “starved” for reagents: i.e., hydrogen which is introduced into the system is reacted very quickly, such that the overall rate of reaction is controlled by the rate at which hydrogen is supplied to the reactor. As the flow rate of hydrogen supplied to the system increases, other mechanisms (such as pore diffusion) begin to limit the rate of reaction, and supplying additional hydrogen no longer reduces the time for complete reaction.

7.3 Comparison of Reduction Kinetics of Molecular and Atomic Hydrogen

Figure 7.11 (on the next page) presents a comparison between the time for complete reaction for pellets heated to a given temperature by the microwave plasma and pellets exposed to molecular hydrogen which have been heated radiatively by the resistance furnace. This plot thus serves as an attempt to answer one of the major outstanding questions identified in Chapter 2: i.e., are there kinetic advantages to using atomic hydrogen (as is produced within the plasma) to reduced metal oxides which can also be reduced by molecular hydrogen? This plot indicates that there is not an appreciable difference between the atomic and molecular hydrogen at high pellet temperatures. There does appear to be a difference between the two heating methods at lower temperatures. However, this is likely an artifact of the different temperature histories of the pellets: for the plasma-heated samples, the pellet began at room temperature and the reaction was initiated by supplying microwave power to the reactor. For the furnace-heated samples, however, the pellet was heated to the initial temperature and the reaction was initiated by supplying hydrogen gas to the reactor. Thus, the initial portion of the plasma-heated experiments occurs at a relatively low temperature—likely too low for the reduction to proceed, due to kinetic limitations of the solid-state reaction. This is not a significant factor for the higher steady-state
temperature experiments because the larger heat flux to the pellet means that the transient “heating time” is short relative to the total reaction time. However, for the lowest temperature points in Figure 7.11, the transient heating time represents a significant portion of the total reaction time. Examining e.g. Figure C-1 and Figure C-19 in Appendix C indicates that no reaction occurred in the initial 40 minutes following ignition of the plasma, whereas the furnace-heated sample began to react almost immediately. This 40-minute period accounts for the difference between the lowest temperature samples heated by the plasma and by the furnace in Figure 7.11.

Figure 7.11: Comparison of effects of plasma and furnace heating on reaction-time and steady-state temperature. Experiments conducted with total pressures of 5.7-6 Torr, hydrogen flow rates of 210 SCCM, and argon flow rates of 10 SCCM.

Thus, there does not appear to be a significant difference between environments containing atomic hydrogen and those containing only molecular hydrogen with respect to the
kinetics of the reduction of pellets of cupric oxide. One interpretation of this behavior is provided by the penetration depth model described in Chapter 4: as one moves deeper into the pellets from the surface, the recombination of atomic hydrogen on the grains continues to reduce the concentration of atomic hydrogen. At depths further from the surface than the penetration depth—where that depth $\delta$ is defined by equation (4.46), with $\delta$ depending on the relative rate of the recombination reaction of atomic hydrogen to the rate of diffusion of atomic hydrogen within the porous pellet, as well as the ratio of the concentration of atomic hydrogen in the bulk plasma to the minimum concentration of atomic hydrogen necessary to reduce cupric oxide to copper—the concentration of atomic hydrogen is too low to influence the recombination reaction.

If the penetration depth $\delta$ is small relative to the radius of the pellets, then there will be no appreciable difference between the reduction kinetics of cupric oxide in the environments containing atomic and molecular hydrogen. Since molecular hydrogen is still able to reduce cupric oxide to copper under the conditions used in these experiments, the overall reduction kinetics will be comparable. If there is a difference between the reduction kinetics of cupric oxide in these two distinct gaseous environments, it would only be apparent at very short reaction times (during the initial phases of the reaction, when the exterior region of the pellet is reacting) or for very small particles whose characteristic lengths are of comparable size to the penetration depth $\delta$.

7.4 Sintering Phenomena and Structural Changes

Different post-reaction morphologies were observed in the pellets processed under different conditions. Notably, the copper pellets which were exposed to increased temperatures during the reaction exhibit reduced intragranular porosity and increased intergranular sintering.
Micrographs of a few selected post-reaction pellets are presented in Figure 7.12 through Figure 7.14. Figure 7.12 shows a magnified image of a collection of grains processed at a relatively low temperature (attaining a maximum temperature of 281 degrees Celsius). The grains appear to be nearly circular in cross section. They are joined to nearby grains via limited “necks,” if at all. Within the individual grains, appreciable porosity is evident from the small dark areas within the bright metallic grain. These pores result from the decrease in molar volume that occurs as the original copper oxide (12.59 cubic centimeters per mole) grains are reduced to copper metal (7.09 cubic centimeters per mole).

![Micrograph of individual grains in a fully-reacted copper sample](image)

**Figure 7.12**: Light optical micrograph of individual grains in a fully-reacted copper sample processed at a relatively low temperature (steady-state temperature 243 degrees Celsius, maximum temperature 281 degrees Celsius). The sample was processed with 200 watts of applied microwave power at 5.8 Torr total pressure, with a hydrogen flow rate of 210 SCCM and an argon flow rate of 10 SCCM. This sample was unetched.

At moderately increased temperatures, the intragranular porosity is reduced by means of sintering. As shown in Figure 7.13 (on the next page), a pellet exposed to a maximum temperature of 594 degrees Celsius has less apparent porosity within the individual grains.
Increased necking between adjacent grains is also apparent, but it is still possible to differentiate between the grains. The intergranular porosity appears to be marginally reduced relative to the pellet processed at low temperatures.

Figure 7.13: Light optical micrograph of individual grains in a fully-reacted copper sample processed at an intermediate temperature (steady-state temperature 484 degrees Celsius, maximum temperature 594 degrees Celsius). The sample was processed with 500 watts of applied microwave power at 5.8 Torr total pressure, with a hydrogen flow rate of 210 SCCM and an argon flow rate of 10 SCCM. This sample was unetched.

For pellets processed at even higher temperatures, intragranular porosity appears to be totally eliminated and increased sintering between adjacent grains is evident. As presented in Figure 7.14, the grains in a pellet processed at a maximum temperature of 761 degrees Celsius seem to be fully densified copper (apart from scratches induced during the polishing process). Furthermore, the increased intergranular sintering has resulted in the formation of irregularly shaped, globular multi-grain complexes. It is not possible to identify all of the original grains which contributed to the formation of these complexes.
Figure 7.14: Light optical micrograph of individual grains in a fully-reacted copper sample processed at a relatively high temperature (steady-state temperature 718 degrees Celsius, maximum temperature 761 degrees Celsius). The sample was processed with 800 watts of applied microwave power at 5.8 Torr total pressure, with a hydrogen flow rate of 210 SCCM and an argon flow rate of 10 SCCM. This sample was unetched.

The pellets also exhibited a decrease in diameter as they underwent reduction. This diameter-decrease likely results from the two effects discussed previously (e.g., the decrease in molar volume as the cupric oxide reacts to form copper and the sintering between grains). This effect is also dependent on temperature, with increased steady-state temperatures corresponding to a larger decrease in the diameter of the pellets. Figure 7.15 (on the next page) demonstrates this effect by plotting the percentage decrease in pellet diameter against the steady-state temperature attained by the pellets. While there is a direct relationship between the reduction in size and the steady-state temperature relationship (with a slope of 1.57 percent diameter reduction per 100 Kelvin), the linear fit has a coefficient of determination of only $R^2=0.687$. Thus, comparison of the macroscopic dimension changes of the pellets supports the
microstructural observations of increased sintering at higher temperatures, as expected given the activated nature of the sintering process, c.f. (Julian Szekely, Evans, and Sohn 1976).

![Graph showing the relationship between steady-state temperature and diameter reduction percent.](image)

Figure 7.15: Comparison of cupric oxide/copper pellet diameter change during reaction and steady-state temperature achieved by the pellets.

### 7.5 Accelerating Rate of Reaction: Nucleation versus Exothermic Feedback

This section presents a mathematical model describing the couple heat- and mass-transfer phenomena which occur during the reduction of copper oxide by hydrogen. It is presented as a means of understanding the sigmoidal behavior of the extent of reaction curves, and of the transient temperature peak observed during the extent of the reduction reaction. As discussed earlier, the sharp reaction-interface observable in the micrograph of the partially-reacted cupric oxide pellet presented in Figure 7.5 indicates that it is reasonable to approximate the reduction behavior of the pellet as a shrinking-core model in which the overall rate of reaction is controlled by diffusion of the reactant and product gases through the porous-reacted layer. A derivation of this model follows.
This model considers the evolution of a spherical pellet of radius \( r = R \) which is undergoing reaction; the reaction interface lies at \( r = r_c \). The conservation equation for molecular hydrogen within the reacted shell region (i.e., at radii \( \tilde{r} \) such that \( r_c < \tilde{r} < R \)) is given by:

\[
c_{\text{tot}} \frac{\partial X_{H_2}}{\partial t} = - \frac{\partial N_{H_2}}{\partial r}
\]

where \( c_{\text{tot}} \) is the total concentration of gaseous species, \( X_{H_2} \) is the mole fraction of hydrogen, and \( N_{H_2} \) is the flux of hydrogen, \( r \) is the radial coordinate, and \( t \) is time. Employing the quasi-steady state approximation discussed in Chapter 4, it is possible to set the left-hand side of equation (7.2) to zero such that:

\[
4\pi R^2 N_{H_2} \bigg|_{r=R} = 4\pi \tilde{r}^2 N_{H_2} \bigg|_{r=\tilde{r}} = 4\pi r_c^2 N_{H_2} \bigg|_{r=r_c}
\]

(7.3)

The flux of molecular hydrogen can be related to the rate of reaction of the pellet by writing:

\[
- \frac{\partial M_{\text{CuO}}}{\partial t} = -4\pi r_c^2 N_{H_2} \bigg|_{r=r_c}
\]

(7.4)

where \( M_{\text{CuO}} \) is the moles of cupric oxide remaining in the pellet; note that equation (7.4) appeals to the stoichiometry of the reduction reaction in which one mole of hydrogen is capable of reducing one mole of cupric oxide. Using equations (7.3) and (7.4), it is possible to write:

\[
- \frac{\partial M_{\text{CuO}}}{\partial t} = -4\pi \tilde{r}^2 N_{H_2} \bigg|_{r=\tilde{r}}
\]

(7.5)

Using Fick’s Law for the case of equimolar counter-diffusion (applicable since one mole of water vapor leaves the pellet for each mole of hydrogen that enters), it is possible to substitute the relationship \( N_{H_2,r} = -D_e c_{\text{tot}} \left( \frac{\partial X_{H_2}}{\partial r} \right) \) into equation (7.5) such that:

\[
\frac{dM_{\text{CuO}}}{dt} = -4\pi \tilde{r}^2 D_e c_{\text{tot}} \left( \frac{\partial X_{H_2}}{\partial r} \right) \bigg|_{r=\tilde{r}}
\]

(7.6)
Note that $\mathcal{D}_e$ is the “effective diffusivity” of molecular hydrogen within the porous product layer.

Equation (7.6) can be integrated:

$$
\frac{dM_{CuO}}{dt} \int_{R}^{r_c} \frac{1}{\bar{r}^2} \partial \bar{r} = -4\pi \mathcal{D}_e c_{tot} \int_{X_{H2,0}}^{0} \partial X_{H2}
$$

which can be evaluated to yield:

$$
\frac{dM_{CuO}}{dt} \left( \frac{1}{r_c} - \frac{1}{R} \right) = -4\pi \mathcal{D}_e c_{tot} X_{H2,g}
$$

For the traditional derivation of the shrinking-core model, this equation is integrated with respect to $t$. However, the situation under consideration involves an exothermic reaction and a potential change in the temperature of the pellet. The effective diffusivity can be considered to be the diffusivity of the hydrogen-water vapor couple with a modifying term accounting for the tortuosity of the pores within the product layer. Given that the diffusion coefficient of gases exhibits a $T^{3/2}$ dependency per (Poirier and Geiger 1994), it is reasonable to define $\mathcal{D}_e(T) = \mathcal{D}_{e,T_0} \left( \frac{T}{T_0} \right)^{3/2}$ (where $\mathcal{D}_{e,T_0}$ is the effective diffusivity at temperature $T_0$) so that:

$$
\frac{dM_{CuO}}{dt} = -4\pi \mathcal{D}_{e,T_0} \left( \frac{T}{T_0} \right)^{3/2} c_{tot} X_{H2,g} \frac{R r_c}{R - r_c}
$$

Relating the rate of reaction with the movement of the reaction interface via the simple stoichiometric equation $-dM_{CuO}/dt = -\rho_{CuO} 4\pi r_c^2 (dr_c/dt)$ where $\rho_{CuO}$ is the molar density of cupric oxide (approximating the change in molar volume during the reduction reaction as zero), it is possible to write:

$$
\frac{dr_c}{dt} = -\mathcal{D}_{e,T_0} \left( \frac{T}{T_0} \right)^{3/2} c_{tot} X_{H2,g} \frac{R}{\rho_{CuO} r_c} \frac{R}{r_c(R - r_c)}
$$

with initial condition $r_c(t = 0) = R$. The evolution of the temperature of the pellet can be expressed by considering a heat balance on the pellet. In the limit of small Biot number (i.e., in the limit of high thermal conductivity of the pellet), it is possible to approximate the entire pellet
as being at a single temperature $T$. Considering the heat produced by the exothermic reduction reaction and the heat lost to the environment by convective/conductive heat transfer, it is possible to write:

$$mC_p \frac{dT}{dt} = (-\Delta H_{rxn}) \left( -\frac{dM_{CuO}}{dt} \right) - h(T - T_0)$$

