INFORMATION TO USERS

This reproduction was made from a copy of a document sent to us for microfilming. While the most advanced technology has been used to photograph and reproduce this document, the quality of the reproduction is heavily dependent upon the quality of the material submitted.

The following explanation of techniques is provided to help clarify markings or notations which may appear on this reproduction.

1. The sign or “target” for pages apparently lacking from the document photographed is “Missing Page(s)”. If it was possible to obtain the missing page(s) or section, they are spliced into the film along with adjacent pages. This may have necessitated cutting through an image and duplicating adjacent pages to assure complete continuity.

2. When an image on the film is obliterated with a round black mark, it is an indication of either blurred copy because of movement during exposure, duplicate copy, or copyrighted materials that should not have been filmed. For blurred pages, a good image of the page can be found in the adjacent frame. If copyrighted materials were deleted, a target note will appear listing the pages in the adjacent frame.

3. When a map, drawing or chart, etc., is part of the material being photographed, a definite method of “sectioning” the material has been followed. It is customary to begin filming at the upper left hand corner of a large sheet and to continue from left to right in equal sections with small overlaps. If necessary, sectioning is continued again–beginning below the first row and continuing on until complete.

4. For illustrations that cannot be satisfactorily reproduced by xerographic means, photographic prints can be purchased at additional cost and inserted into your xerographic copy. These prints are available upon request from the Dissertations Customer Services Department.

5. Some pages in any document may have indistinct print. In all cases the best available copy has been filmed.
GASEOUS CORROSION OF MAGNESIUM OXIDE IN HYDROGEN

The Ohio State University

University Microfilms International 300 N. Zeeb Road, Ann Arbor, MI 48106
PLEASE NOTE:

In all cases this material has been filmed in the best possible way from the available copy. Problems encountered with this document have been identified here with a check mark \( \checkmark \).

1. Glossy photographs or pages \( \checkmark \)
2. Colored illustrations, paper or print ______
3. Photographs with dark background \( \checkmark \)
4. Illustrations are poor copy ______
5. Pages with black marks, not original copy ______
6. Print shows through as there is text on both sides of page ______
7. Indistinct, broken or small print on several pages \( \checkmark \)
8. Print exceeds margin requirements ______
9. Tightly bound copy with print lost in spine ______
10. Computer printout pages with indistinct print ______
11. Page(s) __________ lacking when material received, and not available from school or author.
12. Page(s) ___36___ seem to be missing in numbering only as text follows.
13. Two pages numbered ______. Text follows.
14. Curling and wrinkled pages ______
15. Dissertation contains pages with print at a slant, filmed as received ______
16. Other__________________________________________________________________________

_____________________________________________________________________________

University
Microfilms
International
GASEOUS CORROSION OF MAGNESIUM OXIDE
IN HYDROGEN

DISSERTATION

Presented in Partial Fulfillment of the Requirements for
the Degree doctor of Philosophy in the Graduate School of
The Ohio State University

By
Veerabhadra Rao Bheemineni, B.Tech.

*****
The Ohio State University
1985

Reading Committee:
Prof. Dennis W. Readey
Assoc. Prof. Eric R. Kreidler
Assoc. Prof. Charles E. Semler

Approved By
Adviser
Department of
Ceramic Engineering
TO

My parents, who have endured so much
I would like to thank my academic adviser, Dr. Dennis W. Readey, for his invaluable guidance and the unending patience he has showed in guiding me. I would also like to thank the National Science Foundation for sponsoring the project, under which this work is done.

Thanks are also due to Dr. Charles E. Semler who has afforded me his experience and guidance during my first year at Ohio State.

I would like to take this opportunity to express my appreciation to my fellow graduate students, especially Ken Williams, Kris Liang and Bill Hong, for their help during the preparation of this volume.

Last, but not least, I would like to thank my roommate Sarat Edupuganti for his invaluable help and understanding. Thanks are also due to Jagannath Satyavolu with whom I have had many enlightening discussions.
VITA

November 4, 1955
Born - Sattenapalle, India.

June 1977
B.Tech., Ceramic Engineering, Banaras Hindu University.

Sept. 1978 - Jan. 1985
Research Associate,
Department of Ceramic Engineering
The Ohio State University

PUBLICATION


FIELD OF STUDY

Ceramic Engineering.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACKNOWLEDGEMENT</td>
<td>iii</td>
</tr>
<tr>
<td>VITA</td>
<td>iv</td>
</tr>
<tr>
<td>TABLE OF CONTENTS</td>
<td>v</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>viii</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>ix</td>
</tr>
<tr>
<td>1. INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>1.1 Refractory Corrosion</td>
<td>1</td>
</tr>
<tr>
<td>1.2 Kinetics</td>
<td>2</td>
</tr>
<tr>
<td>1.3 Objectives</td>
<td>4</td>
</tr>
<tr>
<td>2. LITERATURE SURVEY</td>
<td>5</td>
</tr>
<tr>
<td>2.1 Stability of Oxides</td>
<td>5</td>
</tr>
<tr>
<td>2.2 Kinetics and Mechanisms</td>
<td>6</td>
</tr>
<tr>
<td>2.2.1 Gas Solid Reactions</td>
<td>6</td>
</tr>
<tr>
<td>2.3 Surface Morphology</td>
<td>13</td>
</tr>
<tr>
<td>3. THEORY</td>
<td>15</td>
</tr>
<tr>
<td>3.1 Thermodynamic Considerations</td>
<td>15</td>
</tr>
<tr>
<td>3.2 Kinetics</td>
<td>19</td>
</tr>
<tr>
<td>3.2.1 Possible Mechanism</td>
<td>19</td>
</tr>
<tr>
<td>3.2.2 Gaseous Diffusion Control</td>
<td>20</td>
</tr>
<tr>
<td>3.3 Gaseous Diffusion Controlled Reduction</td>
<td>25</td>
</tr>
</tbody>
</table>
3.3.1 Influence of the Flow Conditions ..........25
3.3.2 Enthalpy and Free Energy of the Reaction ..28
3.3.3 Effect of Water Vapor on Reduction .............31
3.4 Microstructure ........................................33

4. EXPERIMENTAL METHOD .................................35
4.1 Sample Preparation .....................................35
4.1.1 Single Crystal Samples ..............................35
4.1.2 Polycrystalline Samples .........................37
4.2 Thermogravimetry ......................................38
4.3 Measurements ..........................................41
4.4 Optical and Scanning Electron Microscopy ........43

5. RESULTS AND DISCUSSION ..........................44
5.1 Results ...................................................44
5.1.1 Weight Loss Data ..................................44
5.1.2 Effect of Gas Flow Rate .............................49
5.1.3 Effect of Temperature ..............................49
5.1.4 Effect of Water Vapor Pressure ....................59
5.1.5 Surface Morphology of Reacted MgO ............59
   (i) Polycrystalline MgO ................................59
   (ii) Single Crystal MgO ................................67
5.2 Discussion of the Results ...........................88
5.2.1 Weight Loss Data .................................88
5.2.2 Effect of Gas Flow Rate ............................96
5.2.3 Effect of Temperature ..............................96

vi
5.2.4 Effect of Water Vapor Pressure ...............97
5.2.5 Morphology of Reduced MgO ..................111
   (i) Effect of Impurities ......................113
   (ii) Effect of Dislocations and Sub-grain
        Boundaries ...............................114
   (iii) Effect of Temperature Gradients
        in the Sample ...........................114
   (iv) Effect of Perturbations in the
        Boundary Layer ..........................120

6. CONCLUSIONS AND SUGGESTIONS FOR FURTHER RESEARCH ...122
   6.1 Conclusions ....................................122
   6.2 Suggestions for Further Research .............123

REFERENCES .........................................124
# LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Spectroscopic analysis of Type 1 and Type 2 single crystal magnesium oxide samples</td>
<td>36</td>
</tr>
<tr>
<td>2. Analysis of flux as a function of square root of gas gas velocity</td>
<td>51</td>
</tr>
<tr>
<td>3. Enthalpy data for single crystal magnesium oxide</td>
<td>57</td>
</tr>
<tr>
<td>4. Enthalpy data for polycrystalline magnesium oxide</td>
<td>58</td>
</tr>
<tr>
<td>5. Slopes of plots of flux versus measured water vapor pressure</td>
<td>61</td>
</tr>
<tr>
<td>6. Free energy values calculated by using Equation 35</td>
<td>63</td>
</tr>
<tr>
<td>7. Spectroscopic analysis of reacted magnesium oxide</td>
<td>81</td>
</tr>
<tr>
<td>8. X-ray diffraction pattern of Type 2 Magnesium oxide</td>
<td>83</td>
</tr>
<tr>
<td>9. Diffraction pattern of the residue left after the reduction of Type 1 magnesium oxide crystal</td>
<td>84</td>
</tr>
<tr>
<td>10. Diffraction pattern of the residue left after the reduction of Type 2 magnesium oxide crystal</td>
<td>85</td>
</tr>
<tr>
<td>11. Results of EDAX analysis on reduced single crystal magnesium oxide</td>
<td>87</td>
</tr>
<tr>
<td>12. Slopes of plots of flux versus equilibrium water vapor pressure for Type 1 plates and spheres of magnesium oxide</td>
<td>102</td>
</tr>
<tr>
<td>13. Slopes of plots of flux versus equilibrium water vapor pressure for Type 2 plates of magnesium oxide</td>
<td>103</td>
</tr>
<tr>
<td>14. Equilibrium constant obtained by fitting the data to Equation 42</td>
<td>107</td>
</tr>
<tr>
<td>15. Equilibrium constant obtained by fitting the data to Equation 43</td>
<td>108</td>
</tr>
</tbody>
</table>
Table

16. Results of the analysis of the data with Equation 46 ........................................112
<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Partial pressures of vapor species versus temperature</td>
<td>17</td>
</tr>
<tr>
<td>2.</td>
<td>Partial pressures of vapor species versus partial pressure of water vapor at 1800°K</td>
<td>18</td>
</tr>
<tr>
<td>3.</td>
<td>Concentration profiles for diffusion controlled and reaction controlled reduction</td>
<td>22</td>
</tr>
<tr>
<td>4.</td>
<td>Boundary layer for a flat plate in parallel flow</td>
<td>23</td>
</tr>
<tr>
<td>5.</td>
<td>Schematic of the experimental setup</td>
<td>39</td>
</tr>
<tr>
<td>6.</td>
<td>Weight loss data as a function of time and temperature for plates and spheres</td>
<td>45</td>
</tr>
<tr>
<td>7.</td>
<td>Weight loss data for spheres for large weight loss</td>
<td>46</td>
</tr>
<tr>
<td>8.</td>
<td>Weight loss data as a function of water vapor pressure</td>
<td>47</td>
</tr>
<tr>
<td>9.</td>
<td>Weight loss data as a function of flow rate of gas</td>
<td>48</td>
</tr>
<tr>
<td>10.</td>
<td>Effect of gas flow rate on the flux</td>
<td>50</td>
</tr>
<tr>
<td>11.</td>
<td>Effect of temperature on flux for spheres of Type 1 magnesium oxide</td>
<td>53</td>
</tr>
<tr>
<td>12.</td>
<td>Effect of temperature on flux for plates of Type 1 magnesium oxide</td>
<td>54</td>
</tr>
<tr>
<td>13.</td>
<td>Effect of temperature on flux for plates of Type 2 magnesium oxide</td>
<td>55</td>
</tr>
<tr>
<td>14.</td>
<td>Effect of temperature on flux for plates of polycrystalline magnesium oxide</td>
<td>56</td>
</tr>
<tr>
<td>15.</td>
<td>Plot of flux versus measured water vapor pressure</td>
<td>60</td>
</tr>
<tr>
<td>16.</td>
<td>Microstructure of unreacted polycrystalline MgO</td>
<td>65</td>
</tr>
<tr>
<td>17.</td>
<td>Microstructure of reacted polycrystalline specimen showing the fallout of the grains</td>
<td>66</td>
</tr>
<tr>
<td>18.</td>
<td>Microstructure of as cleaved single crystal MgO</td>
<td>68</td>
</tr>
</tbody>
</table>
Figure Page

19. Microstructure of reacted crystal of Type 1 magnesium oxide .................................................. 69

20. Microstructure of reacted crystal of Type 2 magnesium oxide .............................................. 70

21. Morphology of single crystal magnesium oxide cleaved after reaction .................................... 71

22. Morphology of single crystal MgO showing severe attack at the edge of the crystal ................. 72

23. Morphology of single crystal of Type 2 MgO reduced at 1450°C and -21°C dew point ................. 73

24. Morphology of single crystal of Type 1 MgO reduced at 1450°C and -21°C dew point ............... 76

25. Morphology of single crystal of Type 2 MgO reduced at 1450°C and +18°C dew point ............... 79

26. Morphology of single crystal of Type 1 MgO at 1500°C and +20°C dew point ......................... 80

27. Morphology of Type 1 MgO single crystal showing the areas analysed with EDAX .................. 86

28. The change in the morphology of the surface of MgO crystal with the progress of reduction ........ 89

29. The change in the morphology of the surface of MgO crystal with the progress of reduction ........ 91

30. Weight loss versus time curves for diffusion controlled and surface reaction controlled reactions .......................................................... 95

31. Plot of flux versus equilibrium water vapor pressure for plates and spheres of Type 1 MgO ....... 99

32. Plot of flux versus equilibrium water vapor pressure for plates of Type 2 MgO ..................... 100

33. Plot of flux versus equilibrium water vapor pressure for plates of Type 2 MgO below 1340°C ...... 104

34. Temperature profile through flowing gas, boundary layer and single crystal magnesium oxide .... 119
1. INTRODUCTION

1.1 Refractory Corrosion

The primary function of the class of ceramic materials known as refractories is to withstand high temperatures and to provide structural integrity in high temperature processes above the temperature range of metals. Many physical processes in metallurgical, ceramic and chemical industries require such high temperatures. The efficiency of these processes depends upon various factors, including: the maximum operating temperature, the time of uninterrupted operation between shut downs and the extent of contamination from the external agents. In all the cases the performance of the refractories plays an important role. For this reason it is extremely important to evaluate and understand the performance of refractory ceramics in conditions that simulate the use environments.