(7.11)

where $m$ is the mass of the pellet, $C_p$ the heat capacity of the pellet (approximated to be the same for both copper and copper oxide), $\Delta H_{rxn}$ the molar heat of the reduction reaction, and $h$ the heat transfer coefficient. Note that using this expression for the heat flux to/from the environment is tantamount to assuming that convection and conduction are more important energy transfer modes than radiation; otherwise, an expression of the form $(T - T_0)^4$ would likely be necessary to take into account the radiative effects. Substituting for the mass of the pellet and using the expression previously developed for $dM_{CuO}/dt$, it is possible to write:

$$\frac{4}{3} \pi R^3 \rho_{CuO} m_{CuO} C_p \frac{dT}{dt} = \Delta H_{rxn} \rho_{CuO} 4\pi r_c^2 \frac{dr_c}{dt} - h(T - T_0)$$

(7.12)

with $m_{CuO}$ the molar mass of copper. Note that the mass of the pellet is assumed to be unchanging in this expression (tantamount to approximating the density of cupric oxide to be the same as the density of copper). This expression can be re-arranged to yield:

$$\frac{dT}{dt} = \frac{3\Delta H_{rxn}}{R^3 C_p m_{CuO}} r_c^2 \frac{dr_c}{dt} - \frac{3h}{4\pi R^3 \rho_{CuO} C_p m_{CuO}} (T - T_0)$$

(7.13)

with initial condition $T(t = 0) = T_0$. By defining the dimensionless variables $\theta \equiv T / T_0$, $\xi \equiv r_c / R$, and $\tau \equiv t \frac{D_e \tau_0}{R^2}$, it is possible to transform equations (7.10) to yield

$$\frac{d\xi}{d\tau} = -\gamma_1 \frac{\theta^{3/2}}{\xi(1 - \xi)}$$

(7.14)

with initial condition $\xi(\tau = 0) = 1$, where $\gamma_1 \equiv c_{tot} X_{H_2, g} / \rho_{CuO}$. Similarly, equation (7.13) can be transformed to yield:
\[
\frac{d\theta}{d\tau} = -\lambda_1 \xi^2 \frac{d\xi}{d\tau} - \lambda_2 (\theta - 1) \tag{7.15}
\]

with initial condition \(\theta(\tau = 0) = 1\), where \(\lambda_1 \equiv -3 \Delta H_{rxn} / (T_0 C_p m_{CuO})\) and \(\lambda_2 \equiv 3 h / (4 \pi D_e \tau_0 R \rho_{CuO} C_p m_{CuO})\). Hence, the solution to the system of equations given by equations (7.14) and (7.15) with their associated boundary conditions will describe the behavior of the coupled heat-and mass-transfer phenomena which occur in the reduction of cupric oxide by hydrogen.

Representative extent-of-reaction and temperature traces for a simulation conducted using this model are presented in Figure 7.16. Several of the conspicuous features observable in the experimental results can also be seen in this figure. Notably, the extent-of-reaction trace
exhibits the same sigmoidal shape observed during the lower-power experiments. Furthermore, the temperature trace starts at a low value, increases during the course of the (exothermic) reaction, reaches a peak, and then begins to decline. Comparison of Figure 7.2 and Figure 7.16 shows that these two features are captured by the analytic model. There are, however, some differences between the qualitative appearance of the two sets of traces, especially in the temperature trace.

These differences likely exist due to features not considered in the development of the model; e.g., radiation, detailed modelling of the heat transfer phenomena, consideration of the other reaction steps (i.e., fluid-film diffusion and chemical reaction), and the internal structure of the porous pellet (i.e., the fact that it is not homogeneous and actually consists of many smaller grains). Furthermore, the analytic model does not consider the fact that the experimental samples started at room temperature, but rather assumes that they begin the reaction at the eventual steady-state temperature. Despite the fact that these simplifications were employed during the construction of the model, it is still capable of qualitatively reproducing the features observed in the experimental data.

Adjusting the ratio of \( \lambda_1 \) and \( \lambda_2 \) is equivalent to changing the relative importance of the exothermicity of the reaction and the other heat-transfer effects which can influence the pellet. Thus, the limit of large \( \lambda_1 \) amounts to a highly exothermic reaction with the expectation of a strong coupling between the extent-of-reaction and temperature profiles, producing a highly-sigmoidal extent-of-reaction trace. The limit of small (but non-negative) \( \lambda_1 \) represents the case of a slightly-exothermic reaction. It is expected that this case will demonstrate less change in the temperature profile during the reaction and an attendant less-sigmoidal extent-of-reaction curve.
The limit of negative $\lambda_1$, not considered here, would represent the case of an endothermic reaction. Figure 7.17 depicts the extent-of-reaction traces for several different values of $\lambda_1$. The expected behavior is reproduced, with the largest values of $\lambda_1$ corresponding to the most sigmoidal curves. There does seem to be a bifurcation in the qualitative shape of the curves, with a relatively sudden transition from a fairly sigmoidal shape to a non-sigmoidal shape occurring between $\lambda_1 = 700$ and $\lambda_1 = 0$.

![Figure 7.17: Comparison of the effect of changing the parameter $\lambda_1$ on the shape of the extent-of-reaction traces. The parameters employed during these simulations were $\gamma_1 = 0.001$, $\lambda_1$ as specified, and $\lambda_2 = 10$. The reaction times have been normalized to the time for complete reaction for each curve.](image)

Comparison of Figure 7.3 with Figure 7.16 shows that the analytic results accurately reproduce this change in shape, with the highest-power curves corresponding to those with the smallest $\lambda_1$. This makes sense intuitively, since increasing the power applied to the pellet via the plasma is analogous to increasing the importance of the other heat transfer effects relative to the
heat produced by the exothermic reaction. Hence, the highest power trials are analogous to situations described by the model in which there is a small ratio of $\lambda_1$ to $\lambda_2$.

The fidelity of this model is significant because it describes the occurrence of these features using only macroscopic phenomena which do not depend upon the pellet reacting in the plasma environment. That is to say, the same sigmoidal extent-of-reaction curves can be found in the course of reactions with molecular hydrogen; see Figure C-19 in Appendix C for an example. This disagrees with the assessment presented by previous researchers (Sabat, Paramguru, and Mishra 2016) which asserted that the sigmoidal extent of reaction curves are a result of microscopic nucleation phenomena which occur at an increased rate within the plasma. The presentation of an alternative explanation for this phenomenon, as well as the similarity observed between the reaction kinetics for atomic and molecular hydrogen, suggest that the plasma environment does not necessarily increase the nucleation kinetics of the copper product phase.

7.6 Discussion and Summary

In summary, the reduction experiments of porous cupric oxide pellets did not demonstrate a significant advantage of atomic hydrogen over molecular hydrogen. The similarity between the reduction behavior in these two different environments might be explained by the large size of the pellets relative to the penetration depth $\delta$: if the pellet radius is large relative to $\delta$, then no atomic hydrogen will be able to penetrate to the inner regions of the pellet, such that the reaction kinetics will be similar to those obtained in the case of molecular hydrogen. The influence of applied power, pressure, and flow rate on the reaction kinetics and steady-state pellet temperatures was investigated. The most important consideration influencing the reaction kinetics appears to be the temperature of the pellets, whether that temperature is achieved by heating via a microwave plasma or by radiative heating from a resistance furnace. The steady-
state temperature achieved by the pellets also influenced the degree of sintering and pellet-shrinkage which occurred during the reaction. The shrinking-unreacted core model provides a reasonable description of the reaction kinetics, and a computational model incorporating the coupling between the heat- and mass-transfer effects in this system was able to accurately reproduce the qualitative features of the experimental data.
CHAPTER 8
PROCESSING OF MOLYBDENUM DIOXIDE: RESULTS AND DISCUSSION

Porous cylindrical pellets of molybdenum dioxide were prepared and processed in the thermo-gravimetric reactor. These experiments were intended to investigate potential differences in the reduction of molybdenum dioxide to molybdenum metal in atmospheres containing atomic hydrogen and those containing solely molecular hydrogen.

8.1 Reduction of Molybdenum Dioxide: Atomic versus Molecular Hydrogen

Images of a pre-reaction and post-reaction molybdenum dioxide sample processed with atomic hydrogen is presented in Figure 8.1. A thin gray crust is evident on the surface of the post-reaction sample while the interior of the sample remains the original red/purple color. This sample reached a maximum internal temperature of 706 degrees Celsius, as reported by the embedded thermocouple.

![Figure 8.1](image1.png)

**Figure 8.1:** Pre-reaction (left) and post-reaction (right) molybdenum dioxide pellet. The sample was processed with up to 1100 watts of applied microwave power, at a total pressure of 6 Torr, with flow rates of 210 SCCM of hydrogen and 10 SCCM of argon. Total plasma exposure time was 2 hours and 11 minutes, with an additional 1 hour and 28 minutes of cooling time under hydrogen flow.

In order to quantify the thickness of the reduced molybdenum layer, a cross-sectional micrograph was prepared. This image is presented in Figure 8.2. The reduced layer appears to be
about 10 micrometers in thickness. While the existence of this finite-depth-of-reduction agrees with the penetration-depth model discussed in Chapter 4, it is not clear that the reduced layer is limited by the recombination of atomic hydrogen: other factors such as pore-sintering, or the deposition of a volatilized species within the pores, could have prevented further reaction of the pellets.

Figure 8.2: Cross-sectional optical micrograph of the surface-region of a plasma-processed molybdenum dioxide pellet. The sample was reacted with up to 1100 watts of applied microwave power, at a total pressure of 6 Torr, with flow rates of 210 SCCM of hydrogen and 10 SCCM of argon. Note the light-colored region demarcating the mounting polymer (to the left) and the unreacted portion of the pellet (to the right).
In order to verify that pore sintering was not the limiting factor of the observed extent of reaction, a loosely-packed bed of molybdenum dioxide powder was prepared in an alumina boat. An image of the pre- and post-reaction bed is presented in Figure 8.3. The extent of reduction is still limited to the surface region of the powder bed. This suggests that pore sintering is likely not the limiting factor in the extent of reaction, given that the individual molybdenum oxide grains were not tightly joined to each other but the reaction was still constrained to the surface region.

![Image of unreacted and plasma-processed molybdenum dioxide powder](image)

Figure 8.3: Photograph of unreacted (left) and plasma-processed (right) molybdenum dioxide powder in alumina boat. The surface of the powder has been displaced to provide an indication of the depth of reduction. The sample was reacted with up to 600 watts of applied microwave power, at a total pressure of 6 Torr, with flow rates of 210 SCCM of hydrogen and 10 SCCM of argon.

However, a light-gray coating is apparent on the boat, and the reacted portion of the powder formed a semi-coherent crust (as evidenced by some of the larger agglomerates within the boat). Furthermore, a metallic coating was formed on the interior of the quartz reactor tube during some of the experiments in which molybdenum dioxide samples were exposed to the plasma; an image of such a coating is presented in Figure 8.4. These factors indicate that a volatile species may have formed during the reduction process: this species could have formed the coating on the boat, and it could also have joined adjacent grains to each other within the bed. It is possible that the deposition of this species could have reduced the permeability of the bed such that no further reaction past the surface region could occur. The work of (Kangsadan 2004) suggests that no appreciable concentrations of volatile species should be formed during the
reduction of molybdenum dioxide by molecular hydrogen, so perhaps the formation of this volatile species is formed only via interaction with the plasma environment (via, e.g., sputtering of molybdenum by argon ions within the plasma).

Figure 8.4: Section of quartz reactor tube employed for reducing molybdenum dioxide samples. Note the formation metallic-lustered coating on the interior of the tube; this coating formed in the approximate vicinity of the molybdenum dioxide sample. The sample was processed with up to 1100 watts of applied microwave power, at a total pressure of 6 Torr, with flow rates of 210 SCCM of hydrogen and 10 SCCM of argon.

In order to evaluate if the same features (i.e., reaction in a thin surface region and evidence of volatilization) are apparent in the reduction of molybdenum dioxide by molecular hydrogen, another molybdenum dioxide pellet was prepared and exposed to an environment containing only molecular hydrogen, with the other conditions the same as those for the pellet processed using molecular hydrogen (i.e., an internal temperature of 706 degrees Celsius, a total pressure of 6 Torr, and flow rates of 210 SCCM of hydrogen and 10 SCCM of argon). An image of this sample before and after treatment is presented in Figure 8.5. There is still evidence of the formation of the same reduced crust layer as that present in the sample exposed to atomic
hydrogen. Furthermore, a coating is also observed on the interior of the reaction tube; an image of this coating is presented in Figure 8.6.

![Figure 8.5: Pre-reaction (left) and post-reaction (right) molybdenum dioxide pellet. The sample was heated with the resistance furnace until it obtained an internal temperature of 706 degrees Celsius at a total pressure of 6 Torr, with flow rates of 210 SCCM of hydrogen and 10 SCCM of argon.](image)

Despite the fact that only the exterior region of the molecular-hydrogen-reduced sample exhibited visual signs of reduction (i.e., the reaction was constrained to a thin, easily-removed surface region), the sample mass decreased over 17% during the course of the reaction (from 2.030 g to 1.672 g). Presumably this mass loss can be attributed to the material which was volatilized. Hence, it is clear that despite the different heating methods (microwave plasma versus resistance furnace), the same features are apparent in both processes: an appreciable quantity of the sample is volatilized, and only a thin surface region of the remaining solid is reduced. A comparison of X-Ray diffraction patterns from the two samples and the initial unreacted molybdenum dioxide powder is presented in Figure 8.7. As can be seen in these
patterns, some molybdenum metal has formed in both the atomic- and molecular-hydrogen-reduced samples.