The primary reasons for the degradation of refractories at high temperatures are mechanical and thermal stresses and chemical degradation. In many instances the combination of high temperature and adverse chemical environment will markedly shorten the performance life of the refractory ceramics. For this reason, corrosion studies of
Refractories are used to generate valuable information pertinent to the design and performance of refractories.

The corrosion of refractories can be generally classified into the following groups:

(i) Gaseous (vapor) corrosion involving reaction(s) between solid material and one or more gaseous species.

(ii) Aqueous corrosion involving reaction(s) between solid material and aqueous chemical agents.

(iii) Liquid corrosion involving reactions between refractories and molten metals or slags.

Because the corrosion of refractories is a heterogenous process, involving mass transport, the diffusion of reactants and products plays an important role in the kinetics of the corrosion process.

1.2 Kinetics

The rate at which any process occurs depends on a number of pertinent variables. At any time there may be more than one path by which the process can be completed and commonly the contribution of one of the paths is larger by many orders of magnitude than that of any of the other paths available. The kinetics of the reaction, then, are dictated by the slowest step in this path. Some of these rate limiting steps may be:
a. Availability of the reactants, i.e. mass transfer of the slowest moving reactant species.

b. The reaction between the reactants and the products which may include more than one step.

c. Dissipation of the products from the reaction site to prevent the build up of the products.

d. Transfer of energy to and from the reaction site depending on whether the reaction is endothermic or exothermic.

In aqueous corrosion, which typically occurs at roughly room temperature, the reaction between the products and reactants is generally slower than the diffusion of reactants and products. However in liquid and gaseous corrosion, where there can be higher temperatures, the diffusion tends to be slower than the reaction making corrosion a diffusion controlled process.

A gas-solid system is ideal to study the corrosion phenomenon because (i) equilibrium thermodynamic data are available, (ii) mass transfer coefficients can be calculated with a reasonable degree of accuracy and (iii) if the products are gases the surface effects of the corrosion can be easily studied. It is also possible to obtain thermodynamic data for systems for which the data are not available. This knowledge would prove to be useful in areas of crystal growth from vapors, sintering and other solid-gas
systems. For these reasons, a gas-solid system, i.e. MgO-H$_2$, was chosen for study. Magnesium oxide is one of the major industrial refractory materials that is widely used worldwide.

1.3 Objectives

The purpose of the study is to determine whether the kinetics in the system MgO-H$_2$ are reaction controlled or diffusion controlled. The main variables in the study are temperature, gas flow conditions and water vapor content of the H$_2$ gas. Related thermodynamic properties, such as free energy of reaction and enthalpy of reaction, will be obtained in this study for comparison with the published values. The surface morphology of both single crystal and polycrystalline MgO will be studied for the complete range of reaction and corrosion conditions included in this study.
2. LITERATURE SURVEY

2.1 Stability of Oxides

The behaviour of ceramic materials in reducing environments was studied qualitatively by Ahmad(1) and Trostel(2) in the mid-sixties. Ahmad(1) analyzed the white whiskery wool deposited in the colder parts of an alundum tube after dry hydrogen had passed through the tube and found that the wool was essentially NaOH.H₂O. Ahmad concluded that Na₂O from the tube was being removed by reduction to Na vapor and that the temperature of the tube (1320°C) was not high enough to observe the reduction of MgO and SiO₂. Trostel(2) studied the stability of alumina and zirconia refractories at higher temperatures in hydrogen and concluded that the mechanism of weight loss was the reduction to volatile suboxides and metals by hydrogen. Trostel(2) had also studied the effect of the water vapor content of the hydrogen gas (dew point) and concluded that there exists a temperature dependent equilibrium dew point for each oxide. If the dew point of the gas is higher than the equilibrium dew point the oxide would be stable. The relative stability of different oxides in alumina refractories was in the increasing order Na₂O, SiO₂, MgO and
Al₂O₃. In zirconia refractories CaO was more stable, making the calcia-stabilized zirconia more desirable. The order of stability (in increasing order) in zirconia was 
SiO₂, TiO₂, ZrO₂, and CaO (2). Crowley (3) investigated the behaviour of silica refractories in hydrogen and observed loss in weight and strength of refractories containing free or combined silica above 1200°C.

2.2 Kinetics and Mechanisms

Systematic acquisition of data and its analysis with an appropriate model is necessary to understand the kinetics and mechanisms of the process in question. Sharp, Brindly and Achar (14) summarized the equations commonly used to analyze solid state reaction kinetics. The equations relate a function of the fraction of the material reacted to time. The proportionality constant in these equations is the reaction rate constant. An Arrhenius plot of the reaction rate constant would give the activation energy. The function of the fraction reacted reflects the geometry of the models and the kinetics.

2.2.1 Gas Solid Reactions

Investigations have been made in a number of systems to determine the kinetics and mechanisms involved (4, 5, 7, 8, 11, 12, 13, 15-18).

Kinetics of vaporization of Cr₂O₃ in oxidizing environments was studied by Graham and Davis (15). The data
showed that the vaporization of Cr$_2$O$_3$ occurs by the
formation of volatile CrO$_3$ and that the rate of vaporization
was controlled by the diffusion of the product through the
stagnant boundary layer surrounding the Cr$_2$O$_3$ pellets.

The studies done on the reduction of hematite spheres in
hydrogen were summarized by Spitzer, Manning and Philbrook
(17) and as pointed out in that paper the conclusions of
different investigators vary widely. Spitzer et al.
developed a model taking into account the resistance of the
gaseous boundary layer to diffusion, the resistance of the
porous iron layer to diffusion and finally the resistance
offered by the interface reaction. In the case of dominant
interface reaction control the model predicts a constant
interface velocity. In other cases the interface velocity
would be a function of the radius of the core. Spitzer et
al. also noted that in the cases of mixed control, the
variation in the interface velocity would be small and
practically constant. Therefore a reaction yielding a
constant interface velocity (referred to as the phase
boundary-controlled reaction by Sharp et al. (14) ) is not
necessarily being controlled by an interface reaction. To
explain the effect of hydrogen pressure and particle size on
the reduction rate it was necessary to assume that the
reduction was under mixed control (17). The surface
reaction itself seemed to be controlled by the chemisorption
of water vapor. Allender and De Jonghe (18) in their study
of the hydrogen reduction of Ni(Al,Fe)$_2$O$_4$ measured the time dependence of the growth of the product layer and found that the rate of growth of the layer was constant. They also calculated the relative control exerted by both the surface reaction and diffusion through the porous product layer and found that the relative control of diffusion increased with increasing temperature. They concluded that the reaction was mainly under interface reaction control when the thickness of the product layer was small and diffusion controlled the process when the product layer thickness was large. Turkdogan and Vinters (16) on the other hand concluded that gas diffusion through the porous iron layer plays the dominant role in the reduction of hematite by hydrogen.

Crowley (4) made a more thorough study of the reduction of silica (in hydrogen) by studying the effect of temperature, pressure, dew point and gas flow rate. He concluded that the reaction is mass transfer controlled because the hydrogen flow rate and pressure individually had greater effects on the rate of weight loss than the did the temperature. Crowley reasoned that if the interfacial reaction kinetics were the dominant factor, the temperature would have much more effect than either the flow rate or pressure. The effect of water vapor was to retard but not completely stop the reaction. The plots of log percent weight loss versus temperature were linear except for the
change in the slope at about 1000°C. The weight loss above 1000°C was thought to be due to the reduction of silica, whereas the weight loss below 1000°C was due to the reduction of other oxides in the silica bricks.

Readey and Kuczynski (5) studied the sublimation of single-crystal Al$_2$O$_3$ spheres and plates in dry hydrogen by monitoring the dimensions of the samples. Their data indicated that the reduction of alumina occurs by the formation of volatile A10. The controlling step of the reaction was determined to be the diffusion of gaseous products through a stagnant boundary layer as described by Langmuir (6).

Schwerdtfeger (7) made a detailed study of silica reduction in reducing gases (hydrogen and CO-CO$_2$ mixtures) by monitoring the weight of the silica spheres and analyzed his data assuming that the reaction was diffusion controlled. Although the fit between the data and the theory was reasonable, the measured rates were less than the predicted rates by a factor of two. The discrepancy was thought to be due to the assumptions made in the theory about the diffusion coefficients and to the use of inaccurate thermodynamic data. The discrepancy may also have been caused because the analysis ignored the change in the radii of the silica spheres with time. The data for the reduction in CO-CO$_2$ mixtures did not fit the diffusion controlled model and the mechanism in this case was thought
to be a surface reaction.

Gardner (8) studied the kinetics of silica reduction in hydrogen by monitoring the weight of silica rods, tubes and high purity quartz powder with a microbalance in flowing hydrogen. Gardner analyzed his data with the generalized equation for solid state reaction kinetics as prescribed by Hancock and Sharp (9). Following this scheme Gardner plotted \(-\ln(\ln(1-x))\) versus \(\ln(\text{time})\). The \(x\) in the expression was the fraction of the sample reacted. The slope of the plots were indicative of the mechanism of the reaction. Gardner’s data gave a slope of about 1.0 indicating that the reduction process is phase boundary controlled. The activation energy obtained by plotting \(\ln(\text{reaction rate})\) versus inverse temperature was 85 Kcal/mole (357 KJ/mole) in dry hydrogen and was 135 Kcal/mole (567 KJ/mole) in water saturated (dew point 24°C) hydrogen. The value of 135 Kcal/mole (567 KJ/mole) is close to the heat of reaction (about 125 Kcal/mole or 525 KJ/mole) assuming that the volatile suboxide is SiO (10). In any case, Gardner concluded that a slow surface reaction is rate controlling and that the difference in activation energies in wet and dry hydrogen atmospheres was due to the formation of Si-OH groups on the surface of the sample, lowering the number of sites available for hydrogen adsorption. It is hard to substantiate the conclusion about the mechanism because the fact that the interface moves at
a constant velocity does not necessarily mean that the reduction is being controlled by an interface reaction (17). More useful and firm conclusions could have been drawn had the data been analyzed with Langmuir's model of evaporating spheres (6,5).

Recently Tso and Pask (11, 12) studied the reaction of fused silica (11), silicate glasses and mullite (12) with hydrogen gas. The data for the fused silica showed dependency on the hydrogen gas flow rate at lower flow rates and leveled off at higher flow rates. Because the reduction rates leveled off at higher gas flow rates, the reduction was deemed not to be controlled by diffusion of the products or the reactants. The apparent activation energy in the temperature range 1200°C was 82 Kcal/mole (344.4 KJ/mole) which is almost identical to that obtained by Gardner for the activation energy of reduction of silica in dry hydrogen (8). Tso and Pask (11) also found that the reaction rate was directly proportional to the partial pressure of hydrogen and concluded that the adsorption of hydrogen was not the slowest step in the reduction. The likely candidate was thought to be either some surface reaction step or desorption of the products. The study of the reduction of silicate glasses and mullite by Tso and Pask (12) showed that aluminosilicate glasses and mullite were more resistant to reduction. The apparent activation energies for reduction in dry hydrogen were 85.7 Kcal/mole.
(360 KJ/mole) and 93 Kcal/mole (390.6 KJ/mole) for aluminosilicate glasses and mullite respectively. From the high alumina content of the porous reaction zone it was evident that alumina is highly resistant to reduction by hydrogen in the temperature range 1300°C to 1500°C.

In a study of the reduction of silica and mullite in hydrogen by Chen(13), the results indicated a diffusion controlled process. The rate of the reaction was proportional to the square root of the velocity as, expected for a diffusion controlled process. The activation energy for the reduction of silica, which according to Chen is also the standard enthalpy of the reaction, was 135 Kcal/mole (567 KJ/mole) and comparable to the data from the JANAF tables (125 Kcal/mole or 525 KJ/mole). Similarly the activation energy of 238 Kcal/mole (999.6 KJ/mole) for the reduction of mullite was reasonably close to the standard enthalpy of the reaction of 254 Kcal/mole (1066.8 KJ/mole). The porous reaction layer (of the reduction of mullite) contained no silica but alumina.

Cheng and Cutler (19) studied the vaporization of silica disks in steam and attributed it to formation of gaseous Si(OH)₄. The data showed that the steam flow rate had no effect on the vaporization and the rate of weight loss varied essentially linearly with steam pressure, suggesting that the vaporization is controlled by surface reaction. The activation energy for the process was found to be 25
Kcal/mole (105 KJ/mole).

2.3 Surface Morphology

The microstructure of the product layer from a solid-gas reaction has been studied in connection with corrosion of ceramic materials in reducing environments (12,16,18). Most often the product layer has a porous microstructure with its pore structure changing with the temperature of the reaction (16,18). The reduction of silicate glasses in hydrogen (12) leaves a layer of alpha-alumina. Allender and De Jonghe (18) observed preferential reduction at grain boundaries in the reduction of Ni(Al,Fe)$_2$O$_4$. This was thought to be the result of the buildup of the less reducible ion (Al$^{3+}$) ahead of the advancing reaction interface. It was thought that the extent of this chemical polarization depended on the relative magnitudes of the interface velocity and the solid-state diffusion rates.

The surface of a solid that is reacting with a gas and producing only gas phase products, is expected to be relatively smooth except for preferred attack at dislocations and high index planes (5). Dome shaped grains were found on the surface of quartz (recrystallized to cristobalite at the reaction temperature) reduced in hydrogen (8). This microstructure was thought to the result of the preferential attack of hydrogen at the grain boundaries. The surface of fused silica reacted with
hydrogen was covered with pin-holes which appeared in the early stages of the reaction and grew deeper (11,13). The surface was also covered with a network of cells (13). Tso and Pask (11) explained the pin-holes assuming that heat transfer by radiation heats the sample and the hydrogen gas was at a lower temperature. The interior of the sample would then be hotter than the surface making the reaction favorable at the apex of the pin-hole. No such morphology was however observed in hydrogen containing large amounts of water vapor (13). Chen (13) assumed that the cell structure (on the surface of the reduced silica) was formed by the alumina impurity which is more resistant to reduction by hydrogen. Thermal and mechanical history of the surface was not the cause of the surface morphology because samples with different surfaces gave similar morphology. Formation and growth of rectangular holes on the surface of silver cyanamide decomposing in air was observed by Montagu-Pollock (20). A majority of the holes were associated with silver specks and a few of the holes observed did not need silver specks to form and grow. No satisfactory explanation was found for the presence of the holes.
3.1 Thermodynamic Considerations

In any chemical process there are a number of reactions involved. If the reactions occur simultaneously (in parallel), the reaction that is fastest controls the kinetics of the process. On the other hand if the reactions occur consecutively (in series), the reaction that is slowest dictates the kinetics of the process.