Figure 8.6: Section of quartz reactor tube employed for reducing molybdenum dioxide samples. Note the bi-colored tube coating; the brown portion of the coating was formed at the locations nearest the sample. This coating was produced during an experiment in which the sample attained an internal temperature of 706 degrees Celsius at a total pressure of 6 Torr, with flow rates of 210 SCCM of hydrogen and 10 SCCM of argon.

It is perhaps not surprising that some reduction was observed under both processing conditions. While the industrial reduction and deoxidation of molybdenum dioxide are conducted at temperatures in the range of 1100 °C, per (Roine 2002), the standard Gibbs free energy change of the reaction:

\[
\text{MoO}_2 + 2\text{H}_2(\text{g}) = \text{Mo} + 2\text{H}_2\text{O}(\text{g})
\]
is given by $\Delta G^\circ_{700°C} = 5.682$ kcal/mol. Given that the (limiting) partial pressure of water vapor within the reactor is on the order of $10^{-6}$ atmospheres and the partial pressure of molecular hydrogen is on the order of $10^{-2}$ atmospheres, it is reasonable that even molecular hydrogen will be able to reduce molybdenum dioxide under these conditions, as can be seen by considering the Gibbs Reaction Isotherm:

$$\Delta G = \Delta G^\circ + RT \log(Q)$$

(8.1)
\[
\Delta G = \left( 5.682 \frac{\text{kcal}}{\text{mol}} \right) + \left( 1.986 \times 10^{-3} \frac{\text{kcal}}{\text{mol K}} \times 973 \text{ K} \right) \times \log(10^{-8})
\]  

(8.2)

\[
\Delta G = -29.9 \frac{\text{kcal}}{\text{mol}}
\]  

(8.3)

Since \( \Delta G \) < 0, this reaction has a thermodynamic potential to occur under these conditions.

8.2 Discussion and Summary

In summary, the molybdenum dioxide experiments have shown that both atmospheres containing atomic hydrogen as well as those containing molecular hydrogen are capable of reducing molybdenum dioxide to molybdenum metal. A large degree of volatilization is observed for both reducing atmospheres; this volatilization is somewhat surprising, given the results reported by (Kangsadan 2004) which indicated that volatile species did not play an appreciable role in the reduction reaction at atmospheric pressure. The extent of reaction is constrained to a thin surface region in both cases, indicating that this limited depth of reduction is not a result of the penetration depth phenomenon discussed in Chapter 4 (since the reduction reaction involving molecular hydrogen should not possess a finite depth of penetration). Thus, one possible explanation for the limited depth of reduction observed in these studies is that the unknown volatile species is condensing near the surface region, thereby reducing the local porosity and preventing further penetration of the reducing gas.
CHAPTER 9

PROCESSING OF TITANIUM OXIDE: RESULTS AND DISCUSSION

This section presents the experimental results obtained during the investigation of the reduction of titanium oxide in nonequilibrium hydrogen plasmas. These results begin with a discussion of the preliminary experiments on the reduction of porous titanium oxide pellets. Motivated by the limited penetration depth observed in these samples, subsequent studies investigated the reduction of thin-films of titanium oxide grown on a variety of substrates. These thin-film oxide samples were intended to study the reduction of titanium oxide on length scales such that the recombination of hydrogen atoms (and the attendant finite depth-of-penetration described in Chapter 4) would not be a limiting factor in the extent of conversion.

9.1 Processing of Bulk Samples of Titanium Dioxide

The initial experiments on the reduction of titanium oxide were conducted with porous pellets of titanium dioxide. Photographs of two post-reaction pellets are presented in Figure 9.1, while X-ray diffraction plots of the surface regions of these pellets are presented in Figure 9.2. In both samples, the surface region is converted from the initial white color to a dark color. In the sample processed at low power for a shorter time, a gray region exists at the boundary between the unreacted interior and the dark surface region. In the sample processed at a higher power for a longer time, the gray region extends throughout the entirety of the sample, with no unreacted white region remaining. However, the thickness of the black surface region does not appear to increase appreciably in the higher-power sample. These results are similar to those reported by (Daniel Edward Bullard 1993). He asserted that the black surface region resulted from interactions with excited species from the plasma, while the grey region resulted from interactions solely with molecular hydrogen. This is consistent with the penetration depth model.
developed in Chapter 4: the plasma-affected region will not grow past the penetration depth, just as the black surface region does not increase in thickness even for longer reaction times. The gray layer, however, if it results from the reaction of TiO$_2$ with molecular hydrogen (possibly to form a non-stoichiometric titanium suboxide) can increase in thickness over longer reaction times, as this reaction should follow traditional (e.g., shrinking core) reaction kinetics.

Figure 9.1: Photographs of titanium dioxide pellets exposed to plasma reactor. Pictures on the left depict a pellet exposed to 600 watts of applied power at a pressure of 6.5 Torr of hydrogen for 30 minutes, while pictures on the right depict a pellet exposed to 1000 watts of applied power at a pressure of 6.5 Torr of hydrogen for one hour.

In Figure 9.2, it can be seen that the higher power/longer time sample has been partially reduced to Ti$_2$O$_3$. The diffraction pattern of the lower power/shorter time sample does not show
evidence of the formation of a new phase, despite the apparent change in its visual appearance. This would be consistent with the formation of a nonstoichiometric suboxide which maintains the same crystal structure as the original rutile.

Figure 9.2: Comparison X-Ray diffraction plot for bulk titania samples. The “low power” sample was exposed to 600 watts of applied power at a pressure of 6.5 Torr of hydrogen for 30 minutes, while the “high power sample” was exposed to 1000 watts of applied power at a pressure of 6.5 Torr of hydrogen for one hour. Note the presence of the Ti₂O₃ peaks (e.g., at 24°) only in the high-power sample.

In summary, the bulk oxide reduction experiments have shown the successful partial reduction of titanium dioxide to Ti₂O₃, reproducing the results of earlier researchers. The plasma-affected region is constrained to a thin surface region of the samples. Thus, subsequent experiments should be constrained to length scales shorter than the thickness of this penetration.
depth in order to properly elucidate the efficacy of atomic hydrogen as a reducing agent.

9.2 Processing of Thin Films of Titanium Dioxide: Glass Substrates

This section presents the results of an experiment performed on a titanium dioxide thin film prepared on a glass substrate from a sol-gel precursor. Figure 9.3 presents before and after images of the sample; the transparent region towards the bottom right of the slide was covered by tape during the sol-gel coating process. Clearly, the film has become darker. There is a gradient in the color change, with the darkest region occurring near the top of the slide. Due to the temperatures experienced by the sample, the substrate began to warp and deform; the largest degree of warping occurred at the top of the sample. This inhomogeneous warping may indicate that the sample did not experience uniform heating. Indeed, the top portion of the sample was

Figure 9.3: Photographs of thin films of titania grown on a glass substrate: unreacted (left) and post-reaction (right). This sample was processed with 200 W of applied power at a total pressure of 22 Torr, with a hydrogen flow rate of 1000 SCCM and an argon flow rate of 10 SCCM. The sample reached approximately 600 degrees Celsius during the course of the reaction.
closer to the highest-intensity section of the plasma.

A four-point probe was used to measure the sheet resistivity of the thin film layer. The sheet resistivity did vary along the sample, with the lowest resistivity being found at the top and the highest at the bottom; numerical values of these measurements are presented in Table 9.1. Both the darker color and the higher conductivity observed near the top of the sample are consistent with a greater degree of reduction having occurred there, likely resulting in the formation of a semiconducting titanium suboxide. The unreacted thin film and the uncoated glass slide both had resistances too large to quantify using the four-point probe.

<table>
<thead>
<tr>
<th>Approximate Distance from Sample Edge (top), mm</th>
<th>Sheet Resistance, Ω □⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>227</td>
</tr>
<tr>
<td>10</td>
<td>249</td>
</tr>
<tr>
<td>15</td>
<td>284</td>
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<td>20</td>
<td>398</td>
</tr>
<tr>
<td>25</td>
<td>742</td>
</tr>
<tr>
<td>30</td>
<td>5200</td>
</tr>
<tr>
<td>35</td>
<td>74700</td>
</tr>
</tbody>
</table>

In summary, the experiments conducted on titanium dioxide films on glass substrates substantiate the fact that some degree of reduction occurs within the plasma. They do not provide a direct measurement of that degree of reduction, but it might be possible to correlate the degree of oxygen removal with the increase in conductivity. Furthermore, the inhomogeneous nature of the reduction indicates that the plasma is not uniformly distributed within the reactor, and it has demonstrable variations in reducing power over length scales of a few centimeters.
9.3 Processing of Thin Films of Titanium Dioxide: Copper Substrates

This section presents the results from the experiments conducted on titanium oxide films grown on copper substrates by a sol-gel process. These results consist of photographs, micrographs, grazing-incidence X-Ray diffraction patterns, and X-Ray photoelectron spectra. Figure 9.4 presents photographs of a sample before and after processing in the hydrogen plasma. The unreacted sample appears smooth and uniform, with a slightly darker region where the film has been deposited. The reacted sample appears to have a rougher appearance, as well as a silver-colored coating over a portion of the sample. This silver-colored coating is observable on both sides of the copper substrate, despite the fact that only one side of the sample was coated with titanium oxide. Some macroscopic deformation of the substrate occurred during processing as well, likely due to softening at elevated temperatures.

Figure 9.4: Photographs of thin films of titania grown on a copper substrate: the thin-film side of the unreacted sample (left), the thin-film side of the post-reaction sample (center), and the “back” side of the post-reaction sample. The sample was processed with 200 W of applied power at a total pressure of 19 Torr, with a hydrogen flow rate of 1000 SCCM and an argon flow rate of 10 SCCM for a period of 20 minutes.

Figure 9.5 presents an optical micrograph of the titanium-oxide bearing surface, post-reaction. The thin film coating has achieved a crazed appearance, with a network of fine cracks.
spreading throughout the coating. It is postulated that these cracks formed due to a mismatch in the coefficients of thermal expansion of the copper substrate and the overlying film: as the temperature of the sample increased and it began to expand, the substrate expanded to a greater degree than the film, resulting in internal stresses and fracturing. It is worth noting that though the film is noticeably different in appearance on the microscale, the macroscopic sample still appears to be copper-colored. This implies that the film is mostly transparent/translucent.

Figure 9.5: Optical micrograph of thin film of titania grown on a copper substrate, post-reaction. The sample was processed with 200 W of applied power at a total pressure of 19 Torr, with flow rates of 1000 SCCM H\textsubscript{2} and 10 SCCM Ar for a period of 20 minutes.

Grazing-incidence X-ray diffraction was employed to investigate the crystalline phase of the thin-film coating: by using a small incident angle, this technique preferentially investigates
the near-surface region of the sample. However, due to the deformation of the sample—both on the macroscopic scale, and possible due to the microscopic crazing mentioned earlier—it was not possible to detect any phases other than that of the copper substrate; diffraction patterns evidencing this are presented in Figure 9.6. No peaks are identified other than those belonging to copper in either the before-reaction or after-reaction patterns. Though the before-reaction sample was uniform and flat, the sol-gel coating was likely amorphous to X-Rays since it was not

Figure 9.6: Comparison of X-Ray diffraction patterns of thin films of titania grown on a copper substrate: unreacted (front) and post-reaction (back). The post-reaction sample was processed with 200 W of applied power at a total pressure of 19 Torr, with a hydrogen flow rate of 1000 SCCM and an argon flow rate of 10 SCCM. The angle of incidence employed for the X-Ray measurements was $\omega = 0.5^\circ$. 
annealed prior to reaction. The post-reaction film, however, should be crystalline due to the elevated temperatures (in the range of 600 degrees Celsius) it experienced during the course of the reaction. Thus, the lack of signal from the surface region in the post-reaction sample likely results from non-uniformities in the sample geometry.

In order to determine the composition (and the state of reduction) of the film, X-Ray photoelectron spectroscopy was employed to characterize the surface region of the sample; survey scans of the unreacted and post-reaction sample are shown in Figure 9.7 and Figure 9.8.

![Figure 9.7: XPS spectrum of thin film of titania grown on a copper substrate, unreacted.](image)

The unreacted sample possesses an unsurprising spectrum, showing oxygen and titanium as well as copper from the underlying substrate. However, the spectrum of the post-reaction sample is surprising, as it shows no evidence of titanium. Instead, a large signal from silicon is detected. Given the previous evidence of the volatilization of silica from the reactor walls—observed in the course of this research as noted in Chapter 6, as well as by
Figure 9.8: XPS spectrum of thin film of TiO$_2$ grown on a Cu substrate, post-reaction. This sample was processed with 200 W at 19 Torr, under 1000 SCCM H$_2$ and 10 SCCM Ar.

(Daniel Edward Bullard 1993; McTaggart 1964)—in addition to the appearance of the silvery coating on both sides of the sample (i.e., even on the side which did not possess the titanium oxide thin film), it seems that this coating is composed of silica/silicon which has condensed after being volatilized from the reactor walls. By sputtering away some of this silicon-bearing coating, it is possible to investigate the oxidation state of titanium in the underlying film and to compare it to the oxidation state of titanium in the unreacted film. This comparison is presented in Figure 9.9.

There is not a significant difference between the two spectra in Figure 9.9 in terms of peak location: per (Moulder et al. 1992), fully reduced titanium has a Ti-2p$_{3/2}$ peak at 454.1 eV, while fully oxidized TiO$_2$ has a Ti-2p$_{3/2}$ peak at 458.8 eV. Neither spectra have a strong peak near 454 eV, though the post-reaction sample might have stronger intensity at lower binding
energies (intermediate between 454 eV and 459 eV), thereby indicating possible partial-reduction of the titanium species. That being said, the sputtering process employed to remove the silicon coating from the surface of the reacted sample may have preferentially sputtered oxygen from the sample, thereby inducing the partial reduction effect observed here. Given that oxygen is preferentially sputtered over titanium (Counsell et al. 2014), the fact that there is still only minor (if any) evidence of reduction post-sputtering means that the pre-sputtered state was minimally reduced (at best).
In summary, the experiments investigating the reduction of titania thin films on copper substrates have demonstrated no significant reduction in the hydrogen plasma. While the diagnostic efforts were hampered by the deposition of silica and the deformation of the sample, XPS analysis of the titanium film indicates that no appreciable reduction occurred. The confounding presence of volatile silicon-bearing species within the presence adds some complexity to the situation, but it appears that the hydrogen plasma (under the conditions investigated here) is incapable of reducing even very thin films of titanium oxide when they are on copper substrates.