The possible reactions in the reduction of magnesium oxide are:

\[ \text{MgO} + \text{H}_2(g) \rightarrow \text{Mg}(g) + \text{H}_2\text{O}(g) \]
\[ \text{H}_2(g) = 2\text{MgOH}(g) \]  

\[ K_1 = \frac{p^*_{\text{Mg}} \cdot p^*_\text{H}_2\text{O}}{p^*_\text{H}_2 \cdot a^*_{\text{MgO}}} \]  

\[ 2\text{MgOH}_2(g) = \text{Mg(OH)}_2(g) + \text{Mg}(g) \]

\[ K_2 = \frac{p^*_{\text{Mg(OH)}_2} \cdot p^*_{\text{Mg}}}{p^*_\text{H}_2 \cdot a^2_{\text{MgO}}} \]  

\[ 2\text{MgO} + \text{H}_2(g) = 2\text{MgOH}(g) \]
\[ K_3 = \frac{(p^*_{\text{MgOH}})^2}{p^*_{\text{H}_2} \cdot a^2_{\text{MgO}}} \] (6)

where the superscript * represents equilibrium partial pressures.

\( K_1, K_2 \) and \( K_3 \) are equilibrium constants for Reactions 1, 3 and 5 respectively.

From the available thermodynamic data (10) the vapor pressures of all the products in the above reactions have been calculated and plotted against temperature in Figure 1. In making these calculations it has been assumed that the partial pressure of hydrogen was 1.0 atmosphere and the activity of MgO was 1.0. The calculations have been done for two cases: (i) the partial pressure of water vapor is equal to that of Mg vapor, i.e. the ambient atmosphere has no water vapor; (ii) the partial pressure of water vapor is 10^{-2} atm. As can be seen from the figure the partial pressure of Mg vapor from Reaction 1 is greater than that of Mg(OH)\(_2\) from Reaction 3 and that of MgOH from Reaction 5 by at least two orders of magnitude throughout the temperature range considered for both cases. Figure 2 shows the dependence of the partial pressures of Mg, MgOH and Mg(OH)\(_2\) vapors on the partial pressure of water vapor at 1800\(^\circ\)K. The plot clearly shows that the vapor pressure of Mg is higher than the vapor pressures of Mg(OH)\(_2\) and MgOH throughout the
Figure 1. Effect of temperature on equilibrium vapor pressures of Mg, MgOH and Mg(OH)$_2$. 
Figure 2. Effect of water vapor on the equilibrium vapor pressures of Mg, MgOH and Mg(OH)$_2$.
range of the water vapor pressures considered. The vapor pressure of Mg(OH)$_2$ and that of the water vapor are related through the equation:

$$\text{MgO} + \text{H}_2\text{O}(g) = \text{Mg(OH)}_2(g)$$  \hspace{1cm} (7)

$$K_4 = \frac{P^{*}\text{Mg(OH)}_2}{P^{*}\text{H}_2\text{O} \cdot a\text{MgO}}$$  \hspace{1cm} (8)

From the above thermodynamic data it is clear that the reaction described by Equation 1 is the most favorable reaction in the reduction of MgO in the presence of hydrogen.

3.2 Kinetics

3.2.1 Possible Mechanism

In the reactions between solids and gases the rates can be controlled by one of the following steps.

a. Mass transfer through the boundary layer next to the solid surface.

b. Heat transfer through the boundary layer.

c. Adsorption of the reactants on to the solid surface.

d. Surface diffusion of the adsorbed reactants or products to the reaction site.

e. Reaction at the reaction site.

f. Desorption of the reactants from the solid surface.
If the rate of the reaction is controlled by (a) the reaction is diffusion controlled and if the rate is controlled by (c) - (f) the reaction is surface reaction controlled.

3.2.2 Gaseous Diffusion Control

The rate of mass transfer of a diffusing species is given by Fick's first law:

\[ J_i = \frac{1}{A} \cdot \frac{dm_i}{dt} = D_i \frac{dc_i}{dx} \]  (9)

Where

- \( J_i \) = mass flux of species i
- \( dm_i \) = rate of change of mass of species i
- \( A \) = area normal to the direction of diffusion
- \( \frac{dc_i}{dx} \) = concentration gradient parallel to the direction of diffusion
- \( D_i \) = diffusion coefficient of species i in the surrounding medium.

This equation presents no difficulty if the concentration gradient \( \frac{dc}{dx} \) is clearly defined. In most practical situations, as in the case of mass transfer from a sphere into the surrounding medium, only the concentrations at the solid surface and in the surrounding medium are known. It is not clear how the concentrations vary with the
spatial coordinate in the vicinity of the solid surface or at what distance from the solid surface the concentrations reach those of the surrounding medium. For these reasons Fick's first law is often written in the form:

\[-(\frac{dm}{dt}) = S \cdot D_i \cdot (C_i - C^o_i)\]  \hspace{1cm} (10)

where \(S\) is the shape factor and depends on the geometry of the system. For diffusion from a plane surface \(S\) is equal to \(A/\delta\), where \(\delta\) is the distance over which the concentrations drop from the values at the interface to those of the surrounding medium.

For mass transfer from solid surfaces into moving fluids the concentration drop from interface value to the bulk value is assumed to occur within a thin film of fluid next to the solid surface. As illustrated in Figure 3 everywhere outside this film the concentrations and the velocities are equal to those of the bulk fluid. This film is referred to as the boundary layer and the boundary layer thickness is a function of the velocity and properties of the fluid and the geometry of the solid. Figure 4 shows the boundary layer for parallel flow along a thin plate. The reactants and products have to diffuse in and out of this film since within this film the fluid velocity normal to the surface is zero. The expression for the mass flux then becomes:
Figure 3. Concentration profiles for diffusion controlled and surface reaction controlled reductions.
Figure 4. Boundary layer for flat plate in parallel flow.
Where \( k \) is the mass transfer coefficient and is equal to \( D/\delta \).

Even though the values of \( \delta \) are not available, use can be made of the principle of similarity (21). For geometrically similar situations (for fluid flow around similar bodies) the boundary layer thickness and the mass transfer coefficient are a function of a dimensionless group of properties of the fluid and have been computed empirically. For parallel flow over flat plates the boundary layer thickness and the mass transfer coefficient are given by the equations: (references (22) and (23))

\[
\delta = \delta_0 + 3.09 \text{Re}^{-1/2}\text{Sc}^{-1/3} \quad (12)
\]

\[
\text{Sh} = 0.664 \text{Re}^{1/2}\text{Sc}^{1/3} \quad (13)
\]

where \( \text{Re} = \frac{L \cdot V}{\mu} \) (Reynold's number)

\( L \) = a characteristic dimension (diameter for spheres and length for plates)

\( V \) = bulk velocity of the fluid

\( \mu \) = kinematic viscosity of the fluid

\( \text{Sc} = \frac{\mu}{D} \) (Schmidt number)

\( D \) = diffusion coefficient
\[ Sh = \frac{k \cdot L}{D} \quad \text{(Sherwood number)} \]

\( \delta_0 \) has been incorporated into Equation 12 to account for the diffusional mass transport into a stagnant fluid (22). Such a term has not been incorporated into Equation 13 and does not give rise to much error at high Reynold's numbers and when the Schmidt number is greater than 0.6 (23). However at low Reynold's numbers the Equation should be modified to:

\[ Sh = Sh_0 + 0.664 Re^{1/2} Sc^{1/3} \quad (14) \]

\( Sh_0 \) accounts for the diffusion into a stagnant fluid and is a constant depending on the geometry of the system. For mass transfer from spheres (24) the Sherwood number is given by:

\[ Sh = 2.0 + 0.6 Re^{1/2} Sc^{1/3} \quad (15) \]

3.3 Gaseous Diffusion-Controlled Reduction

3.3.1 Influence of the Flow Conditions

If the reaction between MgO and hydrogen at the interface is sufficiently fast and the diffusion through the
boundary layer is slow the kinetics of reduction of MgO are controlled by diffusion. Under these circumstances all the species involved are in equilibrium at the solid surface. The concentrations (partial pressures) at the solid surface are then related through Equations 1-8 and can be computed from the available thermodynamic data (10). The equilibrium constants in Equations 2, 4 and 6, and hence the concentrations, are a function of temperature only. The interface concentration $C_i$ in Equation 11 is then equal to the equilibrium concentration. Expressing the concentration in terms of partial pressures:

$$C_i^* = \frac{p_i^*}{RT} \quad (16)$$

The molar flux of species $i$ is given by:

$$J_i = \left( \frac{k_i}{RT} \right) \cdot (p_i^* - p_i^0) \quad (17)$$

$k_i$ is the only variable that is a function of the flow rate (velocity of the hydrogen gas) on the right hand side of Equation 17. The dependence of the mass transfer coefficient on the velocity of the gas is given by Equations 14 and 15 and can be simplified to:

$$k_i = a_1 + a_2 \cdot v^{0.5} \quad (18)$$
\[ a_1 = \text{a constant depending on the geometry of the system} \]

\[ a_2 = \frac{0.664D_0^{0.67}}{L^{0.5} \mu^{0.17}} \quad \text{for plates (23).} \]

Therefore,

\[ J_i = a_3 + a_4 \cdot v^{0.5} \quad (19) \]

for isothermal reduction.

Hence for a diffusion controlled reduction the rate of weight loss would be proportional to the square root of the velocity of the gas.

For flat plates the rate of weight loss \( \frac{dm}{dt} \) would be invariant with time (assuming that the bulk gas concentration does not change with time) because the geometry of the interface does not change significantly and none of the other variables change with time. For mass transfer from spheres however, the sphere size changes with time and this change would result in \( \frac{dm}{dt} \) being a function of time:

\[ \frac{dm}{dt} = \rho \cdot 4\pi r^2 \cdot \frac{dr}{dt} = 4\pi r^2 \cdot \frac{k_i}{RT} \cdot (p^* - p_i) \quad (20) \]

where \( \rho \) is density.

\[ \rho \cdot \frac{dr}{dt} = \frac{k_i}{RT} \cdot (p^* - p_i) \quad (21) \]
For spheres the mass transfer coefficient is given by:

\[ k_i = 2.0 \left( \frac{\text{D}_i}{r} \right) + \frac{0.6 \sqrt{0.5} \text{D}_i^{0.67}}{r^{0.5} \mu^{0.17}} \]  

(22)

Since the mass transfer coefficient, and hence \( \frac{dr}{dt} \), is a function of the radius of the sphere the rate of weight loss, \( \frac{dm}{dt} \), would be a function of time for mass transfer from spheres. If the second term on the right hand side of Equation 22 is small compared to the first term, then

\[ \left( \frac{dm}{dt} \right) = 4 \pi r^2 \cdot \left( \frac{dr}{dt} \right) = a_5 \cdot r \]  

(23)

where \( a_5 \) is a constant. So at low Reynolds' numbers the rate of weight loss from spheres in a diffusion controlled reaction is directly proportional to the radii of the spheres.

3.3.2 Standard Enthalpy and Free Energy of the Reaction

Assuming \( p^*_{\text{H}_2} = 1.0 \) (in pure hydrogen) and \( a^*_{\text{MgO}} = 1.0 \) (pure MgO crystal) the equilibrium constant for Reaction 1 is given by:

\[ K_{eq} = p^*_{\text{Mg}} \cdot p^*_{\text{H}_2\text{O}} \]  

(24)

If the flow rate is high enough to prevent buildup of the products in the bulk gas, \( p^0_{\text{Mg}} = 0 \) for the bulk gas. The
molar flux of Mg vapor is then given by:

\[ J_{\text{Mg}} = \left( \frac{k_{\text{Mg}}}{RT} \right) \cdot p^*_{\text{Mg}} \]  

(25)

For stoichiometric reduction of MgO

\[ J_{\text{Mg}} = J_{\text{H}_2\text{O}} = -J_{\text{H}_2} \]  

(26)

\[ \left( \frac{k_{\text{H}_2\text{O}}}{RT} \right) \cdot (p^*_{\text{H}_2\text{O}} - p^0_{\text{H}_2\text{O}}) = \left( \frac{k_{\text{Mg}}}{RT} \right) \cdot p^*_{\text{Mg}} \]  

(27)

Assuming that \( k_{\text{H}_2\text{O}} = k_{\text{Mg}} \)

(Strictly speaking the diffusion coefficients \( D_{\text{H}_2\text{O}-\text{H}_2} \) and \( D_{\text{Mg}-\text{H}_2} \) are not equal because the properties of the monatomic Mg vapor are different from those of water vapor. Using Chapman-Enskog formula (29) the values calculated are:

\[ D_{\text{H}_2\text{O}-\text{H}_2} = 17.9 \text{ Cm}^2/\text{Sec. at 1500}^\circ\text{C} \]

\[ D_{\text{Ar}-\text{H}_2} = D_{\text{Mg}-\text{H}_2} = 15.4 \text{ Cm}^2/\text{Sec. at 1500}^\circ\text{C} \]

The diffusion coefficient of Ar has been used as an estimate for the diffusion coefficient of Mg\(_g\). From the above comparison it can be seen that the diffusion coefficients of water vapor and magnesium vapor would be close.)
If the partial pressure of water vapor in the bulk hydrogen gas (incoming gas) is very low (<<K_{eq}^{0.5}) then p_{H_{2}O}^{0} can be taken as zero.

From Equations 28 and 24

\[ p_{Mg}^{*} = p_{H_{2}O}^{*} = K_{eq}^{0.5} = \exp(-\frac{\Delta G^{0}}{2RT}) \]  

(29)

and the flux is given by:

\[ J_{Mg} = \frac{k_{Mg}}{RT} \exp(-\frac{\Delta G^{0}}{2RT}) \]  

(30)

In the temperature range 1350 to 1500°C the pre-exponential coefficient on the right in Equation 30 remains more or less constant. Therefore the slope of a plot of \(\log(J)\) versus \(1/T\) can be used to calculate the standard enthalpy of the reaction. These relationships are somewhat different when the bulk hydrogen gas contains appreciable amounts of water vapor. In this case Equation 29 would be incorrect and the correct relation between equilibrium partial pressure of magnesium vapor and that of water vapor would be

\[ p_{H_{2}O}^{*} = p_{H_{2}O}^{0} + p_{Mg}^{*} \]  

(31)
From Equations 31, 24 and 25

\[ J_{\text{Mg}} = \left( \frac{k_{\text{Mg}}}{2RT} \right) \cdot \left\{ \left( p_{\text{H}_2\text{O}}^0 \right)^2 + 4k_{\text{eq}} \right\}^{0.5} - p_{\text{H}_2\text{O}}^0 \]  

(32)

This relation simplifies to Equation 30 at very low partial pressures of water vapor \( K_{\text{eq}} \gg p_{\text{H}_2\text{O}}^2 \). On the other hand, at high \( p_{\text{H}_2\text{O}}^0 \),

\[ p_{\text{H}_2\text{O}}^* - p_{\text{H}_2\text{O}}^0 \]

and Equation 32 becomes,

\[ J_{\text{Mg}} = \left( \frac{k_{\text{Mg}}}{RTp_{\text{H}_2\text{O}}^0} \right) \cdot \exp \left( - \frac{\Delta G_{\text{eq}}^0}{RT} \right) \]  

(33)

3.3.3 Effect of Water Vapor on the Reduction

From Equations 24 and 25 the molar flux of Mg vapor can be expressed as:

\[ J_{\text{Mg}} = \left( \frac{k_{\text{Mg}}}{RT} \right) \cdot \left( \frac{K_{\text{eq}}}{p_{\text{H}_2\text{O}}^*} \right) \]

(34)

Since \( p_{\text{H}_2\text{O}}^* \) is not known from the experiments and since \( p_{\text{H}_2\text{O}}^0 \) and \( p_{\text{H}_2\text{O}}^* \) are approximately equal \( p_{\text{H}_2\text{O}}^0 \) can be used for \( p_{\text{H}_2\text{O}}^* \) in the above equation.
The measured fluxes can then be checked for compliance with Equation 34.

The standard free energy of the reaction can be obtained (reference 13) by combining Equations 31, 24 and 25.

\[ K_{eq} = \left( \frac{J_{Mg}RT}{k_{Mg}} \right) \cdot \left( \frac{J_{Mg}RT}{k_{Mg}} + p_{H2O} \right) \]  

\[ (35) \]

\( K_{eq} \) is a constant for isothermal reduction and \( k_{Mg} \) is a function of sample dimensions, gas flow rate and properties of the gas. At constant temperature the properties of the gas remain invariant (incompressible flow). So Equation 34 can be solved for \( K_{eq} \) and \( k_{Mg} \) from the reduction data of one sample at constant temperature and gas flow rate. The standard free energy of the reaction can then be obtained from \( K_{eq} \).

At high partial pressures of water vapor the contribution of Reaction 3 could be significant and the partial pressure of \( Mg(OH)_2 \) could begin to become comparable to that of \( Mg \) vapor. At very high partial pressures of water vapor the partial pressure of \( Mg(OH)_2 \) would be much higher than that of \( Mg \) vapor. Since the partial pressure of \( Mg(OH)_2 \) would be directly proportional to that of water vapor (Equation 8), the flux would increase with the partial pressure of water vapor. On the other hand water vapor has no effect on Reaction 3 and if Reaction 3 were to
be the dominant process the flux would not be a function of
the partial pressure of water vapor at all.

3.4 Microstructure

The microstructure of reacted single crystal and
polycrystalline magnesium oxide depends on impurities,
mechanically and thermally induced stresses and the relative
stability of the various crystallographic planes.

Calcium oxide, which is normally an impurity in
magnesium oxide and is thought to segregate to the surface
(30), is more resistant to reduction and could effect the
microstructure evolution during the reduction of MgO.
Aluminum oxide is highly resistant to reduction at these
temperatures and could remain as a solid reaction product
influencing the microstructure to a great extent. As the
reduction proceeds aluminum oxide accumulates on the surface
and forms a porous layer. Segregation of the impurities on
the surface could lead to uneven and localized reduction on
the solid surface. In polycrystalline magnesium oxide low
melting impurities tend to segregate in the grain boundaries
if SiO$_2$ is present. This could lead to increased attack at
the grain boundaries.

Since dislocations are associated with high energy, the
reduction would be more favourable at the sites where the
dislocations emerge to the surface. The slip lines in a
mechanically strained crystal and the sub-grain boundaries are also more susceptible to attack by hydrogen.
4. Experimental Method

4.1 Sample Preparation

4.1.1 Single Crystal Samples

Single crystal samples of magnesium oxide were cleaved from the bulk samples received from two sources. One set of single crystal magnesium oxide samples, referred to as "Type 1", were received from Dr. Y. Chen of Oak Ridge National Laboratory. The second set of samples, referred to as "Type 2" were received from Dr. C. E. Semler of Ohio State University. The spectroscopic analysis of the samples is given in Table 1. The cleaved crystals were of different sizes varying from 0.5 to 1.0 cm in width and length. The thickness of the samples was approximately 1.0 mm. For some of the qualitative work, samples (plates) of irregular geometry were used. All the crystals were cleaved along [100] directions to expose (100) crystallographic planes. Spherical samples were also prepared from Type 1 magnesium oxide for quantitative study. The spheres were made by grinding the edges and corners of the cubes cut from the single crystals. In the early stages of the work cleaved samples were chemically polished in 85% orthophosphoric acid.
for 1 to 2 minutes in order to obtain smooth surfaces. As a result a thin film of magnesium orthophosphate occasionally was observed on the chemically polished crystals. This film proved to be more stable in hydrogen at high temperatures. The chemical polishing also rounded the edges of any cleavage steps present on the surface of the crystal and produced plates with rounded edges and corners. In a majority of the cases the cleaving was done with meticulous care and did not produce any cleavage steps with excessive thickness. Because of the tendency of the crystals to hydrate, experiments were done on samples that were cleaved and immediately stored in air-tight vials. The surfaces of the samples remained shiny even two to three months after the cleaving process, indicating that there was not any appreciable hydration.

4.1.2 Polycrystalline Samples

Polycrystalline samples were prepared from reagent grade magnesium oxide powder obtained from Fisher Scientific. The powder was ball milled using polyethylene balls with metallic cores to avoid contamination. The ball milling was done in polyurethane bottles. Green pellets 3.175 centimeters in diameter and 0.1 to 0.2 centimeters in thickness were pressed at 10,000 psi (68.8 MN/sq. meter). These green pellets were pre-fired at 1000°C. Rectangular plates approximately 0.65 cm. in width and 1.0 cm. in length were
cut from these prefired pellets with a diamond wafering blade. The rectangular plates were then sintered at 1550°C. The resulting samples were polished mechanically and were used in the thermogravimetric studies.

4.2 Thermogravimetry

A Cahn 2000 microbalance was used to measure the weight loss of the samples. The microbalance was connected to a strip chart recorder to continuously monitor the weight change of the sample. A complete schematic of the experimental setup is shown in Figure 5. The microbalance is capable of producing a full scale pen travel when the change in weight of the sample was 100 micrograms. Unfortunately, because of the disturbance caused by the gas flow and because of the general building vibrations, it was found that the most sensitive range of the balance that could be used without too much noise was 1.0 milligram full scale. Most of the experiments were run with 1.0 and 10.0 milligrams full scale. When a sample loses more weight than the full scale range, electronic suppression was used to bring the recorder pen back within range. In this way, weight losses of 100 milligrams or more were monitored with a high degree of precision.

The microbalance is enclosed in a vacuum glass bottle which is connected to a 99.9% Alumina tube (2 inches in diameter and 1.15 meters in length) with a glass tube. To
Figure 5. Schematic diagram of experimental setup.
Figure 5 (contd). Schematic diagram of experimental setup.

1. Furnace
2. Microbalance
3. MgO sample and suspending molybdenum wire
4. Alumina tube
5. Hygrometer
6. Water trap for exiting gas
7. Thermocouple
8. Water trap to introduce water vapor
9. Liquid nitrogen tank to freeze out the water vapor
make the connections gas tight rubber "0" rings are used. The alumina tube passed through a Lindberg tubular furnace. The other end of the alumina tube was connected to a hygrometer and a water trap as shown in Figure 5. The hygrometer (Panametrics Co) was capable of measuring dew points of the flowing gas in the range -80°C to +20°C. The rate of flow of the gas was measured with flowmeters before the gas entered the system. To prevent the leakage of air into the system a slight positive pressure was maintained in the system.

A thin (0.05 cm diameter) molybdenum wire was used to suspend the sample from the microbalance. The wire was made into links of 10 to 15 cm. long and the links were joined together to make a chain long enough to reach the hot zone of the furnace. The samples were suspended from this chain with a 0.0125cm. diameter molybdenum wire. The molybdenum wire was extremely stable in hydrogen at high temperature. The links weighed the same to the nearest milligram after they were used in hydrogen at high temperatures. The temperature of the hot zone was measured with a type R (Pt-13%Rh87%Pt) thermocouple placed inside the alumina tube. The same thermocouple was also connected to the temperature controller used to control the temperature of the furnace.
4.3 Measurements

The samples were ultrasonically cleaned in isopropyl alcohol and in distilled water immediately before loading them onto the balance. Care was taken not to contaminate the sample surface after cleaning. After suspending the samples from the microbalance into the hot zone, all the openings were sealed and the entire system was purged with helium gas. Hydrogen was then passed through the system at a rate of about 500 cc./min.. The furnace was then heated to the desired temperature. Most of the experiments were run between 1350°C and 1500°C. The weight of the sample was monitored from the start of the heatup. During the heatup the balance recorded a slight increase in weight. This increase in weight can be attributed to the increase in the drag on the sample as the velocity of the gas through the system increased. This weight change reversed during cooling of the furnace. In any case the weight gain was about 1.0 milligram in going from room temperature to 1500°C. A similar apparent gain in weight was observed when the gas flow rate was increased while maintaining a constant temperature.

The rate of weight loss was measured as function of gas flow rate, temperature and the dew point of the hydrogen gas. The water vapor content of the hydrogen gas was varied by first cooling the hydrogen gas in liquid nitrogen to extract the water and then bubbling the gas through
distilled water. The dew point was measured (with the Panametrics Hygrometer) as the gas exited from the system.

4.4 Optical and Scanning Electron Microscopy

The surface morphology of the reduced single crystal and polycrystalline magnesium oxide samples was studied as a function of weight loss. A given area of the sample was examined with a metallographic microscope after successively increasing amounts of weight loses. In this way, the changes in the morphology of the surface of the samples were studied as the reduction progressed. The examination of the sample surface with a scanning electron microscope was not feasible because of the charging problems associated with uncoated ceramics. After the final weight loss the samples were coated with either carbon or a gold-palladium alloy and examined in the scanning electron microscope. X-ray microprobe analysis was done on the carbon coated samples. Auger electron spectroscopy was also performed on selected reacted and unreacted single crystals.
5. Results and Discussion

5.1 Results

5.1.1 Weight Loss Data

The weight loss as a function of time for single crystal plates is shown in Figure 6. The rate of weight loss $\frac{dm}{dt}$ is constant for both plates and spheres for small weight losses. The weight versus time plot for a spherical sample that has lost a significant fraction (~30%) of its weight is shown in Figure 7. It can be seen from the figure that the rate of weight loss decreases with time.

Figures 6, 8 and 9 show the weight loss of magnesium oxide single crystals as a function of temperature, dew point of the hydrogen gas (measured as the gas exits from the alumina tube) and the flow rate of the hydrogen gas. These plots show that the rate of weight loss increases as the temperature increases, decreases with increasing dew point and increases with increasing flow rate. These results are discussed in more detail in the following sections.
Figure 6. Weight loss data as a function of time and temperature.
Figure 7. Weight loss data as a function of time for spheres of Type 1 MgO.
Figure 8. Weight loss data as a function of water vapor pressure.
Figure 9. Weight loss data as a function of flow rate of gas.
5.1.2 Effect of Gas Flow Rate

The effect of gas flow rate was measured at different temperatures and different water vapor pressures. The weight loss flux (moles/cm²sec) is plotted against the square root of the gas velocity in Figure 10. The weight loss flux increases with the square root of the gas flow rate. The data show some scatter which may be due to the edge effects of the sample. The equations are empirical and are subject to some error for flow parallel to flat plates for which a 10% error is not uncommon (31). It was not possible to pool the data from all the samples because of the different sizes (width and thickness) of the samples used.

The expression for the slope of the plot can be obtained from Equations 14, 17 and 19.

\[
a_4 = \frac{0.664D^{0.67}(p^{H_2O} - P^{H_2O})}{RTL^{0.5} \mu^{0.17}}
\]

(36)

From the experimental values of \(a_4\), the values of \(p^{H_2O}\), \(K_{eq}\) and standard free energy are calculated and tabulated in Table 2.

5.1.3 Effect of Temperature on the Reduction

The influence of temperature on the reduction is studied by measuring the rate of weight loss at various temperatures.
Figure 10. Dependence of flux on gas flow rate.
Table 2. Analysis of weight loss data as a function of flow rate.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>101N</td>
<td>-18.0</td>
<td>1475</td>
<td>5.116E-09</td>
<td>2.191E-04</td>
<td>1.449E-03</td>
<td>3.174E-07</td>
<td>52.37</td>
</tr>
<tr>
<td>101P</td>
<td>18.0</td>
<td>1475</td>
<td>1.286E-09</td>
<td>5.505E-05</td>
<td>2.176E-02</td>
<td>1.779E-06</td>
<td>45.02</td>
</tr>
<tr>
<td>101M</td>
<td>0.0</td>
<td>1450</td>
<td>1.103E-09</td>
<td>4.637E-05</td>
<td>6.075E-03</td>
<td>2.817E-07</td>
<td>52.04</td>
</tr>
<tr>
<td>102M</td>
<td>19.0</td>
<td>1425</td>
<td>1.937E-09</td>
<td>8.175E-05</td>
<td>2.014E-02</td>
<td>1.108E-06</td>
<td>47.99</td>
</tr>
</tbody>
</table>
for spheres and plates made of Type 1 magnesium oxide single crystals and for plates of Type 2 magnesium oxide single crystals.

The data are plotted as log(flux) versus reciprocal temperature in Figures 11, 12 and 13 for spheres of Type 1 magnesium oxide crystals, for plates of Type 1 magnesium oxide and for plates of Type 2 magnesium oxide respectively. Similar plots are shown for polycrystalline magnesium oxide plates in Figure 14.