9.4 Processing of Thin Films of Titanium Dioxide: Titanium Substrates

This section presents the results obtained in the course of the experiments on the reduction of titanium oxide films on titanium substrates. Photographs, micrographs, X-Ray diffraction patterns, and X-Ray photoelectron spectra are presented as means of characterizing the samples before and after reaction. The samples prepared and characterized here are similar to those investigated by (Sakamoto and Ishibe 1980), but this research performs a more-thorough characterization of the pre- and post-reaction samples, and also directly contrasts the reducing power of atomic and molecular hydrogen.

Figure 9.10 presents images of the samples. In the unreacted and the molecular-hydrogen-processed samples, a variety of color are visible, resulting from interference effects produced by the thin oxide film on the surface. Per (Sakamoto and Ishibe 1980), the second-order blue regions visible here should be approximately 180 nanometers thick, as calculated using the refractive index of TiO$_2$ and the interference conditions for the appropriate wavelength of light. The molecular-hydrogen-processed and unreacted samples appear to be quite similar in
Figure 9.10: Photographs of thin films of titania grown on titanium substrates: unreacted (left), processed using molecular hydrogen (center) and processed using atomic hydrogen (right). The molecular-hydrogen-processed-sample was reacted at 600 °C and a total pressure of 20 Torr, with a hydrogen flow rate of 600 SCCM and an argon flow rate of 10 SCCM, for a total reaction time of 30 minutes. The atomic-hydrogen-processed-sample was reacted at 200 W of applied power (producing a temperature of at most 619 °C), a total pressure of 18.3 Torr, a flow rates of 1000 SCCM H\textsubscript{2} and 10 SCCM, for a total reaction time of 20 minutes.

appearance, though the surface of the former does appear to be more uneven, with a slight scale appearing on the surface. It seems unlikely that this could be the silica-bearing coating discussed previously, as there was no evidence of volatilization of the quartz reactor wall during experiments with molecular hydrogen (i.e., silica coatings on the tube wall and dimpling/softening were only observed when the microwave plasma was employed).

The atomic-hydrogen-processed sample has a metallic luster and shows no colors; its surface is noticeably rougher, though. The absence of colors indicates that the titanium oxide film is no longer present. It is possible that the oxide film could have been sputtered away or volatilized within the plasma. However, given the fact that no volatilization of the titanium layer was evidenced in the copper experiments, it seems unlikely that titania could have volatilized from the titanium samples under the same conditions.
Figure 9.11 presents a collection of optical micrographs of the unreacted and molecular-hydrogen-processed samples. These images provide some clarity into the nature of the surface roughness apparent in the molecular-hydrogen-processed sample. It appears that another phase (the semi-transparent irregular shapes that appear to be on top of the regularly shaped background) has started to grow on the surface; examination of the higher-magnification image makes it appear as if the new phase is growing from the grain boundaries of the underlying sample.

Figure 9.12 presents a comparison of the diffraction patterns of the titanium oxide on titanium samples. The strongest rutile peak (at around 27°) is present in both the unreacted and molecular-hydrogen-processed samples. However, it is absent in the atomic-hydrogen-processed sample; this confirms that there is no longer rutile present. Furthermore, the increase in the intensity of the peak at about 35° from the atomic-hydrogen-reduced sample relative to the peak from the other two samples indicates that titanium hydride may have been formed at the surface of the sample, as this is the location of the strongest diffraction peak of titanium hydride.

X-Ray photoelectron spectroscopy confirms that the titanium species at the surface of the atomic-hydrogen-processed sample has been reduced relative to the titanium species in the other two samples, as shown in Figure 9.13. The atomic-hydrogen-processed peaks have been shifted to lower binding energies, indicative of the titanium atoms being more reduced in this sample. Admittedly, some ambiguity exists in the interpretation of this spectrum: it was necessary to sputter the silica-bearing coating from the surface, just as in the copper-substrate sample. It is possible that this sputtering went too far and is actually revealing the bulk of the sample. The X-Ray diffraction patterns and the photographs, however, were taken on the sample as-obtained from the plasma, so their validity is not compromised by the necessity of this sputtering process.
In summary, the investigation of the processing of titanium oxide films on titanium substrates have confirmed that a greater degree of reduction is achieved in samples processed with atomic hydrogen than in those processed with molecular hydrogen, with all other variables held constant (temperature, pressure, and gas flow rates). These experiments have also confirmed the production of volatile silica-bearing species (and the deposition of those species on solids within the plasma), as mentioned previously in the context of the experiments on copper.
Figure 9.12: Comparison of XRD patterns of thin films of TiO$_2$ grown on Ti substrates: unreacted (front), processed using molecular H$_2$ (center), and processed using atomic H (back). The molecular-hydrogen-processed-sample was reacted at 600 °C and a total pressure of 20 Torr, with a H$_2$ flow rate of 600 SCCM and an Ar flow rate of 10 SCCM, for a total reaction time of 30 minutes. The atomic-hydrogen-processed-sample was reacted at 200 W of applied power (producing a temperature of at most 619 °C), a total pressure of 18.3 Torr, a hydrogen flow rate of 1000 SCCM, and an argon flow rate of 10 SCCM, for a reaction time of 20 minutes. These measurements were conducted with an incident X-Ray angle of $\omega = 0.5^\circ$.

substrates. These experiments have extended the results of (Sakamoto and Ishibe 1980) by investigating the post-reaction samples more explicitly (i.e., these conclusions are supported by grazing-incidence X-Ray diffraction patterns and X-Ray photoelectron spectra, whereas the previous results were supported only by visual inspection) and by directly comparing this reduction process against that achievable with molecular hydrogen.
Figure 9.13: Comparison X-Ray photoelectron spectra of thin films of TiO$_2$ grown on Ti substrates: unreacted (bottom), processed using molecular H$_2$ (center), and processed using atomic H (top). The molecular-hydrogen-processed-sample was reacted at 600 °C and a total pressure of 20 Torr, with a H$_2$ flow rate of 600 SCCM and an Ar flow rate of 10 SCCM, for a total reaction time of 30 minutes. The atomic-hydrogen-processed-sample was reacted at 200 W of applied power (producing a temperature of at most 619 °C), a total pressure of 18.3 Torr, a hydrogen flow rate of 1000 SCCM, and an argon flow rate of 10 SCCM, for a total reaction time of 20 minutes. The atomic-hydrogen-processed sample was sputtered for 10.5 minutes at a 5kV accelerating voltage in order to remove the silica-surface layer.

9.5 Discussion and Summary

This chapter has investigated the reduction of titanium oxide in a variety of forms: as bulk samples, as thin films prepared by sol-gel processes on glass and copper substrates, and as thin films prepared by thermal oxidation on titanium substrates. In bulk samples, reduction was only achieved in a thin surface layer, as predicted by the penetration-depth model of Chapter 4; this reduction was also limited in extent (i.e., at most the samples were reduced to Ti$_2$O$_3$) The thin film samples on glass and copper substrates may have been partially reduced, but not to a
significant extent, despite the fact that the thickness of these films should have been small relative to the penetration depth. However, reduction to titanium hydride was achieved in the titanium oxide films grown on titanium substrates. This differential reduction behavior indicates that the substrate plays an essential role in the observed reduction process.

One possible explanation for that role is that the bulk of the titanium metal substrate acts as an oxygen sink: given the large solubility of oxygen in titanium—c.f., e.g., (Lefebvre and Baril 2018)—it is possible that the oxide anions in the surface oxide could have been oxidized (and the titanium cations reduced) such that the resulting neutral oxygen atoms could dissolve within the titanium lattice. This explanation could be feasible from the macroscopic perspective: a thermodynamic driving force could exist for the reduction of the surface oxide based on the overall reaction:

\[
\begin{align*}
\text{TiO}_2 &= \text{Ti} + 2\text{O} \text{(surface)}, \quad \Delta G_{\text{reduction}} \\
2\text{O} \text{(surface)} &= 2\text{O} \text{(bulk)}, \quad \Delta G_{\text{dissolution}}
\end{align*}
\]

provided that the sum \(\Delta G_{\text{reduction}} + \Delta G_{\text{dissolution}} = \Delta G_{\text{net}} < 0\). However, the specific reaction mechanism by which the initial reduction-oxidation reaction occurs is not clear.

Furthermore, given that the titanium oxide film was not removed when processed under identical conditions with molecular hydrogen, it seems that the substrate is not the only factor which influences the reaction. There is a synergistic effect which requires both the titanium substrate and the plasma in order to reduce the oxide: neither a titanium substrate alone nor the presence of the plasma alone is capable of reducing the oxide layer, as shown by the titanium substrate/molecular hydrogen experiment and the copper substrate/atomic hydrogen experiment. The nature of this synergistic interaction is as-yet unclear; a possible mechanistic explanation of this phenomenon will be discussed in Chapter 11.
CHAPTER 10

PROCESSING OF NEODYMIUM OXIDE: RESULTS AND DISCUSSION

This chapter presents the experimental results obtained during the investigation of the reduction of neodymium oxide in non-equilibrium hydrogen plasmas. Several forms of neodymium oxide were investigated, including pressed pellets of neodymium powder, as well as thin films of neodymium oxide grown on a variety of substrates, including neodymium metal and titanium metal. The extent of reduction was evaluated by means of visual inspection, X-Ray diffraction, and X-Ray photoelectron spectroscopy.

10.1 Processing of Bulk Samples of Neodymium Oxide

This section presents the results obtained during the investigation of the reduction of bulk samples of neodymium oxide. Figure 10.1 presents images of bulk neodymium oxide pellets, before- and after-reaction with atomic hydrogen. The pre-reaction sample is the pale-blue color characteristic of neodymium oxide. The post-reaction sample shows some evidence of change, with the development of a dark gray color on the surface of the sample. Once again, this reduced layer is constrained to a thin region, presumably determined by the penetration depth of atomic hydrogen within the sample. This is consistent with the partial reduction of the surface region, given that the non-stoichiometric rare-earth oxides are often darkly colored per (Adachi, Imanaka, and Kang 2006) whereas the stoichiometric oxides are generally light or pastel-colored. Heuristically, this coloration may occur due to the formation of color centers (Farbe centers) due to the oxygen vacancies which result from the partial reduction process: electrons trapped in these oxygen vacancies are effective absorbers of radiation, resulting in an apparent dark coloration.
In order to evaluate if a new phase was formed during the reduction process, X-Ray diffraction was performed on these bulk samples; the results of these measurements are presented in Figure 10.2. There is no evidence of reduction from the diffraction pattern. At least two possible explanations exist for the lack of change in crystal structure. First, that the reduced layer is too thin, such that the X-Rays penetrate deep into the sample relative to the thickness of the reduced layer, reporting only the signal from the underlying bulk (note that the measurements in Figure 10.2 were taken using a traditional goniometric arrangement, and were not conducted using grazing-incidence X-Rays). A second possibility is that only a partial reduction process has occurred, resulting in the formation of a sub-stoichiometric oxide. This nonstoichiometric oxide would have the same crystal structure as that of the original oxide, such that it would produce the same diffraction pattern.
In summary, the experiments on the reduction of bulk neodymium oxide samples show some visual evidence of a partial reduction. However, this reduction is constrained to a thin surface region, and likely resulted only in the formation of a nonstoichiometric suboxide.

10.2 Processing of Thin Films of Neodymium Oxide: Neodymium Substrates

This section presents the results obtained during the course of the experiments of the reduction of thin films of neodymium oxide on neodymium substrates (prepared by thermal oxidation). Given the limited depth of penetration observed in the bulk samples of neodymium oxide, the oxide layers considered in these experiments were intended to be thin relative to this depth. Photographs of the samples pre- and post-reaction are presented in Figure 10.3.
reaction sample, a series of colors can be observed on the surface of the sample. These result from the same interference effect described in the context of the titanium films prepared in Chapter 9. The film is approximately 240 nanometers thick in the blue region, as calculated using a refractive index of $n = 1.86$ for neodymium oxide, per (Fan et al. 2015). No colors are evident on the surface of the sample exposed to high-applied microwave powers: its surface is dark and reflective. The sample exposed to low microwave powers has developed an extremely irregular, darkly colored surface.

Figure 10.3: Photographs of thin films of neodymium oxide grown on neodymium substrates: unreacted (left), exposed to a high-power microwave plasma (center), and exposed to a low-power microwave plasma (right). The high-power sample was exposed to 600 watts of microwave power at a pressure of 6.5 Torr with a hydrogen flow rate of 70 SCCM and an argon flow rate of 10 SCCM for 60 minutes. The low-power sample was exposed to 100 watts of microwave power at a pressure of 20 Torr with a hydrogen flow rate of 700 SCCM and an argon flow rate of 10 SCCM for 30 minutes.

Due to the deformation of the underlying substrate, it is difficult to ascertain the fate of the thin film on the surface of the sample exposed to low applied powers. Furthermore, the deformation and decrepitation of the neodymium-substrate samples processed at low applied powers became more severe as time elapsed post-reaction; this continuing decrepitation process is depicted in Figure 10.4: the sample expands, flakes, and eventually becomes a coarse, ochre-colored powder. The deformation of the underlying neodymium substrate made it impossible to conduct grazing-incidence X-Ray diffraction on the post reaction samples, and the increased
surface area resulting from the decrepitation process likely resulted in oxidation of the substrate.