The slopes of these plots can be derived from Equation 30 when the partial pressure of water vapor is very low and from Equation 33 when the partial pressure of water vapor is high. Because the pressure of water vapor was not less than $10^{-4}$ atm. ($10^{-5}$ MN/sq. meter) in the experiments, the slopes of these plots are given by Equation 33 and are equal to $\Delta H^0/2.303R$. The slopes of the plots and the calculated values of the standard enthalpy of the reaction are tabulated in Table 3 for single crystals and in Table 4 for polycrystalline magnesium oxide. The tables also record the dew point, temperature range of the experiment and the standard deviation for the standard enthalpy of the reaction. The standard enthalpy varies between 85 Kcal/mole ($357$ KJ/mole) to 135 Kcal/mole ($567$ KJ/mole) for both single crystals and for polycrystalline plates.
Figure 11. Effect of temperature on flux for spheres of Type 1 MgO.
Figure 12. Effect of temperature on flux for plates of Type 1 MgO.
Figure 13. Effect of temperature on flux for plates of Type 2 MgO.
Figure 14. Effect of temperature on flux for polycrystalline MgO.
Table 3. Enthalpy Data for Single Crystal MgO.

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>TEMPERATURE RANGE °C</th>
<th>DEW PT. °C</th>
<th>SLOPE</th>
<th>ENTHALPY (Kcal/mole)</th>
<th>ST. DEV.</th>
</tr>
</thead>
<tbody>
<tr>
<td>TYPE 1 MgO PLATES</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>D085T</td>
<td>1480-1420</td>
<td>-32.0</td>
<td>-1.886</td>
<td>86.9</td>
<td>1.76</td>
</tr>
<tr>
<td>D086T</td>
<td>1490-1450</td>
<td>-30.0</td>
<td>-1.902</td>
<td>87.6</td>
<td>5.21</td>
</tr>
<tr>
<td>D087T</td>
<td>1410-1360</td>
<td>-32.0</td>
<td>-2.788</td>
<td>128.4</td>
<td>5.02</td>
</tr>
<tr>
<td>D087X</td>
<td>1490-1370</td>
<td>-32.0</td>
<td>-2.285</td>
<td>105.2</td>
<td>2.13</td>
</tr>
<tr>
<td>D088T</td>
<td>1480-1365</td>
<td>-30.0</td>
<td>-2.285</td>
<td>105.2</td>
<td>2.02</td>
</tr>
<tr>
<td>D089T</td>
<td>1490-1365</td>
<td>-34.0</td>
<td>-2.013</td>
<td>92.7</td>
<td>0.47</td>
</tr>
<tr>
<td>D203T</td>
<td>1500-1375</td>
<td>-10.0</td>
<td>-2.203</td>
<td>101.5</td>
<td>4.67</td>
</tr>
<tr>
<td>D203X</td>
<td>1500-1325</td>
<td>-30.0</td>
<td>-1.895</td>
<td>87.3</td>
<td>10.77</td>
</tr>
</tbody>
</table>

| TYPE 2 MgO PLATES |
| D108T  | 1499-1370             | +20.0      | -2.021 | 93.1                | 3.71     |
| D108X  | 1499-1326             | -22.0      | -2.378 | 109.5               | 2.29     |
| D109T  | 1499-1400             | +18.0      | -2.023 | 93.2                | 2.80     |
| D109X  | 1499-1350             | -21.5      | -2.299 | 105.9               | 1.93     |
| D113T  | 1499-1375             | -20.0      | -2.712 | 124.9               | 2.74     |
| D113X  | 1496-1410             | +9.0       | -2.921 | 134.5               | 4.68     |
| D114T  | 1497-1385             | -10.5      | -2.949 | 135.8               | 2.95     |

| TYPE 1 MgO SPHERES |
| D142T  | 1455-1367             | +1.0       | -2.310 | 106.4               | 2.49     |
| D142X  | 1450-1370             | -1.0       | -2.405 | 110.8               | 4.18     |
| D142Y  | 1435-1355             | -1.0       | -2.409 | 111.0               | 2.89     |
| D143T  | 1440-1360             | -2.0       | -2.858 | 131.7               | 2.72     |
| D143X  | 1445-1385             | -3.5       | -2.623 | 120.8               | 10.91    |
| D143Y  | 1447-1345             | -3.0       | -2.467 | 113.6               | 5.77     |
Table 4. Enthalpy Data for Polycrystalline MgO Plates.

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>TEMPERATURE RANGE °C</th>
<th>DEW PT. °C</th>
<th>SLOPE</th>
<th>ENTHALPY ST. DEV. (Kcal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P101</td>
<td>1495-1350</td>
<td>-21</td>
<td>-1.501</td>
<td>69.12</td>
</tr>
<tr>
<td>P102</td>
<td>1499-1330</td>
<td>-26</td>
<td>-1.688</td>
<td>77.72</td>
</tr>
<tr>
<td>P103</td>
<td>1450-1300</td>
<td>-28</td>
<td>-1.640</td>
<td>75.53</td>
</tr>
<tr>
<td>P104</td>
<td>1600-1350</td>
<td>-25</td>
<td>-2.070</td>
<td>95.32</td>
</tr>
<tr>
<td>P105</td>
<td>1630-1566</td>
<td>-31</td>
<td>-2.114</td>
<td>97.36</td>
</tr>
<tr>
<td>P105</td>
<td>1535-1350</td>
<td>-42</td>
<td>-1.604</td>
<td>73.89</td>
</tr>
<tr>
<td>P107</td>
<td>1630-1515</td>
<td>-8</td>
<td>-2.843</td>
<td>130.91</td>
</tr>
<tr>
<td>P108</td>
<td>1580-1428</td>
<td>-29</td>
<td>1.774</td>
<td>81.70</td>
</tr>
</tbody>
</table>
5.1.4 Effect of Water Vapor Pressure on the Reduction

The effect of the partial pressure of water vapor on the reduction was studied by measuring the rate of weight loss of single crystal spheres and plates as a function of the partial pressure of water vapor at constant temperatures and flow rates. The logarithm of flux is plotted against logarithm of measured partial pressure of water vapor in Figure 15 and the slopes of the plots (along with the standard deviations) are tabulated in Table 5. The temperature and the range of the dew points are also given in Table 5. The average of the slopes is $-0.82 \pm 0.16$.

The weight loss data at constant temperature was fitted to Equation 35 and the resulting values of $K_{eq}$ and the standard free energy of the reaction are tabulated in Table 6.

5.1.5 Surface Morphology of Reacted Magnesium Oxide

(i) Polycrystalline Magnesium Oxide

The microstructure of the unreacted polycrystalline specimen and that of the reacted polycrystalline specimen are shown in Figures 16 and 17 respectively. Figure 17 shows preferred attack at the grain boundaries and this preferred reduction at the grain boundaries extends into the bulk of the specimen and leads to the fallout of whole
Figure 15. Effect of water vapor pressure on flux.
Table 5. Log(Flux) vs. Log(water vapor)

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>TEMP °C</th>
<th>DEW PT. RANGE °C</th>
<th>SLOPE</th>
<th>STANDARD DEVIATION</th>
</tr>
</thead>
<tbody>
<tr>
<td>D084A</td>
<td>1450</td>
<td>-36.5 0.0</td>
<td>-0.649</td>
<td>0.0143</td>
</tr>
<tr>
<td>D085A</td>
<td>1425</td>
<td>-35.0 -2.0</td>
<td>-0.825</td>
<td>0.0417</td>
</tr>
<tr>
<td>D086A</td>
<td>1450</td>
<td>-36.0 -0.5</td>
<td>-0.746</td>
<td>0.0411</td>
</tr>
<tr>
<td>D086E</td>
<td>1450</td>
<td>-35.5 -2.0</td>
<td>-0.698</td>
<td>0.0299</td>
</tr>
<tr>
<td>D087A</td>
<td>1450</td>
<td>-39.0 -2.0</td>
<td>-0.628</td>
<td>0.0527</td>
</tr>
<tr>
<td>D088A</td>
<td>1425</td>
<td>-33.0 -29.0</td>
<td>-0.954</td>
<td>0.0465</td>
</tr>
<tr>
<td>D088D</td>
<td>1450</td>
<td>-36.0 -21.0</td>
<td>-0.852</td>
<td>0.0505</td>
</tr>
<tr>
<td>D089A</td>
<td>1450</td>
<td>-35.5 -21.0</td>
<td>-0.703</td>
<td>0.0423</td>
</tr>
<tr>
<td>D089D</td>
<td>1490</td>
<td>-35.2 -20.0</td>
<td>-0.495</td>
<td>0.0504</td>
</tr>
<tr>
<td>D090A</td>
<td>1490</td>
<td>-35.5 -10.0</td>
<td>-0.635</td>
<td>0.0283</td>
</tr>
<tr>
<td>D097A</td>
<td>1450</td>
<td>+4.0 +15.5</td>
<td>-0.986</td>
<td>0.0385</td>
</tr>
<tr>
<td>D097D</td>
<td>1450</td>
<td>+1.0 +19.5</td>
<td>-0.886</td>
<td>0.0148</td>
</tr>
<tr>
<td>D098A</td>
<td>1450</td>
<td>-28.0 -11.0</td>
<td>-0.807</td>
<td>0.0320</td>
</tr>
</tbody>
</table>

**TYPE 1 SPHERES**

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>TEMP °C</th>
<th>DEW PT. RANGE °C</th>
<th>SLOPE</th>
<th>STANDARD DEVIATION</th>
</tr>
</thead>
<tbody>
<tr>
<td>D142A</td>
<td>1444</td>
<td>-10.0 +17.0</td>
<td>-1.126</td>
<td>0.0480</td>
</tr>
<tr>
<td>D142B</td>
<td>1464</td>
<td>-8.0 +18.5</td>
<td>-0.943</td>
<td>0.0120</td>
</tr>
<tr>
<td>D142C</td>
<td>1457</td>
<td>-11.0 +18.5</td>
<td>-0.901</td>
<td>0.0094</td>
</tr>
<tr>
<td>D143A</td>
<td>1447</td>
<td>-18.0 +19.5</td>
<td>-0.818</td>
<td>0.0261</td>
</tr>
</tbody>
</table>
Table 5 (contd.) Log(Flux) vs. Log(water vapor)

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>TEMP °C</th>
<th>DEW PT. RANGE °C</th>
<th>SLOPE</th>
<th>STANDARD DEVIATION</th>
</tr>
</thead>
<tbody>
<tr>
<td>D099A</td>
<td>1300</td>
<td>-35.0 -17.5</td>
<td>-0.967</td>
<td>0.1022</td>
</tr>
<tr>
<td>D100A</td>
<td>1475</td>
<td>-4.5 +17.0</td>
<td>-0.911</td>
<td>0.0652</td>
</tr>
<tr>
<td>D101A</td>
<td>1300</td>
<td>-28.0 -5.5</td>
<td>-1.277</td>
<td>0.0651</td>
</tr>
<tr>
<td>D101D</td>
<td>1475</td>
<td>-26.5 +18.0</td>
<td>-0.721</td>
<td>0.0141</td>
</tr>
<tr>
<td>D102A</td>
<td>1475</td>
<td>-28.0 +15.0</td>
<td>-0.617</td>
<td>0.0421</td>
</tr>
<tr>
<td>D102B</td>
<td>1425</td>
<td>-28.5 -6.0</td>
<td>-0.816</td>
<td>0.0118</td>
</tr>
<tr>
<td>D113A</td>
<td>1450</td>
<td>-21.0 +19.0</td>
<td>-0.785</td>
<td>0.0105</td>
</tr>
<tr>
<td>D114A</td>
<td>1426</td>
<td>-29.5 +2.5</td>
<td>-0.719</td>
<td>0.0192</td>
</tr>
<tr>
<td>D114B</td>
<td>1346</td>
<td>-31.0 +2.0</td>
<td>-0.870</td>
<td>0.0308</td>
</tr>
<tr>
<td>D116A</td>
<td>1475</td>
<td>-30.0 -8.5</td>
<td>-0.545</td>
<td>0.0318</td>
</tr>
<tr>
<td>D116B</td>
<td>1453</td>
<td>-28.5 -8.5</td>
<td>-0.712</td>
<td>0.0240</td>
</tr>
<tr>
<td>D116C</td>
<td>1427</td>
<td>-30.0 -8.0</td>
<td>-0.773</td>
<td>0.0215</td>
</tr>
<tr>
<td>D119A</td>
<td>1401</td>
<td>-32.0 +0.5</td>
<td>-0.789</td>
<td>0.0024</td>
</tr>
<tr>
<td>D119B</td>
<td>1377</td>
<td>-30.0 -5.5</td>
<td>-0.850</td>
<td>0.0191</td>
</tr>
<tr>
<td>D120A</td>
<td>1340</td>
<td>-32.5 -10.0</td>
<td>-0.927</td>
<td>0.0302</td>
</tr>
<tr>
<td>D120B</td>
<td>1340</td>
<td>-33.5 -6.5</td>
<td>-0.869</td>
<td>0.0565</td>
</tr>
<tr>
<td>D120C</td>
<td>1350</td>
<td>-31.0 -7.5</td>
<td>-1.026</td>
<td>0.0617</td>
</tr>
</tbody>
</table>
Table 6. Free Energy values calculated using Equation 35.

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>TEMP °C</th>
<th>K\textsubscript{eq} (cm/sec)</th>
<th>k \text{ST.DEV. for } 1/k</th>
<th>DEW POINT RANGE °C</th>
<th>FREE ENERGY OF REACTION Kcal/Mole</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>*10^{-8}</td>
<td>*10^{-2}</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**TYPE 1 PLATES**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temp °C</th>
<th>K\textsubscript{eq}</th>
<th>k</th>
<th>ST.DEV.</th>
<th>Dew Point Range °C</th>
<th>Free Energy of Reaction Kcal/Mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>D084A</td>
<td>1450</td>
<td>34.610</td>
<td>19.198</td>
<td>3.974</td>
<td>-36.5 0.0</td>
<td>51.265</td>
</tr>
<tr>
<td>D085A</td>
<td>1425</td>
<td>9.206</td>
<td>39.929</td>
<td>3.051</td>
<td>-36.0 -2.0</td>
<td>55.018</td>
</tr>
<tr>
<td>D086A</td>
<td>1450</td>
<td>14.820</td>
<td>38.241</td>
<td>3.781</td>
<td>-36.0 -0.5</td>
<td>54.187</td>
</tr>
<tr>
<td>D087A</td>
<td>1450</td>
<td>19.710</td>
<td>41.521</td>
<td>1.914</td>
<td>-39.0 -2.0</td>
<td>53.205</td>
</tr>
<tr>
<td>D088A</td>
<td>1425</td>
<td>0.166</td>
<td>1620.000</td>
<td>0.236</td>
<td>-33.0 -20.5</td>
<td>68.660</td>
</tr>
<tr>
<td>D088D</td>
<td>1450</td>
<td>0.880</td>
<td>330.310</td>
<td>0.084</td>
<td>-36.0 -21.0</td>
<td>63.917</td>
</tr>
<tr>
<td>D089A</td>
<td>1450</td>
<td>3.133</td>
<td>165.540</td>
<td>0.040</td>
<td>-35.5 -21.0</td>
<td>59.542</td>
</tr>
<tr>
<td>D089D</td>
<td>1490</td>
<td>10.750</td>
<td>99.713</td>
<td>0.050</td>
<td>-35.0 -20.0</td>
<td>56.577</td>
</tr>
<tr>
<td>D090A</td>
<td>1490</td>
<td>14.000</td>
<td>91.902</td>
<td>0.404</td>
<td>-35.5 -10.0</td>
<td>55.646</td>
</tr>
<tr>
<td>D097A</td>
<td>1450</td>
<td>96.360</td>
<td>12.926</td>
<td>36.730</td>
<td>+4.0 +19.0</td>
<td>47.736</td>
</tr>
<tr>
<td>D097D</td>
<td>1450</td>
<td>933.900</td>
<td>1.199</td>
<td>25.981</td>
<td>+1.0 +19.5</td>
<td>39.909</td>
</tr>
<tr>
<td>D098A</td>
<td>1450</td>
<td>12.760</td>
<td>56.746</td>
<td>0.990</td>
<td>-28.0 -11.0</td>
<td>54.703</td>
</tr>
<tr>
<td>D098D</td>
<td>1450</td>
<td>11.700</td>
<td>52.774</td>
<td>0.709</td>
<td>-32.0 -10.0</td>
<td>55.002</td>
</tr>
</tbody>
</table>

**TYPE 1 SPHERES**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temp °C</th>
<th>K\textsubscript{eq}</th>
<th>k</th>
<th>ST.DEV.</th>
<th>Dew Point Range °C</th>
<th>Free Energy of Reaction Kcal/Mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>D142B</td>
<td>1464</td>
<td>160.800</td>
<td>19.269</td>
<td>3.000</td>
<td>-8.0 +18.5</td>
<td>46.345</td>
</tr>
<tr>
<td>D142C</td>
<td>1457</td>
<td>208.700</td>
<td>12.615</td>
<td>3.437</td>
<td>-11.0 +18.5</td>
<td>45.256</td>
</tr>
<tr>
<td>D143A</td>
<td>1447</td>
<td>199.600</td>
<td>11.916</td>
<td>1.992</td>
<td>-18.0 +19.5</td>
<td>45.148</td>
</tr>
</tbody>
</table>
Table 6. (contd.) Free Energy values calculated using Equation 35.

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>TEMP °C</th>
<th>Keq *10^-8</th>
<th>k (cm/sec)</th>
<th>ST. DEV. for 1/k *10^-2</th>
<th>DEW POINT RANGE °C</th>
<th>FREE ENERGY OF REACTION Kcal/Mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>D099A</td>
<td>1300</td>
<td>0.628</td>
<td>33.105</td>
<td>6.602</td>
<td>-35.0 -17.5</td>
<td>59.414</td>
</tr>
<tr>
<td>D100A</td>
<td>1475</td>
<td>431.300</td>
<td>6.280</td>
<td>17.696</td>
<td>-4.5 +17.0</td>
<td>43.189</td>
</tr>
<tr>
<td>D101D</td>
<td>1475</td>
<td>215.400</td>
<td>14.414</td>
<td>1.997</td>
<td>-26.5 +18.0</td>
<td>45.669</td>
</tr>
<tr>
<td>D102A</td>
<td>1475</td>
<td>248.000</td>
<td>12.020</td>
<td>2.514</td>
<td>-28.0 +15.0</td>
<td>45.175</td>
</tr>
<tr>
<td>D102B</td>
<td>1425</td>
<td>15.570</td>
<td>39.135</td>
<td>0.594</td>
<td>-28.5 -6.0</td>
<td>53.233</td>
</tr>
<tr>
<td>D113A</td>
<td>1450</td>
<td>204.300</td>
<td>7.822</td>
<td>2.665</td>
<td>-21.0 +19.0</td>
<td>45.146</td>
</tr>
<tr>
<td>D114A</td>
<td>1426</td>
<td>52.000</td>
<td>16.450</td>
<td>0.848</td>
<td>-29.5 +2.5</td>
<td>49.167</td>
</tr>
<tr>
<td>D114B</td>
<td>1346</td>
<td>15.380</td>
<td>8.580</td>
<td>8.604</td>
<td>-31.0 +2.0</td>
<td>50.796</td>
</tr>
<tr>
<td>D116A</td>
<td>1475</td>
<td>46.560</td>
<td>35.483</td>
<td>0.254</td>
<td>-30.0 -8.5</td>
<td>50.971</td>
</tr>
<tr>
<td>D116B</td>
<td>1453</td>
<td>21.600</td>
<td>44.242</td>
<td>0.310</td>
<td>-28.5 -8.5</td>
<td>52.981</td>
</tr>
<tr>
<td>D116C</td>
<td>1427</td>
<td>12.830</td>
<td>41.525</td>
<td>0.301</td>
<td>-30.0 -8.0</td>
<td>53.954</td>
</tr>
<tr>
<td>D119A</td>
<td>1401</td>
<td>17.530</td>
<td>23.927</td>
<td>3.201</td>
<td>-32.0 +0.5</td>
<td>52.100</td>
</tr>
<tr>
<td>D119B</td>
<td>1377</td>
<td>11.010</td>
<td>25.154</td>
<td>1.463</td>
<td>-30.0 -5.5</td>
<td>52.872</td>
</tr>
<tr>
<td>D120A</td>
<td>1340</td>
<td>2.532</td>
<td>38.062</td>
<td>1.668</td>
<td>-32.5 -10.0</td>
<td>56.428</td>
</tr>
<tr>
<td>D120B</td>
<td>1340</td>
<td>5.312</td>
<td>17.311</td>
<td>8.878</td>
<td>-33.5 -6.5</td>
<td>54.038</td>
</tr>
</tbody>
</table>

TYPE 2 PLATES
Figure 16. Microstructure of unreacted polycrystalline MgO.
(a) As polished 200x
(b) Polished and etched in HCl 2400x
Figure 17. Microstructure of reacted polycrystalline MgO showing preferential attack at the grain boundaries. (1175x)
Temperature of reaction: 1450°C
Dew point: -20°C to -30°C
Weight lost: 20 mg/sq.cm.
grains from the surface of the sample. The plates that were made of high purity magnesium oxide powder were porous and did not lend themselves to morphological study.

(ii) Single Crystal Magnesium Oxide

The two types of crystals used in the study (Type 1 obtained from Dr. Chen of Oak Ridge National Laboratory and Type 2 obtained from Dr. Semler of Ohio State University) show somewhat different microstructures after reaction under similar conditions. The unreacted and as-cleaved microstructures have more or less smooth surfaces except for an occasional cleavage step as shown in Figure 18.

The microstructures of the reacted crystals (of both types) are shown in Figures 19 and 20. The microstructure of the reacted Type 1 crystal (Figure 19) shows a surface that is not smooth but full of holes extending into the bulk of the crystal. The surface of the Type 2 single crystal MgO (Figure 20) shows similar holes. The reduction seems to occur beneath the surface to a large extent as illustrated by Figure 21. The lower halves of both micrographs show the interior of the crystal (exposed by cleaving the crystal after the reaction) and the upper halves show the reacted surface. The subsurface attack is more severe at the edges and corners of the crystal as shown Figures 22 and 23.
Figure 18. Microstructure of as-cleaved single crystal MgO (Type 1). (1000x)
Figure 19. Microstructure of reacted single crystal (Type 1) MgO reduced at 1500°C and -25°C dew point. (700x)
Weight loss = 80 mg/sq.cm.
Figure 20. Microstructure of reacted single crystal (Type 2) MgO reduced. (100x)
Temperature of reaction: 1500°C to 1450°C
Dew point: -10°C to -30°C
Weight loss: 73 mg/sq.cm.
Figure 21. Morphology of single crystal (Type 1) MgO cleaved after reaction at 1500°C and -25°C dew point.
Weight loss: 100 mg/sq.cm.
Figure 22. Morphology of single crystal (Type 1) MgO showing severe attack at the edges of the crystal. (1000x)
Temperature of reaction: 1450°C
Dew point= -20°C
Weight loss= 10 mg/sq.cm.
Central area 1000x

Figure 23. Morphology of reacted single crystal (Type 2) MgO
Temperature of reaction: 1450°C
Dew point: -21°C
Weight loss: 41 mg/sq.cm
Figure 23 (contd) Morphology of reacted single crystal MgO (Type 2).

Close to edge (1000x)
Figure 23 (contd) Morphology of reacted single crystal MgO (Type 2).

Edge (1000x)
Figure 24. Morphology of reduced single crystal (Type 1) MgO
Temperature of reaction: \(1450^\circ\text{C}\)
Dew point: \(-21^\circ\text{C}\)
Weight loss=42 mg/sq.cm.
Figure 24 (contd) Morphology of reduced single crystal MgO (Type 1).

Edge 1000x
Figures 23 and 24 compare the microstructures of Type 2 and Type 1 crystals. Both specimens were reduced under the same conditions (temperature, partial pressure of water vapor and flow rate) and to the same extent (the total weight lost). Type 1 sample (Figure 24) shows severe subsurface reduction and Type 2 sample (Figure 23 shows smaller amount of subsurface reduction in all areas (edges and center) of the specimen.

The effect of the water vapor pressure on the microstructure of the reduced Type 2 crystals can be seen by comparing Figures 23 and 25. Both samples (Type 2) were reduced at the same temperature (1450°C) and lost about the same amount of weight (40mg/cm²). The sample in Figure 23 was reduced at a dew point of -21°C whereas the sample in Figure 25 was reduced at a dew point of +18°C. Figure 26 shows the microstructure of the Type 1 crystal reduced at 1500°C and +20°C dew point. From these micrographs it can be concluded that the partial pressure of water vapor does not have any effect on the morphology.

The reduced samples were analysed by emission spectroscopy and the analysis is given in Table 7. The surface of the reduced and unreduced samples were analysed by ESCA (Electron Spectroscopy for Chemical Analysis), AES (Auger Electron Spectroscopy) and EDAX (Energy Dispersive Analysis of X-Rays).
Figure 25. Morphology of single crystal (Type 2) MgO reduced at 1450°C and +18°C dew point. Weight loss: 40 mg/sq.cm.
Central area

Figure 26. Morphology of Type 1 MgO single crystal reduced at 1500°C temperature and +20°C dew point. (100x)
Weight loss: 25 mg/sq.cm.
Table 7. Chemical Analysis of Reduced Type 2 MgO.

<table>
<thead>
<tr>
<th>ELEMENT</th>
<th>CONCENTRATION RANGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>40.0% - 90.0%</td>
</tr>
<tr>
<td>Si</td>
<td>5.0% - 25.0%</td>
</tr>
<tr>
<td>Ca</td>
<td>5.0% - 25.0%</td>
</tr>
<tr>
<td>Al</td>
<td>1.0% - 10.0%</td>
</tr>
<tr>
<td>Zr</td>
<td>0.05% - 0.5%</td>
</tr>
<tr>
<td>Fe</td>
<td>&lt;0.01%</td>
</tr>
<tr>
<td>Sr</td>
<td>0.005% - 0.05%</td>
</tr>
<tr>
<td>Ti</td>
<td>0.005% - 0.05%</td>
</tr>
<tr>
<td>Cu</td>
<td>&lt;0.01%</td>
</tr>
<tr>
<td>Mo</td>
<td>&lt;0.01%</td>
</tr>
<tr>
<td>B, Sb, As, Mn</td>
<td>NOT</td>
</tr>
<tr>
<td>Pb, Cr, Sn, W</td>
<td>DETECTED</td>
</tr>
<tr>
<td>Ge, In, Ni, Bi</td>
<td></td>
</tr>
<tr>
<td>Be, V, Cd, Ag</td>
<td></td>
</tr>
<tr>
<td>Zn, Co</td>
<td></td>
</tr>
</tbody>
</table>
ESCA indicated about 5 atomic% Al on the surface of the unreduced crystal and 30 atomic% Al on the surface of reduced crystal of Type 1 magnesium oxide. 5 atomic% Al on the surface of the unreduced crystals implies a 5 mole% aluminum oxide impurity throughout the bulk of the sample because the specimen were cleaved from larger crystals. The X-ray diffraction pattern of the powdered crystal (Table 8) did not show any detectable aluminum oxide. The spectroscopic analysis of starting material (Table 1) also does not show much aluminum.

The residue left over after complete reduction of Type 1 crystal was identified as magnesium aluminum spinel by X-ray diffraction. The reduction was assumed to be complete when there was no detectable weight loss. The diffraction pattern of the residue is given in Table 9. The weight of the residue was less than 5mg for a starting crystal of 1.7gm. This makes the concentration of aluminum oxide less than 0.25%. The residue from Type 2 magnesium oxide was identified as alumina (diffraction pattern is given in Table 10). The weight of the residue was about 1mg for 435mg of starting material and this makes the concentration of aluminum oxide about 0.25%, about the same as that of Type 1 magnesium oxide.

EDAX was used to check for the compositional differences of the areas with and without holes on the same specimen. The results of the analysis marked in Figure 27 is given in
Table 8. Diffraction Pattern of as Received
Type 2 MgO.