However, for a short period post-reaction (before decrepitation occurred), it was possible to conduct X-Ray diffraction on the samples; these results are presented in Figure 10.5.

![Figure 10.4: Photographs of plasma-processed Nd coupon, following increasing post-reaction periods: several minutes (left), several days (middle), and several months (right). The coupon was exposed to 100 W at 20 Torr under 700 SCCM H\(_2\) and 10 SCCM Ar for 30 minutes.](image)

The X-Ray patterns show that the decrepitated samples have been at least partially converted to neodymium hydride. This makes sense as a cause of the decrepitation since the molar volume of neodymium hydride is larger than that of neodymium metal by 19.9% according to (Warf and Korst 1956). Indeed, a hydrogen-assisted decrepitation process takes advantage of this volume expansion and is employed in the manufacture and recycling of neodymium-iron-boride magnets (Szymański et al. 2016). For the sample processed at high powers, however, the hydride phase was not formed. Rather, the surface region is composed at least primarily of neodymium oxide. The fact that the tendency to form the hydride decreases as the applied power (and consequently the temperature) of the sample increases makes sense heuristically, as the hydriding process is exothermic:

\[
\text{Nd} + \text{H}_2(\text{g}) = \text{NdH}_2, \quad \Delta H_{600^\circ\text{C}} = -50.176 \text{ kcal/mole}
\]

such that the reaction should have a lower affinity to proceed at increased temperatures.

Furthermore, in the context of Figure 4.8, it is clear that the neodymium oxide phase becomes
Figure 10.5: Comparison XRD patterns of thin films of Nd$_2$O$_3$ grown on Nd substrates: unreacted (front), exposed to a high-power plasma (center), and exposed to a low-power plasma (back). The high-power sample was exposed to 600 W at 6.5 Torr with a flow rate of 70 SCCM H$_2$ and 10 SCCM Ar for 60 minutes. The low-power sample was exposed to 100 watts of power at 20 Torr with flow rates of 700 SCCM H$_2$ and 10 SCCM Ar for 30 minutes.

stable in this system only at elevated temperatures. Unfortunately, no thermocouple data are available from this reduction experiment, but it is possible to estimate the temperatures it experienced using the results from Chapter 6. It is worth noting that the X-Ray diffraction patterns in Figure 10.5 are conducted using a traditional goniometric arrangement, such that they cannot detect the presence of the thin-film of neodymium oxide in the unreacted sample. Grazing incidence diffraction patterns of this unreacted sample are presented in Appendix D, Figures D-24 through D-26.
It is worth noting that molecular hydrogen is also capable of forming neodymium hydride from neodymium metal; an image of a partially-hydrided neodymium metal coupon is presented in Figure 10.6. The partial covering of the metal surface with dark blisters indicates the production of the hydride, though likely to a lesser extent than in the samples exposed to atomic hydrogen. In this case, however, the discrepancy in the extent of reaction may result from differences in the reaction temperature between the two samples. It is interesting that molecular hydrogen is capable of hydriding neodymium metal at these pressures, because examination of the neodymium-oxygen-molecular hydrogen phase diagram indicates that the water partial pressure within the reactor (based on the calculations from Chapter 6) is too high for this hydriding process to occur. Hence, it is postulated that the neodymium metal acts as a “self-getter”: the water within the reactor reacts with a (small) portion of the neodymium metal, forming neodymium oxide. This acts to lower the partial pressure of water vapor within the reactor to a point near the neodymium-neodymium hydride-neodymium oxide invariant (triple) point, at which point the hydriding reaction can continue to occur. The phase-stability diagram relevant to this analysis is presented in Figure 10.7.
In summary, the results from the experiments of the reduction of neodymium oxide thin films on neodymium substrates have indicated that the neodymium substrates react strongly to the plasma, resulting in the formation of neodymium hydride at low applied powers; even molecular hydrogen is capable of effecting this hydriding process. The decrepitation of the neodymium substrate renders accurate characterization of the thin-film on the surface impractical, such that the fate of the surface oxide (i.e., whether or not it was reduced during exposure to the plasma) is uncertain.

![Phase-stability diagram for the Nd-O-H system at 600 °C](image)

Figure 10.7: Phase-stability diagram for the Nd-O-H system at 600 °C, calculated using (Roine 2002). The red arrow depicts the change in conditions effected by the self-gettering effect of neodymium, allowing for the hydriding of neodymium by molecular hydrogen.

10.3 Processing of Thin Films of Neodymium Hydroxide: Neodymium Substrates

This section presents results obtained during the experiments on the processing of thin films of neodymium hydroxide in a non-equilibrium hydrogen plasma. This course of investigation was motivated by the difficulty in identifying the fate of the thin films discussed in
the previous section: those films were so thin that they were rendered unidentifiable by the decrepitation of the neodymium substrate. By choosing a slightly thicker film (one which was still thinner than the penetration depth), it was hoped that it would be possible to identify it post-reaction. Hence, it was decided to investigate the native oxidized film which grows naturally on neodymium metal exposed to the atmosphere. Photographs of the pre- and post-reaction samples are presented in Figure 10.8.

Figure 10.8: Photographs of native film of neodymium hydroxide on a neodymium substrate: unreacted (left) and post-reaction (right). The sample was processed with 100 W of applied power at a total pressure of 22 Torr, with a hydrogen flow rate of 1000 SCCM and an argon flow rate of 14 SCCM for a period of 25 minutes.

The surface of the pre-reaction sample is dark in color and dull in luster. The post-reaction sample, on the other hand, has a blue/gray surface (reminiscent of the pale-blue of neodymium oxide) which possesses a noticeably brighter luster. The post-reaction sample also shows evidence of the same decrepitation phenomena referenced earlier, as demonstrated by the expansion and cracking of the edges of the sample. To verify the identity of these phases, X-Ray
diffraction (in a traditional goniometric arrangement) was conducted; the results of these measurements of the pre- and post-reaction samples are presented in Figure 10.9.

![X-ray diffraction plots](image)

Figure 10.9: Comparison of X-Ray diffraction plots of native film of neodymium hydroxide on a neodymium substrate: unreacted (front) and post-reaction (back). The sample was processed with 100 W of applied power at a total pressure of 22 Torr, with a hydrogen flow rate of 1000 SCCM and an argon flow rate of 14 SCCM for a period of 25 minutes.

Figure 10.9 shows that the pre-reaction sample surface is covered with a native hydroxide, Nd(OH)₃. Following exposure to the plasma, however, the hydroxide is converted to neodymium oxide. This is consistent with the predictions of Figure 4.8, in which neodymium oxide is shown to be more stable than neodymium hydroxide at high temperatures and high water partial pressures. The fact that the surface of the sample is converted to neodymium oxide
while the substrate bulk decrepitates due to hydride formation is interesting: it suggests that even though the conditions are favorable for the formation of the hydride from the metal, the conversion of even relatively thin films of the hydroxide (and oxide) to the hydride is not favorable. This contrasts with the behavior of titanium, in which the presence of the metal substrate (acting as an oxygen sink) allows for the successful reduction of the surface oxide to form a hydride. Thus, even though neodymium has a larger affinity for oxygen than does titanium (as can be quantified by comparing the Gibbs free energy of oxidation for the two metals), neodymium is not able to remove the oxygen as effectively from oxide coatings. This difference in reduction behavior may result from the anomalously high solubility of oxygen in titanium.

In summary, the results obtained in the investigation of films of neodymium hydroxide have shown that hydrogen plasmas (under the conditions investigated here) are incapable of reducing even fairly thin coatings of neodymium oxide/hydroxide, even when in the presence of an effective oxygen getter such as neodymium metal.

10.4 Processing of Thin Films of Neodymium Oxide: Titanium Substrates

This section presents the results obtained in the course of investigations into the reduction of thin films of neodymium oxide prepared on the surface of titanium metal substrates. Given the somewhat surprising fact that titanium metal is able to aid in the reduction of its own surface oxide while neodymium is incapable of this feat, it was prudent to probe deeper into the ability of titanium to act as a reducing agent for other highly stable metal oxides. Hence, thin films of neodymium oxide were prepared on titanium by a sol-gel technique. These samples were exposed to molecular hydrogen or to atomic hydrogen and were subsequently characterized by means of X-Ray diffraction and X-Ray photoelectron spectroscopy.
Figure 10.10 presents images of the pre- and post-reaction samples. The pre-reaction samples are covered with a transparent yellow film; they are smooth and exhibit specular reflection. The post-reaction samples exhibit different appearances based on their method of treatment: samples treated with molecular hydrogen maintain the same yellow coloration, though their surface is no longer smooth and does not exhibit specular reflection. Samples treated with atomic hydrogen, on the other hand, show a dull grey surface with non-uniform blue coloration.
X-Ray diffraction patterns of the pre- and post-reaction samples are presented in Figure 10.11. As can be seen in this figure, neither the unreacted sample nor the sample treated with molecular hydrogen exhibit peaks below 35° or so. It is reasonable that the unreacted sample

Figure 10.11 Comparison of X-Ray diffraction patterns of thin neodymium oxide films grown on titanium substrates: unreacted sample (front), molecular-hydrogen-processed-sample (middle) and atomic-hydrogen-reduced-sample (back). The molecular-hydrogen-processed-sample was reacted at 600 °C and a total pressure of 22 Torr, with a hydrogen flow rate of 900 SCCM and an argon flow rate of 10 SCCM, for a total reaction time of 20 minutes. The atomic-hydrogen-processed-sample was reacted at 200 W of applied power (producing a temperature about 600 °C), a total pressure of 22 Torr, a hydrogen flow rate of 650 SCCM, and an argon flow rate of 10 SCCM, for a total reaction time of 21 minutes. These measurements were conducted with an incident X-Ray angle of ω = 2°.

would not show any peaks here (lacking even the primary neodymium oxide peak at 26.9°) because the unannealed sol-gel-prepared film is likely amorphous to X-Rays. However, it is slightly surprising that the molecular-hydrogen-reacted-sample does not exhibit any peaks in this
region, as one would expect the neodymium oxide film to crystallize when exposed to elevated temperatures, even if does not react chemically. Perhaps the irregularity in the sample surface has made it impossible to detect the phases located there (similar to the lack of signal observed in the diffraction patterns of the titanium-oxide-on-copper experiments) while the other peaks in the diffraction pattern result from the bulk titanium substrate.

The atomic-hydrogen processed sample exhibits a peak at approximately 28°. This is consistent with the presence of neodymium hydride, although there is a slight mismatch in the peak location; it is possible that this mismatch results from lattice strain between the film and the underlying substrate. As verification of the presence of a reduced neodymium species in the atomic-hydrogen-processed sample, X-Ray photoelectron spectra of these samples were collected; these are presented in Figure 10.12. Due to the relatively small difference between the peak location for oxidized and reduced neodymium species (982 eV for Nd₂O₃ and 980.8 eV for Nd), it is difficult to ascertain the oxidation state of the neodymium from these spectra. It may be possible to glean more information by fitting these curves to potential contributing peaks.

In summary, the experiments investigating the reduction of neodymium oxide films on titanium substrates have established different reduction behavior: the neodymium oxide processed with atomic hydrogen has been reduced to neodymium hydride, whereas the neodymium oxide processed with molecular hydrogen does not appear to have reacted. These conclusions are supported by visual inspection and X-Ray diffraction patterns. The X-Ray photoelectron spectra are not conclusive due to the similarity of the peak locations for oxidized and reduced neodymium oxide.
Figure 10.12 Comparison of X-Ray photoelectron spectra of thin neodymium oxide films grown on titanium substrates: unreacted sample (front), molecular-hydrogen-processed-sample (middle) and atomic-hydrogen-reduced-sample (back). The molecular-hydrogen-processed-sample was reacted at 600 °C and a total pressure of 22 Torr, with a hydrogen flow rate of 900 SCCM and an argon flow rate of 10 SCCM, for a total reaction time of 20 minutes. The atomic-hydrogen-processed-sample was reacted at 200 W of applied power (producing a temperature about 600 °C), a total pressure of 22 Torr, a hydrogen flow rate of 650 SCCM, and an argon flow rate of 10 SCCM, for a total reaction time of 21 minutes. The atomic-hydrogen-processed sample was sputtered at an accelerating voltage of 5 kV for a period of 2 minutes to remove the silica signal prior to acquisition of its spectra.

10.5 Discussion and Summary

This chapter has investigated the evolution of neodymium oxide in environments containing atomic hydrogen and in environments containing only molecular hydrogen. The bulk oxide samples may have been reduced to a nonstoichiometric suboxide in the near surface region; however, this conclusion is supported only by visual inspection. Neodymium oxide and hydroxide films on neodymium metal do not appear to be reduced by application of the hydrogen
plasma, though the neodymium metal substrates themselves do react to form neodymium hydride. When neodymium oxide films are grown on titanium substrates, however, it appears that the films are reduced to form neodymium hydride when exposed to atomic hydrogen; this reduction is not achieved when the films are exposed to molecular hydrogen.

Thus, the results from this chapter support the two findings of the titanium oxide investigations: first, that the hydrogen plasmas attainable in this research are not capable of reducing stable metal oxides outright (i.e., independent of substrate). However, there does appear to be a demonstrable advantage of atomic hydrogen over molecular hydrogen, as the use of titanium substrates does not guarantee the reduction of stable oxide films (i.e., independent of hydrogen dissociation). Possible explanations for this phenomenon are discussed in Chapter 11.
CHAPTER 11

CONCLUSION

This chapter forms the final element of the dissertation. It contains a synthesis of a set of conclusions concerning the efficacy of atomic hydrogen in reducing metal oxides, as well as a high-level discussion of the practicality of employing atomic hydrogen as a reducing agent on an industrial scale. Limitations of this work are itemized as are sources of error. A list of the contributions of this work to the fundamental knowledge-base is enumerated, and a set of recommendations for future work in the field are provided.

11.1 Synthesis and Conclusions

Given the results presented earlier in this dissertation, atomic hydrogen does provide an advantage over molecular hydrogen in its ability to reduce refractory metal oxides. However, atomic hydrogen requires the presence of an appropriate substrate (e.g., titanium) for this advantage to be apparent. One possible explanation of this effect is provided by considering the relative kinetics of the desorption of water vapor from the surface with the kinetics of the reoxidation reaction. Reoxidation occurs when adsorbed water molecules—the products from the reaction between atomic hydrogen and the metal oxide—react with the resulting oxygen vacancies on the surface; this situation is depicted schematically in Figure 11.1. Intuitively, it makes sense that the desorption process should be slow relative to the reoxidation process, since the former must be an activated process while the latter might occur with a relatively small activation energy. If this is indeed an accurate characterization of the relative rates of the reoxidation and desorption phenomena, then it will not be possible to achieve the appreciable reduction of a refractory metal oxide: atomic hydrogen will successfully reduce the oxide, but it is impossible to remove the water molecules from the surface before they reoxidize it. If,
however, there is an oxygen sink accessible via a lower activation-energy route—e.g., surface diffusion to a coherently attached substrate which can function as an oxygen acceptor—then it is possible to achieve the net reduction of the surface oxide, at the cost of an increase in the oxygen content of the substrate.

Figure 11.1: Schematic of competing reoxidation, desorption, and dissolution phenomena.

This proposed mechanism adds the third option depicted in Figure 11.1: a rapid, surface diffusion of water vapor away from the surface oxide and concomitant dissociation/dissolution.

This mechanism is consistent with the experimental results: without atomic hydrogen, the surface oxide is unable to overcome the initial reduction step, but without an oxygen-acceptor-substrate, the oxide immediately reoxidizes. This accurately describes the observed phenomena.
in which both atomic hydrogen and a titanium substrate were required to achieve the net reduction of refractory metal oxides.

Re-visiting the outstanding questions identified in Chapter 2, it is possible to identify some of the major conclusions of this work. With regard to the ability of atomic hydrogen to increase the reduction kinetics of non-refractory metal oxides, the results from this work are unclear. It is possible that atomic hydrogen may be capable of achieving faster reaction kinetics than those attainable using molecular hydrogen. However, these improvements should only be quantifiable when the metal oxide samples have dimensions comparable to the recombination depth $\delta$. For the bulk copper oxide samples investigated in this work (the radii of which were presumably much greater than $\delta$), no kinetic improvements were apparent.

With regard to the ability of atomic hydrogen to reduce refractory metal oxides, the thermodynamic approach presented in Chapter 4 is unsatisfactory and is incapable of predicting which metal oxides can be *in general* reduced by atomic hydrogen. An extension of the kinetic approach sketched in Chapter 4 (incorporating the relative rates of reduction, reoxidation, and recombination) may be capable of analyzing the reducibility of refractory metal oxides. It is unlikely that atomic hydrogen will be capable of reducing refractory metal oxides to their respective metals on industrial scales: outside of niche applications (e.g., the semiconductor industry), it will not be possible to produce useful quantities of these metals because of the (proposed) reoxidation reaction.

With regard to the superficial nature of the reaction observed in refractory metal oxides exposed to atomic hydrogen, the heterogeneous recombination model presented in Chapter 4 and the existence of a finite penetration depth $\delta$ provide a satisfactory explanation of this phenomenon. The recombination model is more convincing than the explanation provided by
Bullard (water re-oxidation from underlying layers) or that provided by Sadedin (limited oxygen-vacancy mobility).

11.2 Limitations and Sources of Error

Clearly, this research was hampered in the range of environments it could investigate due to relatively large leaks into the reactor from the outside atmosphere. This limited the strength of the conclusions which could be drawn from the work, as the water partial pressure within the reactor could not be made arbitrarily small.

Furthermore, the conclusions regarding the advantages of atomic hydrogen over molecular hydrogen rest on the assertion that all other factors are being held constant between the two reactions. This means that accurate knowledge of the temperature of the sample throughout the course of the reaction is essential. The use of a single thermocouple resting against/inside the samples as an accurate representation of the sample temperature thus introduces the possibility for serious errors: if the thermocouple moves during the course of the reaction, or appreciable temperature gradients exist within the sample, the temperature distribution of two nominally identical trials may be quite different in reality.

The thermogravimetric data were also plagued by large, seemingly-random perturbations during some trials (visible in the extent-of-reaction traces in Appendix C). The source of this error has not been identified, but it may result from coupling between the sample and/or the support rod arrangement with the microwaves: any eddy currents that are induced in these portions of the reactor system could result in unintended forces being exerted on the sensitive analytical balance.

The samples employed in this research were relatively small and occasionally experienced deformation during the course of reaction. This led to poor quality data and a low
signal-to-noise ratio in some X-Ray diffraction patterns. Thus, superior sample preparation strategies (e.g., sputtering to produce single crystal films of defined orientations) and inert substrates (i.e., thicker metal substrates or alumina/sapphire ones) could allow for more insightful analysis, especially of the thin film samples.

11.3 Contributions to the Knowledge-Base

- Development of a mathematical model describing the transient evolution of the depth-of-reaction in metal oxide systems exposed to environments containing atomic hydrogen.
- Implementation and testing of a (hypothetical) equilibrium phase-stability-diagram-based approach for predicting the ability of atomic hydrogen to reduce a given metal oxide system.
- Spectroscopic characterization of a large-diameter Surfaguide-type discharge at moderate pressures.
- Identification of a viable alternative to Sabat et al.’s explanation for the sigmoidal extent-of-reaction curves observed in the reduction of cupric oxide by atomic hydrogen.
- Distinguishing the utility of small-length-scale (e.g., thin-film) samples as a means of decoupling the effects of limited penetration depth from other restrictions on the ability of atomic hydrogen to reduce metal oxides.
- Elucidation of the results of previous researchers, especially with regard to the reduction of titanium thin films on titanium substrates (as studied by Sakamoto and Ishibe), and the sudden discontinuity in reduction kinetics reported by Sadedin et al.
11.4 Recommendations for Future Work

While this work has taken a fundamentals-based approach to understanding the ability of atomic hydrogen to reduce metal oxide systems, there are a number of opportunities for future research. These include:

- Implementation of an ultra-high vacuum system to eliminate the confounding effect of atmospheric leaks.
- Implementation of an alternative reactor material (e.g., alumina) instead of silica, to avoid the confounding effects of the volatile silica-bearing species formed during the course of some reactions. While one attempt was made at using an alumina reactor tube, the tube quickly failed upon ignition of the plasma (from a hairline crack). Because alumina has a higher thermal expansion coefficient than silica, it will be necessary to be more conscientious about heating/cooling the system gradually.
- Investigation of isothermal reactions within the plasma reactor (i.e., avoiding the confounding effects of the transient heating phase which follows the initial ignition of the plasma).
- Experimental and computational characterization of the speciation of oxygen-bearing species (such as hydroxyl radicals and oxygen atoms) within the plasma.
- Verification of the coupled heat- and mass-transfer model for the bulk metal oxide samples by investigating other insightful systems (e.g., the only marginally exothermic reduction of nickel oxide).
• Improvement of the moving-boundary analysis for the transient evolution of the penetration depth to account for the effects of diffusion due to bulk flow, and extension of the model to more general geometries.

• Investigation of the reaction kinetics of atomic hydrogen and non-refractory metal oxides on small length scales—i.e., less than the penetration depth of atomic hydrogen. This could be accomplished using a continuous reaction system, such as a spouted or fluidized bed, such as those described by (Karches and Von Rohr 2001; Sathiyamoorthy 2010).

• Development of a true first-principles-based-model of the plasma reactor, à la (Hassouni et al. 1999).

• Accurate characterization of the thickness of the thin-film samples employed in this research via, e.g., ellipsometry or transmission electron microscopy. For that matter, the characterization of some of the post-reaction thin-film samples using transmission electron microscopy would also be beneficial.
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Warf, J.C., and W.L. Korst. 1956. “Studies of the Rare-Earth Hydrides.”


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APPENDIX A
DETAILS OF NUMERICAL SIMULATIONS

This appendix presents the Wolfram Mathematica 11.1 code for conducting the numerical simulations presented in Chapter 4 and in Chapter 7. The first notebook presents the code employed for the moving-boundary simulations, adapted from (Beltukov 2014). It employs a first-order finite difference method for the spatial domain. Per (Wolfram Research 2018), the time-stepping is conducted via “an LSODA approach, switching between a non-stiff Adams method and a stiff Gear backward differentiation formula method.”

\[
\begin{align*}
\frac{\partial \chi}{\partial \tau} &= \frac{\partial^2 \chi}{\partial \xi^2} + \xi \frac{\partial \chi}{\partial \xi} \frac{\partial \xi}{\partial \tau} - \lambda_1 \chi \\
\chi |_{\xi=0} &= 1 \\
\frac{\partial \chi}{\partial \xi} |_{\xi=1} &= \lambda_2 \zeta (\chi |_{\xi=1} - 1) \\
\frac{d\zeta}{dt} |_{\xi=1} &= -\gamma_1 \frac{\partial \chi}{\partial \xi} |_{\xi=1} \\
\zeta (r = 0) &= 0
\end{align*}
\]

\[
\begin{align*}
n &= 1000; \\
\delta \xi &= 1. / n; \\
\lambda_1 &= 10; \\
\lambda_2 &= 10; \\
\gamma_1 &= 0.1; \\
T &= 100000; \\
\beta &= .00001;
\end{align*}
\]

```
ClearAll[dv, \tau, \chi]
dv[v_List] := With[\{\xi = First[v], \chi = Rest[v]\},
With[\{d\xi = If[\chi[[-1]] > 0, (\chi[[-1]] - 0) \lambda_2 \gamma_1, 0], \xi = N@Range[n - 1] / n, 
d1 = ListCorrelate[\{-0.5, 0, 0.5\} / d\xi, \#] & \&, 
d2 = ListCorrelate[\{1, -2, 1\} / d\xi^2, \#] & \&, 
d0 = ListCorrelate[\{0, 1, 0\}, \#] & \}],
Prepend[d2[\#] / \xi^2 + \xi d\xi d1[\#] / \xi - \lambda_1 d\theta[\#] & \& \Join[\{1.\}, \chi, \{0 + d\xi / (\lambda_2 \gamma_1)\}, d\xi]\}],
\theta = 0.0001;
\theta = Prepend[ConstantArray[\theta., n - 1], \xi \theta];
sol = NDSolve[\{v'[\tau] = dv[v[\tau]], v[\theta] == \theta, v, \{\tau, \theta, T\}\}[[1, 1, 2]]];
```

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The following notebook presents the code employed for modelling the coupled heat- and mass-transfer model from Chapter 7. It employs the same LSODA approach described previously for the time-stepping.

```
Needs("DifferentialEquations'InterpolatingFunctionAnatomy");
values = InterpolatingFunctionValuesOnGrid@sol;
valu = Transpose@Join[{#, x[#, 1]} & /@ values, {0, 1}];
vals = InterpolatingFunctionValuesOnGrid[sol][[All, 1]];
ξ = Flatten@InterpolatingFunctionGrid@sol;
ε = Range[0., n] / n;
ξ = ListInterpolation[vals, t];
x[ξ] = ListInterpolation[valu, {ε, ξ}];
x = If[2 < ξ[ε], x[ξ, n2 / ξ[ε]], 0.1] &;
Show[{DensityPlot[x[ξ, ε, t, θ, 0, 10], FrameLabel -> {"t", "n"}],
Plot[x[ε], {ε, θ, T}, PlotStyle -> (Red, Dashed)]}]

Export["Moving_boundary_interface_xi_pt01.xls",
Join[Table[{ε, x[ε, 1, 1, 0.1]}, {ε, 1, 3000, 1}]]
Moving_boundary_interface_xi_pt01.xls

Export["Moving_boundary_trace_pt05.xls", Table[{ε, x[ε, 0.05, 1]}, {ε, 0, 2, 0.01}]]
Moving_boundary_trace_pt05.xls

sol =
NDSolve[{{ξ[ε, t] = Piecewise[{{-γ1
ξ[ε, t] (1 - ξ[ε, t])
0, ξ[ε, t] > 0.001}}],
σ[ε, t] = -λ1 (ξ[ε, t] - λ2 (σ[ε, t] - 1),
ξ[ε, 0] = 0.999, σ[ε, 0] = 1,
{ξ[ε, t], σ[ε, t]}, {ε, 0, 1000}] /.
{γ1 -> 0.001, λ1 -> 1000, λ2 -> 10};
{Plot[Evaluate[ξ[ε, t] / sol], {ε, 0, T}],
Plot[1 - (Evaluate[ξ[ε, t] / sol])^3, {ε, 0, T}, PlotRange -> All],
Plot[Evaluate[σ[ε, t] / sol], {ε, 0, T}]} /.
T -> 0.2

Export["Coupled_heat_mass_transport_lambda1_100.xls",
Table[{ε, Evaluate[1 - ξ[ε, t] / sol[[1]]], Evaluate[σ[ε, t] / sol[[1]]], {ε, 0, 400, 1}]]
Coupled_heat_mass_transport_lambda1_100.xls
```
APPENDIX B

DETAILS OF SPECTROSCOPIC MEASUREMENTS

This appendix presents the raw data gathered from the spectroscopic measurements of the plasma. By quantifying the relative intensity of the various line-emission peaks and using the actinometric techniques described in Chapter 4, this data made possible the quantification of the hydrogen dissociation presented in Chapter 6.