<table>
<thead>
<tr>
<th>TWO THETA (DEGREES)</th>
<th>RELATIVE INTENSITY</th>
<th>d SPACING O_A</th>
<th>hkl1 (MgO)</th>
</tr>
</thead>
<tbody>
<tr>
<td>37.10</td>
<td>9</td>
<td>2.421</td>
<td>111</td>
</tr>
<tr>
<td>43.10</td>
<td>&gt;100</td>
<td>2.102</td>
<td>200</td>
</tr>
<tr>
<td>62.40</td>
<td>64</td>
<td>1.487</td>
<td>220</td>
</tr>
<tr>
<td>74.70</td>
<td>7</td>
<td>1.270</td>
<td>311</td>
</tr>
<tr>
<td>78.70</td>
<td>17</td>
<td>1.215</td>
<td>222</td>
</tr>
</tbody>
</table>
Table 9. Diffraction Pattern of the residue from Type 1 MgO.

<table>
<thead>
<tr>
<th>TWO THETA (DEGREES)</th>
<th>RELATIVE INTENSITY</th>
<th>d SPACING Å</th>
<th>hk1 (SPINEL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>19.25</td>
<td>30</td>
<td>4.607</td>
<td>111</td>
</tr>
<tr>
<td>31.65</td>
<td>42</td>
<td>2.825</td>
<td>220</td>
</tr>
<tr>
<td>37.30</td>
<td>100</td>
<td>2.409</td>
<td>311</td>
</tr>
<tr>
<td>45.30</td>
<td>66</td>
<td>2.001</td>
<td>400</td>
</tr>
<tr>
<td>60.05</td>
<td>56</td>
<td>1.539</td>
<td>511</td>
</tr>
<tr>
<td>66.00</td>
<td>81</td>
<td>1.414</td>
<td>440</td>
</tr>
</tbody>
</table>
Table 10. Diffraction Pattern of the Residue from Type 2 MgO.

<table>
<thead>
<tr>
<th>TWO THETA (DEGREES)</th>
<th>RELATIVE INTENSITY</th>
<th>d SPACING oA</th>
<th>hkl (ALPHA-ALUMINA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25.57</td>
<td>***</td>
<td>3.480</td>
<td>012</td>
</tr>
<tr>
<td>35.19</td>
<td>***</td>
<td>2.547</td>
<td>104</td>
</tr>
<tr>
<td>37.71</td>
<td>**</td>
<td>2.384</td>
<td>110</td>
</tr>
<tr>
<td>43.26</td>
<td>***</td>
<td>2.090</td>
<td>100</td>
</tr>
<tr>
<td>52.58</td>
<td>**</td>
<td>1.738</td>
<td>024</td>
</tr>
<tr>
<td>57.33</td>
<td>***</td>
<td>1.606</td>
<td>116</td>
</tr>
<tr>
<td>61.33</td>
<td>*</td>
<td>1.510</td>
<td>122</td>
</tr>
<tr>
<td>66.38</td>
<td>**</td>
<td>1.407</td>
<td>124</td>
</tr>
<tr>
<td>68.15</td>
<td>**</td>
<td>1.375</td>
<td>030</td>
</tr>
<tr>
<td>79.98</td>
<td>*</td>
<td>1.224</td>
<td>1.0.10</td>
</tr>
<tr>
<td>80.50</td>
<td>*</td>
<td>1.192</td>
<td>220</td>
</tr>
<tr>
<td>84.02</td>
<td>*</td>
<td>1.154</td>
<td>223</td>
</tr>
<tr>
<td>95.35</td>
<td>*</td>
<td>1.040</td>
<td>226</td>
</tr>
</tbody>
</table>
Figure 27. Morphology of Type 1 MgO single crystal. (650x)
Temperature of reaction: 1450°C
Dew point: -20°C to -30°C
EDAX analysis of areas marked (1, 2, 3 and 4) is given in Table 11.
Table 11. EDAX Analysis of the Sample in Figure 27.

<table>
<thead>
<tr>
<th>ELEMENT</th>
<th>AREA 1</th>
<th>AREA 2</th>
<th>AREA 3</th>
<th>AREA 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>0.0</td>
<td>41.28</td>
<td>39.58</td>
<td>40.70</td>
</tr>
<tr>
<td>Al</td>
<td>31.74</td>
<td>3.29</td>
<td>2.48</td>
<td>2.0</td>
</tr>
<tr>
<td>Si</td>
<td>0.0</td>
<td>0.0</td>
<td>0.41</td>
<td>0.53</td>
</tr>
<tr>
<td>P</td>
<td>0.0</td>
<td>1.69</td>
<td>2.86</td>
<td>2.59</td>
</tr>
<tr>
<td>Pd</td>
<td>3.21</td>
<td>1.79</td>
<td>2.01</td>
<td>1.73</td>
</tr>
<tr>
<td>Ca</td>
<td>0.0</td>
<td>0.01</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td>Cu</td>
<td>4.73</td>
<td>0.27</td>
<td>0.14</td>
<td>0.16</td>
</tr>
<tr>
<td>Au</td>
<td>12.72</td>
<td>1.24</td>
<td>1.22</td>
<td>1.01</td>
</tr>
<tr>
<td>O</td>
<td>47.60</td>
<td>50.44</td>
<td>51.28</td>
<td>51.26</td>
</tr>
</tbody>
</table>
Table 11 and shows higher concentration of aluminum on the surface. The interior of the crystal has less aluminum.

Finally, to study the effect of dislocations on the formation and growth of holes on the surface, freshly cleaved crystals were etched with a chemical reagent and reduced in hydrogen. The change in the topology of the surface was documented by removing and examining pre-selected areas of the crystal intermittently during the experiment. The magnification and the clarity of the micrographs was limited by the use of a metallurgical microscope. A scanning electron microscope could not be used because the samples were not coated with a conductive film. Figures 28 and 29 document the changes on the surface of the crystal as the reduction progresses. The holes present in the initial stages were caused by the chemical etching and mark the dislocations. As the reduction progresses these holes disappear. The holes that appear and grow in the later stages of the reduction are not necessarily located at the dislocations.

5.2 Discussion of the Results

5.2.1 Weight loss data

Equation 23 predicts the rate of weight loss to be a function of the radius of a spherical sample. It is more convenient to convert Equation 23 into a relation between
Figure 28. The change in the morphology of the surface of chemically etched single crystal (Type 1) MgO with reduction. (100x)
Figure 28 (contd) The change in the morphology of the surface of chemically etched single crystal MgO (Type 1) with the progress of reduction.
- Temperature: 1400°C
- Dew point: -20°C
- Weight loss: 3.0 mg/sq.cm.
Figure 29. The change in the morphology of the surface of single crystal (Type 1) MgO with of reduction. (400x) Temperature: 1350°C Dew point: -20°C Weight loss: 0.2 mg/sq.cm.
Figure 29. (contd.) The change in the morphology of the surface of single crystal (Type 1) MgO with reduction. (400x)
Temperature: 1350°C
Dew point: -20°C
Weight loss: 0.6 mg/sq.cm.
Figure 29. (contd.) The change in the morphology of the surface of single crystal (Type 1) MgO with reduction. (400x)
Temperature: 1350°C
Dew point: -20°C
Weight loss: 2.0 mg/sq.cm.
the weight of the sphere and time of reaction.

From Equation 23

\[
\frac{dm}{dt} = a_6 \cdot m^{1/3}
\]

and,

\[
m^{2/3} = m_0^{2/3} - a_7 \cdot t
\]  (37)

For interface reaction controlled reduction the rate of weight loss is directly proportional to the area of the sphere. In this case Equation 37 changes to:

\[
\frac{dm}{dt} = 4 \pi \rho \cdot r^2 \frac{dr}{dt}
\]

\[
m^{1/3} = m_0^{1/3} - a_8 \cdot t
\]  (38)

Equations 37 and 38 give the shape of the weight versus time curves for diffusion controlled and interface reaction controlled reductions respectively. These curves are included in Figure 30 along with the experimental curve. The curve corresponding to Equation 38 deviates most from the experimental curve. The curve for diffusion controlled reduction deviates slightly from the experimental curve. This deviation may be due to the pitting observed on the sample. Because of the subsurface reduction the diameter of the sample changes to a lesser extent.
Figure 30. Weight loss data for spheres for large weight loss.
5.2.2 Effect of Gas Flow Rate

For a diffusion controlled reduction, Equation 19 predicts that the flux varies linearly with the square root of the gas velocity. The results, as shown in Figure 10, follow this dependency. The standard free energy of the reaction calculated from the data (Table 2) varies between 45 Kcal/mole (189 KJ/mole) and 52 Kcal/mole (218.4 KJ/mole). The standard free energy of Reaction 1 calculated from available thermodynamic data (10) is 53 Kcal/mole (223 KJ/mole) at 1475°C and is close to the experimentally calculated values, indicating diffusion controlled reduction.

5.2.3 Effect of Temperature on Reduction

The standard enthalpy of the reaction calculated from the weight loss measurements of single crystals (using Equation 33 and tabulated in Tables 3 and 4) is 108.7 Kcal/mole (456.4 KJ/mole) with a standard deviation of 16 Kcal/mole (67.2 KJ/mole). The data for individual samples (Figures 11, 12 and 13) does not show much scatter. There does not seem to be any correlation between the known variables (temperature range, dew point, flow rate and sample size) and the deviation of the experimentally calculated enthalpy from the mean value. The standard enthalpy of the reaction calculated from the data in the
literature (10) is 115 Kcal/mole (483 KJ/mole) and is close to the mean of the experimentally calculated values of standard enthalpy. For polycrystalline plates, the mean standard enthalpy of reaction is 87.7 Kcal/mole (368.3 KJ/mole) with a standard deviation of 20 Kcal/mole (84.6 KJ/mole). Because of the preferential attack at the grain boundaries which dislodges whole grains from the surface, the enthalpy data for polycrystalline MgO are not meaningful.

5.2.4 Effect of Water Vapor Pressure on the Reduction

For diffusion controlled reduction Equation 34 gives the variation of flux with partial pressure of water vapor. The slope of the plot log(J) versus log(p^H2O) would be equal to -1 for a diffusion controlled reaction. The experimental data gives a slope of -0.82, which is higher than the expected value of -1. The source of this error is the assumption made in equation 34. It was assumed that p^H2O ~ p^H2O (since p^H2O is not known from the experiments). Even though the order of magnitude of both p^H2O and p^O H2O are the same, they do not have equal values. In fact p^H2O and p^O H2O are related by the flux equation:

\[ J_{H2O} = \frac{k_{Hg}}{RT} \cdot (p_{H2O}^* - p_{H2O}^O) \] (39)
Since the value of the flux changes by an order of magnitude over the range of the partial pressures of water vapor studied, the quantity \( (p^*_\text{H}_2\text{O} - p^0\text{H}_2\text{O}) \) also varies by an order of magnitude. Therefore, the assumption made in deriving Equation (34) is not valid when the value of the flux, \( J \), is high (i.e. at low partial pressures of water vapor). At low partial pressures of water vapor, the value of \( p^*_\text{H}_2\text{O} \) is greater than the value of \( p^0\text{H}_2\text{O} \) by a factor of 2 or 3. At high partial pressures of water vapor, when the flux is small, the assumption made in Equation 34 does not give rise to much error and the values of \( p^*_\text{H}_2\text{O} \) and \( p^0\text{H}_2\text{O} \) are close. The direct result of this assumption, then, is to increase the slope of the plot \( \log(J) \) versus \( \log(p^0\text{H}_2\text{O}) \).

From Equations 31 and 24

\[
p^*_\text{H}_2\text{O} = 0.5\left[p^0\text{H}_2\text{O} + \left\{(p^0\text{H}_2\text{O})^2 + 4K_{eq}\right\}^{0.5}\right] \quad (40)
\]

Now \( p^*_\text{H}_2\text{O} \) can be calculated from Equation 40 and from the values of the \( K_{eq} \) (available from literature) and used in Equation 34 instead of \( p^0\text{H}_2\text{O} \).

Using Equation 40 and the tabulated values of \( K_{eq} \) (reference (10)), the values of \( p^*_\text{H}_2\text{O} \) are calculated and \( \log(J) \) is plotted as a function of \( \log(p^*_\text{H}_2\text{O}) \) in Figures 31 and 32. The data for plates and spheres of Type 1 magnesium oxide are plotted in Figure 31 and cannot be fitted to one single straight line throughout the range of the partial
Figure 31. Dependence of flux on the equilibrium water vapor pressure for Type 1 MgO.
Figure 32. Dependence of flux on water vapor for Type 2 MgO.
pressures of water vapor investigated. Instead a parabola or two straight lines (one for the data at high vapor pressures and one for the data at low vapor pressures of water vapor) are required to account for the data. Both parabolas and two sets of straight lines are fitted to the data and the resulting errors and coefficients are examined. The errors (sum of the squared errors) are about the same in both cases. The coefficients were consistently close for the sets of straight lines whereas the coefficients for the parabolas varied widely. Also, when the transition from one region to the other is considered, there would be no difference between a parabola and a set of two straight lines. Therefore, the data in Figure 31 are represented as straight lines in the high and low vapor pressure (of water vapor) regions. The slopes of the lines and their standard deviations are given in Table 12. The average slope in the low partial pressure range \( (p^{*}_{\text{H}_2\text{O}} < 10^{-3}) \) is \(-1.78\) (standard deviation=0.27) whereas the slope in the high partial pressure range is \(-0.816\) (standard deviation=0.073).

The data for single crystal plates of Type 2 magnesium oxide are plotted in Figure 32, showing that the data can be fitted to a single straight line throughout the water vapor pressure range investigated. The slopes of these plots are given in Table 13. The average slope is \(-0.909\) (standard deviation 0.093). However, below \(1350^\circ\text{C}\) the data can't be fitted with a single line satisfactorily. As can be seen
Table 12. Slopes of Plots Log(Flux) vs. Log($p^*_{H_2O}$) for Plates and Spheres of Type 1 MgO.