Figure B-1: Emission spectrum from plasma under 100 W of applied power at 5.8 Torr, with a hydrogen flow rate of 210 SCCM and an argon flow rate of 10 SCCM. Spectra was gathered through the open door of the furnace, directed at the location of highest plasma intensity.
Figure B-2: Emission spectrum from plasma under 100 W of applied power at 5.8 Torr, with a hydrogen flow rate of 210 SCCM and an argon flow rate of 10 SCCM. The spectrum was gathered from the first viewing port.

Figure B-3: Emission spectrum from plasma under 200 W of applied power at 5.8 Torr, with a hydrogen flow rate of 210 SCCM and an argon flow rate of 10 SCCM. The spectrum was gathered from the first viewing port.
Figure B-4: Emission spectrum from plasma under 200 W of applied power at 5.8 Torr, with a hydrogen flow rate of 210 SCCM and an argon flow rate of 10 SCCM. The spectrum was gathered from the furnace door.

Figure B-5: Emission spectrum from plasma under 200 W of applied power at 10 Torr, with a hydrogen flow rate of 210 SCCM and an argon flow rate of 10 SCCM. The spectrum was gathered from furnace door.
Figure B-6: Emission spectrum from plasma under 200 W of applied power at 20.7 Torr, with a hydrogen flow rate of 50 SCCM and hydrogen to argon partial pressure ratio of 21:1. The spectrum was gathered from the furnace door.

Figure B-7: Emission spectrum from plasma under 200 W of applied power at 20.7 Torr, with a hydrogen flow rate of 100 SCCM and hydrogen to argon partial pressure ratio of 21:1. The spectrum was gathered from the furnace door.
Figure B-8: Emission spectrum from plasma under 200 W of applied power at 20.7 Torr, with a hydrogen flow rate of 210 SCCM and an argon flow rate of 10 SCCM. The spectrum was gathered from the furnace door.

Figure B-9: Emission spectrum from plasma under 200 W of applied power at 20.7 Torr, with a hydrogen flow rate of 210 SCCM and an argon flow rate of 10 SCCM. The spectrum was gathered from the first viewing port.
Figure B-10: Emission spectrum from plasma under 200 W of applied power at 20.7 Torr, with a hydrogen flow rate of 300 SCCM and a hydrogen to argon partial pressure ratio of 21:1. The spectrum was gathered from the furnace door.

Figure B-11: Emission spectrum from plasma under 200 W of applied power at 20.7 Torr, with a hydrogen flow rate of 500 SCCM and a hydrogen to argon partial pressure ratio of 21:1. The spectrum was gathered from the furnace door.
Figure B-12: Emission spectrum from plasma under 200 W of applied power at 20.7 Torr, with a hydrogen flow rate of 900 SCCM and a hydrogen to argon partial pressure ratio of 21:1. Thus spectrum was gathered from the furnace door.

Figure B-13: Emission spectrum from plasma under 200 W of applied power at 30 Torr, with a hydrogen flow rate of 210 SCCM and an argon flow rate of 10 SCCM. The spectrum was gathered from the furnace door.
Figure B-14: Emission spectrum from plasma under 200 W of applied power at 40 Torr, with a hydrogen flow rate of 210 SCCM and an argon flow rate of 10 SCCM. The spectrum was gathered from the furnace door.

Figure B-15: Emission spectrum from plasma under 200 W of applied power at 50 Torr, with a hydrogen flow rate of 210 SCCM and an argon flow rate of 10 SCCM. The spectrum was gathered from the furnace door.
Figure B-16: Emission spectrum from plasma under 200 W of applied power at 60 Torr, with a hydrogen flow rate of 210 SCCM and an argon flow rate of 10 SCCM. The spectrum was gathered from the furnace door.

Figure B-17: Emission spectrum from plasma under 300 W of applied power at 5.8 Torr, with a hydrogen flow rate of 210 SCCM and an argon flow rate of 10 SCCM. The spectrum was gathered from the first viewing port.
Figure B-18: Emission spectrum from plasma under 100 W of applied power at 5.8 Torr, with a hydrogen flow rate of 210 SCCM and an argon flow rate of 10 SCCM. The spectrum was gathered from the furnace door.

Figure B-19: Emission spectrum from plasma under 400 W of applied power at 5.8 Torr, with a hydrogen flow rate of 210 SCCM and an argon flow rate of 10 SCCM. The spectrum was gathered from the first viewing port.
Figure B-20: Emission spectrum from plasma under 400 W of applied power at 5.8 Torr, with a hydrogen flow rate of 210 SCCM and an argon flow rate of 10 SCCM. The spectrum was gathered from the second viewing port.

Figure B-21: Emission spectrum from plasma under 500 W of applied power at 5.8 Torr, with a hydrogen flow rate of 210 SCCM and an argon flow rate of 10 SCCM. The spectrum was gathered from the first viewing port.
Figure B-22: Emission spectrum from plasma under 500 W of applied power at 5.8 Torr, with a hydrogen flow rate of 210 SCCM and an argon flow rate of 10 SCCM. The spectrum was gathered from the second viewing port.

Figure B-23: Emission spectrum from plasma under 600 W of applied power at 5.8 Torr, with a hydrogen flow rate of 210 SCCM and an argon flow rate of 10 SCCM. The spectrum was gathered from the second viewing port.
Figure B-24: Emission spectrum from plasma under 600 W of applied power at 5.8 Torr, with a hydrogen flow rate of 210 SCCM and an argon flow rate of 10 SCCM. The spectrum was gathered from the third viewing port.

Figure B-25: Emission spectrum from plasma under 600 W of applied power at 5.8 Torr, with a hydrogen flow rate of 210 SCCM and an argon flow rate of 10 SCCM. The spectrum was gathered from the fourth viewing port.
Figure B-26: Emission spectrum from plasma under 600 W of applied power at 5.8 Torr, with a hydrogen flow rate of 210 SCCM and an argon flow rate of 10 SCCM. The spectrum was gathered from the first viewing port.

Figure B-27: Emission spectrum from plasma under 700 W of applied power at 5.8 Torr, with a hydrogen flow rate of 210 SCCM and an argon flow rate of 10 SCCM. The spectrum was gathered from the first viewing port.
Figure B-28: Emission spectrum from plasma under 700 W of applied power at 5.8 Torr, with a hydrogen flow rate of 210 SCCM and an argon flow rate of 10 SCCM. The spectrum was gathered from the second viewing port.

Figure B-29: Emission spectrum from plasma under 700 W of applied power at 5.8 Torr, with a hydrogen flow rate of 210 SCCM and an argon flow rate of 10 SCCM. The spectrum was gathered from the third viewing port.
Figure B-30: Emission spectrum from plasma under 700 W of applied power at 5.8 Torr, with a hydrogen flow rate of 210 SCCM and an argon flow rate of 10 SCCM. The spectrum was gathered from the fourth viewing port.

Figure B-31: Emission spectrum from plasma under 800 W of applied power at 5.8 Torr, with a hydrogen flow rate of 210 SCCM and an argon flow rate of 10 SCCM. The spectrum was gathered from the first viewing port.
Figure B-32: Emission spectrum from plasma under 800 W of applied power at 5.8 Torr, with a hydrogen flow rate of 210 SCCM and an argon flow rate of 10 SCCM. The spectrum was gathered from the second viewing port.

Figure B-33: Emission spectrum from plasma under 800 W of applied power at 5.8 Torr, with a hydrogen flow rate of 210 SCCM and an argon flow rate of 10 SCCM. The spectrum was gathered from the third viewing port.
Figure B-34: Emission spectrum from plasma under 800 W of applied power at 5.8 Torr, with a hydrogen flow rate of 210 SCCM and an argon flow rate of 10 SCCM. The spectrum was gathered from the fourth viewing port.

Figure B-35: Emission spectrum from the Avalight HAL-CAL Mini calibration lamp; this measurement along with the NIST-traceable lamp irradiance data were used to determine the intensity correction coefficients for the spectrometer.
Figure B-36: Transfer function for converting count rate to energy flux (determined using calibration lamp).
APPENDIX C

DETAILS OF COPPER OXIDE REDUCTION EXPERIMENTS

This appendix contains the extent-of-reaction and temperature-trace curves for the experiments investigating the reduction of cupric oxide. The conditions employed for each experiment are described in the caption of the respective figure. The times for 95% reaction and 99% reaction are marked on the top axis of each graph, while the temperature at 99% reaction is marked on the right axis of each graph. It is worth noting that in Figure C-7, the mass data between zero and five minutes is interpolated. Also, the experiments depicted in Figures A-10, A-17, and A-24 exhibit unusual features (the lack of correspondence between the temperature and extent-of-reaction traces) which indicate that the data from these experiments may be suspect.

Figure C-1: CuO Reduction, 200 W, 5.8 Torr, 210 SCCM H₂, 10 SCCM Ar.
Figure C-2: CuO Reduction, 300 W, 5.8 Torr, 210 SCCM H\textsubscript{2}, 10 SCCM Ar.

Figure C-3: CuO Reduction, 400 W, 5.8 Torr, 210 SCCM H\textsubscript{2}, 10 SCCM Ar.
Figure C-4: CuO Reduction, 500 W, 5.8 Torr, 210 SCCM H₂, 10 SCCM Ar.

Figure C-5: CuO Reduction, 600 W, 5.8 Torr, 210 SCCM H₂, 10 SCCM Ar.
Figure C-6: CuO Reduction, 700 W, 5.8 Torr, 210 SCCM H$_2$, 10 SCCM Ar.

Figure C-7: CuO Reduction, 800 W, 5.8 Torr, 210 SCCM H$_2$, 10 SCCM Ar.
Figure C-8: CuO Reduction, 600 W, 10 Torr, 210 SCCM H\textsubscript{2}, 10 SCCM Ar.

Figure C-9: CuO Reduction, 600 W, 20 Torr, 210 SCCM H\textsubscript{2}, 10 SCCM Ar.
Figure C-10: CuO Reduction, 600 W, 30 Torr, 210 SCCM H\(_2\), 10 SCCM Ar.

Figure C-11: CuO Reduction, 600 W, 40 Torr, 210 SCCM H\(_2\), 10 SCCM Ar.
Figure C-12: CuO Reduction, 600 W, 50 Torr, 210 SCCM H\textsubscript{2}, 10 SCCM Ar.

Figure C-13: CuO Reduction, 600 W, 60 Torr, 210 SCCM H\textsubscript{2}, 10 SCCM Ar.
Figure C-14: CuO Reduction, 600 W, 24 Torr, 50 SCCM H₂, 2.4 SCCM Ar.

Figure C-15: CuO Reduction, 600 W, 23.9 Torr, 100 SCCM H₂, 4.8 SCCM Ar.
Figure C-16: CuO Reduction, 600 W, 23 Torr, 300 SCCM H₂, 14.3 SCCM Ar.

Figure C-17: CuO Reduction, 600 W, 24 Torr, 500 SCCM H₂, 23.8 SCCM Ar.
Figure C-18: CuO Reduction, 600 W, 24 Torr, 900 SCCM H₂, 42.9 SCCM Ar.

Figure C-19: CuO Reduction, 400° C, 6 Torr, 210 SCCM H₂, 10 SCCM Ar.
Figure C-20: CuO Reduction, 540° C Furnace, 6 Torr, 210 SCCM H₂, 10 SCCM Ar.

Figure C-21: CuO Reduction, 720° C Furnace, 6 Torr, 210 SCCM H₂, 10 SCCM Ar.
Figure C-22: CuO Reduction, 600 W, 5.8 Torr, 210 SCCM H₂, 10 SCCM Ar.

Figure C-23: CuO Reduction, 600 W, 5.8 Torr, 210 SCCM H₂, 10 SCCM Ar.
Figure C-24: CuO Reduction, 600 W, 5.8 Torr, 210 SCCM H\textsubscript{2}, 10 SCCM Ar.
APPENDIX D

X-RAY DIFFRACTION PATTERNS

This appendix presents the X-Ray diffraction patterns gathered during the course of this research. They are presented in the order in which the corresponding experiments were discussed in the text. Certain samples exhibit anomalous lines; e.g., the aluminum and iron-nickel lines visible in Figures D-2 and D-3 likely result from contamination which occurred during sample preparation (e.g., from the razor blade that was used to even the surface of the powder, and from the aluminum powder holder).

Figure D-1: X-ray diffraction pattern for surface region of molybdenum dioxide sample processed with up to 1100 watts of applied microwave power, at a total pressure of 6 Torr and under flow rates of 210 SCCM of hydrogen and 10 SCCM of argon. The Mo pattern is matched by ICSD 98-005-2267, while the MoO$_2$ pattern is matched by ICSD 98-008-0830.
Figure D-2: X-ray diffraction pattern for a (powdered) molybdenum dioxide sample processed using the furnace at a temperature of 700 °C, a total pressure of 6 Torr, and flow rates of 210 SCCM of hydrogen and 10 SCCM of argon. The Mo pattern is matched by ICSD 98-005-2267, the MoO$_2$ pattern is matched by ICDD 01-074-6246, the Fe$_{0.63}$Ni$_{0.37}$ pattern is matched by ICDD 04-018-7295, and the Al pattern is matched by ICDD 04-018-7295.

Figure D-3: X-ray diffraction pattern for unreacted molybdenum dioxide powder. The MoO$_2$ pattern is matched by ICDD 01-074-6246, the Fe$_{0.63}$Ni$_{0.37}$ pattern is matched by ICDD 04-018-7295, and the Al pattern is matched by ICDD 04-018-7295.
Figure D-4: X-ray diffraction pattern for unreacted bulk titania sample. The TiO$_2$ pattern is matched by ICDD 01-072-4820.

Figure D-5: X-ray diffraction pattern for the low-power treated bulk titania sample. The TiO$_2$ pattern is matched by ICDD 01-072-4820. This sample was processed Pictures on the left depict a pellet exposed to 600 watts of applied power at a pressure of 6.5 Torr of hydrogen for 30 minutes.
Figure D-6: X-ray diffraction pattern for high-power bulk titania sample. The TiO$_2$ pattern is matched by ICDD 01-072-4820, while the Ti$_2$O$_3$ pattern is matched by ICDD 04-005-4651. This sample was processed at 1000 watts of applied power at a pressure of 6.5 Torr of hydrogen for one hour.

Figure D-7: X-ray diffraction pattern for a thin film of titania grown on a copper substrate, unreacted. The Cu pattern is matched by ICDD 04-013-9963; the angle of incidence employed for the X-Ray measurements was $\omega = 5^\circ$. 

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Figure D-8: X-ray diffraction pattern for a thin film of titania grown on a copper substrate, unreacted. The Cu pattern is matched by ICDD 04-013-9963; the angle of incidence employed for the X-Ray measurements was $\omega = 2^\circ$.

Figure D-9: X-ray diffraction pattern for a thin film of titania grown on a copper substrate, unreacted. The Cu pattern is matched by ICDD 04-013-9963; the angle of incidence employed for the X-Ray measurements was $\omega = 0.5^\circ$. 
Figure D-10: X-ray diffraction pattern for a thin film of titania grown on a copper substrate, processed at 200 W, 19 Torr, 1000 SCCM hydrogen, and 10 SCCM argon for a period of 20 minutes. The Cu pattern is matched by ICDD 04-013-9963; the angle of incidence employed for the X-Ray measurements was $\omega = 5^\circ$.

Figure D-11: X-ray diffraction pattern for a thin film of titania grown on a copper substrate, processed at 200 W, 19 Torr, 1000 SCCM hydrogen, and 10 SCCM argon for a period of 20 minutes. The Cu pattern is matched by ICDD 04-013-9963; the angle of incidence employed for the X-Ray measurements was $\omega = 2^\circ$. 
Figure D-12: X-ray diffraction pattern for a thin film of titania grown on a copper substrate, processed at 200 W, 19 Torr, 1000 SCCM hydrogen, and 10 SCCM argon for a period of 20 minutes. The Cu pattern is matched by ICDD 04-013-9963; the angle of incidence employed for the X-Ray measurements was $\omega = 0.5^\circ$.

Figure D-13: X-ray diffraction pattern for a thin film of titania grown on a titanium substrate, unreacted. The TiO$_2$ pattern is matched by ICDD 04-008-7856, the Ti pattern is matched by ICDD 01-071-4632, and the Ti$_3$O pattern is matched by ICDD 04-005-4376; the angle of incidence employed for the X-Ray measurements was $\omega = 5^\circ$. 
Figure D-14: X-ray diffraction pattern for a thin film of titania grown on a titanium substrate, unreacted. The TiO$_2$ pattern is matched by ICDD 04-008-7856, the Ti pattern is matched by ICDD 01-077-3481, and the Ti$_3$O pattern is matched by ICDD 04-005-4376; the angle of incidence employed for the X-Ray measurements was $\omega = 2^\circ$.

Figure D-15: X-ray diffraction pattern for a thin film of titania grown on a titanium substrate, unreacted. The TiO$_2$ pattern is matched by ICDD 04-014-1641, the Ti pattern is matched by ICDD 01-077-3481, and the Ti$_2$O pattern is matched by ICDD 04-021-5544; the angle of incidence employed for the X-Ray measurements was $\omega = 0.5^\circ$. 277
Figure D-16: XRD pattern for a thin film of TiO$_2$ grown on a Ti substrate, exposed to H$_2$; the sample was reacted at 600 °C at 20 Torr, with 600 SCCM H$_2$ and 10 SCCM Ar for 30 minutes. Reference patterns: TiO$_2$/ICSD 98-020-0391; Ti/ICSD 98-005-2522; TiH$_2$/ICSD 98-016-4602; TiO$_{0.325}$/ICSD 98-002-4080; the angle of incidence for the measurement was $\omega = 5^\circ$.

Figure D-17: XRD pattern for a thin film of TiO$_2$ grown on a Ti substrate, exposed to H$_2$; the sample was reacted at 600 °C at 20 Torr, with 600 SCCM H$_2$ and 10 SCCM Ar for 30 minutes. Reference patterns: TiO$_2$/ICSD 98-020-0391; Ti/ICSD 98-005-2522; TiH$_2$/ICSD 98-016-4602; TiO$_{0.325}$/ICSD 98-002-4080; the angle of incidence for the measurement was $\omega = 2^\circ$. 
Figure D-18: XRD pattern for a thin film of TiO$_2$ grown on a Ti substrate, exposed to H$_2$; the sample was reacted at 600 °C at 20 Torr, with 600 SCCM H$_2$ and 10 SCCM Ar for 30 minutes. Reference patterns: TiO$_2$/ICSD 98-020-0391; Ti/ICSD 98-005-2522; TiH$_2$/ICSD 98-016-4602; TiO$_{0.325}$/ICSD 98-002-4080; the angle of incidence for the measurement was $\omega = 0.5^\circ$.

Figure D-19: XRD pattern for a thin film of TiO$_2$ grown on a Ti substrate, exposed to 200 W (a temperature of at most 619 °C) at 18.3 Torr with 1000 SCCM H$_2$ and 10 SCCM Ar for 20 minutes. Reference patterns: Ti/ICSD 98-005-2522; TiH$_2$/ICSD 98-016-4602; the angle of incidence employed for the X-Ray measurements was $\omega = 5^\circ$. 
Figure D-20: XRD pattern for a thin film of TiO$_2$ grown on a Ti substrate, exposed to 200 W (a temperature of at most 619 °C) at 18.3 Torr with 1000 SCCM H$_2$ and 10 SCCM Ar for 20 minutes. Reference patterns: Ti/ICSD 98-005-2522; TiH$_2$/ICSD 98-016-4602; the angle of incidence employed for the X-Ray measurements was $\omega = 2^\circ$.

Figure D-21: XRD pattern for a thin film of TiO$_2$ grown on a Ti substrate, exposed to 200 W (a temperature of at most 619 °C) at 18.3 Torr with 1000 SCCM H$_2$ and 10 SCCM Ar for 20 minutes. Reference patterns: Ti/ICSD 98-005-2522; TiH$_2$/ICSD 98-016-4602; the angle of incidence employed for the X-Ray measurements was $\omega = 0.5^\circ$. 

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Figure D-22: X-ray diffraction pattern for a bulk neodymium oxide pellet, unreacted. The neodymium oxide pattern is matched by ICDD 00-041-1089.

Figure D-23: X-ray diffraction pattern for a bulk neodymium oxide pellet, exposed to 1000 watts of applied power at a pressure of 15 Torr of hydrogen for 60 minutes. The neodymium oxide pattern is matched by ICDD 00-041-1089.
Figure D-24: X-Ray diffraction pattern for thin film of neodymium oxide on a neodymium substrate, unreacted. The Nd peaks are matched by ICDD 04-004-2603 while the Nd$_2$O$_3$ peaks are matched by ICDD 00-041-1089. The angle of incidence used for this measurement was $\omega = 5^\circ$.

Figure D-25: X-Ray diffraction pattern for thin film of neodymium oxide on a neodymium substrate, unreacted. The Nd peaks are matched by ICDD 04-004-2603 while the Nd$_2$O$_3$ peaks are matched by ICDD 00-041-1089. The angle of incidence used for this measurement was $\omega = 2^\circ$. 282
Figure D-26: X-Ray diffraction pattern for thin film of neodymium oxide on a neodymium substrate, unreacted. The Nd peaks are matched by ICDD 04-004-2603 while the Nd$_2$O$_3$ peaks are matched by ICDD 00-041-1089. The angle of incidence used for this measurement was $\omega = 0.5^\circ$.

Figure D-27: X-Ray diffraction pattern for thin film of neodymium oxide on a neodymium substrate, unreacted. The Nd peaks are matched by ICDD 04-004-2603; this measurement was conducted as a traditional goniometer scan with varying incident angle.
Figure D-28: X-Ray diffraction pattern for thin film of neodymium oxide on a neodymium substrate, exposed to 600 watts of microwave power at a pressure of 6.5 Torr with a hydrogen flow rate of 70 SCCM and an argon flow rate of 10 SCCM for 60 minutes. The Nd$_2$O$_3$ peaks are matched by ICDD 00-041-1089; this measurement was conducted as a goniometer scan.

Figure D-29: X-Ray diffraction pattern for thin film of neodymium oxide on a neodymium substrate, exposed to 100 watts of microwave power at a pressure of 20 Torr with a hydrogen flow rate of 700 SCCM and an argon flow rate of 10 SCCM for 30 minutes. The NdH$_2$ peaks are matched by ICDD 04-003-4822; this measurement was conducted as a goniometer scan.
Figure D-30: X-Ray diffraction pattern of the native film of neodymium hydroxide on a neodymium substrate, unreacted. The Nd(OH)$_3$ peaks are matched by ICDD 04-005-8595; this measurement was conducted as a goniometer scan.

Figure D-31: X-Ray diffraction pattern of the native film of neodymium hydroxide on a neodymium substrate, processed with 100 W of applied power at a total pressure of 22 Torr, with a hydrogen flow rate of 1000 SCCM and an argon flow rate of 14 SCCM for a period of 25 minutes. The Nd$_2$O$_3$ peaks are matched by ICDD 00-041-1089;
Figure D-32: X-ray diffraction pattern for a thin film of neodymium oxide grown on a titanium substrate, unreacted. The alternate Ti pattern is matched by ICSD 98-018-3409 and the Ti pattern is matched by ICSD 98-005-2522; the angle of incidence employed for the X-Ray measurements was $\omega = 5^\circ$.

Figure D-33: X-ray diffraction pattern for a thin film of neodymium oxide grown on a titanium substrate, unreacted. The TiH$_2$ pattern is matched by ICSD 98-016-4602, the TiO$_2$ pattern is matched by ICSD 98-020-0391, the alternate Ti pattern is matched by ICSD 98-018-3409 and the Ti pattern is matched by ICSD 98-005-2522; the angle of incidence employed for the X-Ray measurements was $\omega = 2^\circ$. 

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Figure D-34: X-ray diffraction pattern for a thin film of neodymium oxide grown on a titanium substrate, unreacted. The alternate Ti pattern is matched by ICSD 98-018-3409 and the Ti pattern is matched by ICSD 98-005-2522; the angle of incidence employed for the X-Ray measurements was $\omega = 0.5^\circ$.

Figure D-35: XRD pattern for a thin film of neodymium oxide grown on a titanium substrate, reacted with molecular hydrogen at 600 °C and a total pressure of 22 Torr, with a hydrogen flow rate of 900 SCCM and an argon flow rate of 10 SCCM, for a total reaction time of 20 minutes. Reference patterns: TiH$_2$/98-016-4602; TiO$_{0.325}$/98-002-4080; Ti/ 98-005-2522. The angle of incidence used for this measurement was $\omega = 5^\circ$. 
Figure D-36: XRD pattern for a thin film of Nd$_2$O$_3$ grown on a Ti substrate, reacted with H$_2$ at 600 °C and 22 Torr with flow rates of 900 SCCM of H$_2$ and 10 SCCM of Ar for a total reaction time of 20 minutes. Reference patterns: TiH$_2$/98-016-4602; TiO$_{0.325}$/98-002-4080; TiO$_2$/98-020-0391; Ti/ 98-005-2522. The angle of incidence for this measurement was $\omega = 2^\circ$.

Figure D-37: XRD pattern for a thin film of Nd$_2$O$_3$ grown on a Ti substrate, reacted with H$_2$ at 600 °C and 22 Torr with flow rates of 900 SCCM of H$_2$ and 10 SCCM of Ar for a total reaction time of 20 minutes. Reference patterns: TiH$_2$/98-016-4602; TiO$_{0.325}$/98-002-4080; TiO$_2$/98-020-0391; Ti/ 98-005-2522. The incident angle for this measurement was $\omega = 0.5^\circ$. 
Figure D-38: XRD pattern for a thin film of Nd$_2$O$_3$ grown on a Ti substrate, exposed to atomic H under 200 W of applied power at 22 Torr, with flow rates of 650 SCCM H$_2$ and 10 SCCM Ar for 21 minutes. Reference patterns: TiH$_2$/98-016-4602; SiO$_2$/01-073-3461; TiO$_2$/98-020-0391; Ti/ 98-005-2522. The incident angle for this measurement was $\omega = 5^\circ$.

Figure D-39: XRD pattern for a thin film of Nd$_2$O$_3$ grown on a Ti substrate, exposed to atomic H under 200 W of applied power at 22 Torr, with flow rates of 650 SCCM H$_2$ and 10 SCCM Ar for 21 minutes. Reference patterns: TiH$_2$/98-016-4602; SiO$_2$/01-073-3461; TiO$_2$/98-020-0391; Ti/ 98-005-2522. The incident angle for this measurement was $\omega = 2^\circ$. 

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Figure D-40: XRD pattern for a thin film of Nd₂O₃ grown on a Ti substrate, exposed to atomic H under 200 W of applied power at 22 Torr, with flow rates of 650 SCCM H₂ and 10 SCCM Ar for 21 minutes. Reference patterns: TiH₂/98-016-4602; SiO₂/01-073-3461; TiO₂/98-020-0391; Ti/ 98-005-2522. The incident angle for this measurement was \( \omega = 0.5^\circ \).