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>TEMP °C</th>
<th>DEW PT. RANGE °C</th>
<th>SLOPE (STANDARD DEVIATION)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>$p_{H_2O}&lt;10^{-3}$</td>
</tr>
<tr>
<td>D084A</td>
<td>1450</td>
<td>-36.5 0.0</td>
<td>-1.969(0.385)</td>
</tr>
<tr>
<td>D085A</td>
<td>1425</td>
<td>-36.0 -2.0</td>
<td>-1.549(0.055)</td>
</tr>
<tr>
<td>D086A</td>
<td>1450</td>
<td>-36.0 -0.5</td>
<td>-1.990(0.075)</td>
</tr>
<tr>
<td>D087A</td>
<td>1450</td>
<td>-39.0 -2.0</td>
<td>-1.520(0.042)</td>
</tr>
<tr>
<td>D088A</td>
<td>1425</td>
<td>-33.0 -20.5</td>
<td>-1.579(0.089)</td>
</tr>
<tr>
<td>D088D</td>
<td>1450</td>
<td>-36.0 -21.0</td>
<td>-1.972(0.163)</td>
</tr>
<tr>
<td>D089A</td>
<td>1450</td>
<td>-35.5 -21.0</td>
<td>-1.603(0.097)</td>
</tr>
<tr>
<td>D089D</td>
<td>1490</td>
<td>-35.0 -20.0</td>
<td>-1.534(0.070)</td>
</tr>
<tr>
<td>D090A</td>
<td>1490</td>
<td>-35.5 -10.0</td>
<td>-2.307(0.077)</td>
</tr>
<tr>
<td>D097A</td>
<td>1450</td>
<td>+4.0 +19.0</td>
<td></td>
</tr>
<tr>
<td>D097D</td>
<td>1450</td>
<td>+1.0 +19.5</td>
<td></td>
</tr>
<tr>
<td>D098D</td>
<td>1450</td>
<td>-32.0 -10.0</td>
<td>-1.815(0.117)</td>
</tr>
<tr>
<td>D142A</td>
<td>1444</td>
<td>-10.0 +16.0</td>
<td></td>
</tr>
<tr>
<td>D142B</td>
<td>1464</td>
<td>-8.0 +18.5</td>
<td></td>
</tr>
<tr>
<td>D142C</td>
<td>1457</td>
<td>-11.0 +18.5</td>
<td></td>
</tr>
<tr>
<td>D143B</td>
<td>1446</td>
<td>-17.0 +17.0</td>
<td></td>
</tr>
</tbody>
</table>
Table 13. Slopes of Plots Log(Flux) vs. Log($p^{*}_{H_2O}$) for Plates of Type 2 MgO.

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>TEMP $^{\circ}$C</th>
<th>DEW PT. RANGE $^{\circ}$C</th>
<th>SLOPE OF THE PLOT AND STANDARD DEVIATION</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>$p_{H_2O}&lt;10^{-3}$</td>
</tr>
<tr>
<td>D099A</td>
<td>1300</td>
<td>-35.0 -17.5</td>
<td>-0.911 (0.065)</td>
</tr>
<tr>
<td>D100A</td>
<td>1475</td>
<td>-4.5 +17.0</td>
<td>-0.751 (0.015)</td>
</tr>
<tr>
<td>D101D</td>
<td>1475</td>
<td>-26.5 +18.0</td>
<td>-1.078 (0.022)</td>
</tr>
<tr>
<td>D102A</td>
<td>1475</td>
<td>-28.0 +15.0</td>
<td>-0.751 (0.015)</td>
</tr>
<tr>
<td>D102B</td>
<td>1425</td>
<td>-28.5 -6.0</td>
<td>-1.078 (0.022)</td>
</tr>
<tr>
<td>D113A</td>
<td>1450</td>
<td>-21.0 +19.0</td>
<td>-0.758 (0.043)</td>
</tr>
<tr>
<td>D114A</td>
<td>1425</td>
<td>-30.0 +2.5</td>
<td>-0.758 (0.043)</td>
</tr>
<tr>
<td>D114B</td>
<td>1345</td>
<td>-31.0 +2.0</td>
<td>-0.758 (0.043)</td>
</tr>
<tr>
<td>D116A</td>
<td>1475</td>
<td>-30.0 -9.0</td>
<td>-0.973 (0.050)</td>
</tr>
<tr>
<td>D116B</td>
<td>1453</td>
<td>-28.5 -9.0</td>
<td>-0.973 (0.050)</td>
</tr>
<tr>
<td>D116C</td>
<td>1427</td>
<td>-30.0 -8.0</td>
<td>-0.973 (0.050)</td>
</tr>
<tr>
<td>D119A</td>
<td>1401</td>
<td>-32.0 +0.5</td>
<td>-0.944 (0.031)</td>
</tr>
<tr>
<td>D119B</td>
<td>1377</td>
<td>-30.0 -6.0</td>
<td>-0.944 (0.031)</td>
</tr>
<tr>
<td>D120A</td>
<td>1340</td>
<td>-32.5 -10.0</td>
<td>-1.093 (0.080)</td>
</tr>
<tr>
<td>D120B</td>
<td>1340</td>
<td>-30.0 -7.0</td>
<td>-1.093 (0.080)</td>
</tr>
<tr>
<td>D120C</td>
<td>1350</td>
<td>-31.0 -7.5</td>
<td>-1.093 (0.080)</td>
</tr>
</tbody>
</table>
Figure 33. Dependence of flux on the equilibrium water vapor pressure for Type 2 MgO.
from Figure 33, two straight lines are necessary to adequately describe the data.

The free energies calculated using Equation 35 (given in Table 6) have a mean value of 52.17 Kcal/mole (219 KJ/mole) and a standard deviation of 6.16 Kcal/mole (25.9 KJ/mole). The values for those samples whose data falls primarily in the high water vapor pressure region are lower than the mean value. The standard free energy values calculated from the data in low water vapor pressure region are higher than the mean value.

The data, then, seem to indicate that there are two different processes occurring in the reduction of MgO by hydrogen. Depending on the partial pressure of the water vapor one or the other is predominant. By calculating the thermodynamic data from the measurements at low and high regions of water vapor pressure and comparing them, the above conclusion can be confirmed.

Substituting for $P^*_{H_2O}$ in Equation 39,

$$J_{H_2O} = \frac{k_{H_2O}}{2RT} \cdot \{ [(p^o_{H_2O})^2 + 4k_{eq}]^{0.5} - p^o_{H_2O} \} \quad (41)$$

At high water vapor pressures $\{(p^o_{H_2O})^2 > 4k_{eq}\}$ Equation 41 can be simplified to,

$$J_{H_2O} = \frac{b_1}{p^o_{H_2O}} - \frac{b_2}{(p^o_{H_2O})^3} + \frac{b_3}{(p^o_{H_2O})^5} - \cdots + \cdots \quad (42)$$
where
\[ b_1 = \left( \frac{k_{H2O}}{RT} \right) \cdot K_{eq} \]
\[ b_2 = \left( \frac{k_{H2O}}{RT} \right) \cdot (K_{eq})^2 \]
\[ b_3 = 2 \cdot \left( \frac{k_{H2O}}{RT} \right) \cdot (K_{eq})^3 \]

For the low water vapor pressure region \((p_{H2O}^o)^2 < 4K_{eq}\)
Equation 41 becomes:
\[ J_{H2O} = b_0 - b_1(p_{H2O}^o) + b_2(p_{H2O}^o)^2 - b_3(p_{H2O}^o)^4 + \ldots \quad (43) \]

where
\[ b_0 = \left( \frac{k_{H2O}}{RT} \right) \cdot (K_{eq})^{0.5} \]
\[ b_1 = \left( \frac{k_{H2O}}{2RT} \right) \]
\[ b_2 = \left( \frac{k_{H2O}}{8RT} \right) \cdot (K_{eq})^{-0.5} \]
\[ b_3 = \left( \frac{k_{H2O}}{128RT} \right) \cdot (K_{eq})^{-1.5} \]

Using Equations 42 and 43, the data that fall in the high and low regions of water vapor pressure are analysed and the results are given in tables 14 and 15, respectively.
Table 14. $K_{eq}$ Obtained by Fitting the Data to Equation 42.

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>TEMPERATURE $^\circ$C</th>
<th>$K_{eq}$</th>
<th>$k$ cm/sec</th>
<th>FREE ENERGY Kcal/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>D097A</td>
<td>1450</td>
<td>2.535E-05</td>
<td>0.531</td>
<td>36.51</td>
</tr>
<tr>
<td>D097D</td>
<td>1450</td>
<td>1.343E-05</td>
<td>0.842</td>
<td>38.70</td>
</tr>
<tr>
<td>D100A</td>
<td>1475</td>
<td>1.282E-05</td>
<td>2.179</td>
<td>39.43</td>
</tr>
<tr>
<td>D101D</td>
<td>1475</td>
<td>2.265E-05</td>
<td>1.562</td>
<td>37.43</td>
</tr>
<tr>
<td>D102A</td>
<td>1475</td>
<td>1.220E-05</td>
<td>2.637</td>
<td>39.60</td>
</tr>
<tr>
<td>D113A</td>
<td>1450</td>
<td>8.100E-06</td>
<td>2.049</td>
<td>40.45</td>
</tr>
<tr>
<td>SAMPLE</td>
<td>TEMPERATURE °C</td>
<td>$K_{eq}$</td>
<td>$k$ cm/sec</td>
<td>FREE ENERGY Kcal/mole</td>
</tr>
<tr>
<td>--------</td>
<td>----------------</td>
<td>---------</td>
<td>------------</td>
<td>---------------------</td>
</tr>
<tr>
<td>D088A</td>
<td>1425</td>
<td>3.46E-08</td>
<td>112.78</td>
<td>58.42</td>
</tr>
<tr>
<td>D088D</td>
<td>1450</td>
<td>3.40E-08</td>
<td>122.49</td>
<td>59.33</td>
</tr>
<tr>
<td>D089A</td>
<td>1450</td>
<td>4.19E-08</td>
<td>140.30</td>
<td>58.61</td>
</tr>
<tr>
<td>D089D</td>
<td>1490</td>
<td>9.97E-08</td>
<td>105.68</td>
<td>56.84</td>
</tr>
<tr>
<td>D119A</td>
<td>1401</td>
<td>4.28E-08</td>
<td>77.76</td>
<td>56.83</td>
</tr>
<tr>
<td>D120B</td>
<td>1340</td>
<td>3.25E-08</td>
<td>35.31</td>
<td>55.63</td>
</tr>
</tbody>
</table>
The free energies calculated for low water vapor pressures (Table 15) vary from 59.33 Kcal/mole (249.2 KJ/mole) to 55.63 Kcal/mole (233.7 KJ/mole) in the temperature range 1490°C to 1340°C. In comparison, the free energy values calculated from the data in the literature (10) vary from 52 Kcal/mole to 57 Kcal/mole. The standard free energy values from the data in the high water vapor pressure region are much lower and vary from 36.5 Kcal/mole (153.3 KJ/mole) to 40.45 Kcal/mole (170 KJ/mole).

From the above comparison, it can be concluded that the kinetics at high water vapor pressure are different from those at low water vapor pressure. The fluxes in the lower region are adequately described by assuming that Reaction 1 is the most favourable one. At higher water vapor pressures, the measured values are higher than the expected values.

The observed higher values of the flux may result because of the contribution of Reaction 3 or Reaction 5 or both. Even though the contribution of these reactions at low vapor pressures of water vapor are very small (compared to that of Reaction 1), at higher pressures of water vapor the vapor pressures of the products of these reactions may become comparable to those of the products of Reaction 1. For example, at 1700°C and a water vapor pressure of 10⁻², the vapor pressures of Mg(OH)₂, MgOH and Mg are:
\[ p^{*}_{\text{Mg(OH)}_2} = K_4 \cdot p^{*}_{\text{H}_2\text{O}} = 2.9 \times 10^{-8} \text{ atm.} \]

\[ p^{*}_{\text{MgOH}} = (K_3)^{1/2} = 1.6 \times 10^{-6} \text{ atm.} \]

\[ p^{*}_{\text{Mg}} = \left( \frac{K_1}{p^{*}_{\text{H}_2\text{O}}} \right) = 1.0 \times 10^{-5} \text{ atm.} \]

Once again the vapor pressure of Mg(OH)$_2$ is too low to have any effect on the reduction, but the vapor pressure of MgOH is 15\% of the vapor pressure of Mg and could influence the kinetics of the reduction at high water vapor pressures. The vapor pressure of MgOH does not depend on the water vapor pressure and is only a function of temperature. The molar flux due to the diffusion of MgOH into the bulk hydrogen gas is given by:

\[ J_{\text{MgOH}} = \left( \frac{k_{\text{MgOH}}}{RT} \right) \cdot (p^{*}_{\text{MgOH}}) \tag{44} \]

The measured flux is the sum of the diffusional fluxes of Mg and MgOH.

\[ J = \left( \frac{k_{\text{Mg}}}{RT} \right) \cdot (p^{*}_{\text{Mg}} + f_1 \cdot p^{*}_{\text{MgOH}}) \tag{45} \]

where \( f_1 \) is the ratio of mass-transfer coefficients for MgOH and Mg vapors. \( p^{*}_{\text{MgOH}} \) is not dependent upon \( p^{0}_{\text{H}_2\text{O}} \) and
is a constant at a constant temperature. Under these conditions, Equation 45 becomes (after substituting for $p^*_Mg$):

$$J \cdot \left( \frac{RT}{k_{Mg}} \right) - 0.5 \cdot \left[ \left( \frac{p^*_{H_2O}}{k_{Mg}} \right)^2 + 4 K_{eq} \right]^{1/2} - p^*_{H_2O} = b$$

where $b = \left( \frac{k_{MgOH}}{k_{Mg}} \right) \cdot p^*_{MgOH}$

The measured data are fitted to the above equation for different values of $K_{eq}$. The values of $K_{eq}$ for which the best fit is obtained are tabulated in Table 16. The corresponding values of $b$ are also given in the table. These values of $b$ are of the same order of magnitude as that of $p^*_{MgOH}$ calculated from literature. These results, then, indicate that at higher water vapor pressures the reduction of MgO occurs by the formation of Mg and MgOH vapors and is diffusion controlled (since all the equations are set up by assuming a diffusion controlled process).

5.2.5 Morphology of Reduced MgO

The formation of the holes observed on the surface may be due to one of the following reasons:
Table 16. Results of the Analysis of the Data with Equation (46).

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>TEMP °C</th>
<th>$K_{eq} \times 10^{-8}$</th>
<th>k cm/sec</th>
<th>ST. DEV. (for k)</th>
<th>CORR. COEF.</th>
<th>b atm $\times 10^{-6}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>D084A</td>
<td>1450</td>
<td>0.990</td>
<td>251.21</td>
<td>4.9</td>
<td>0.9992</td>
<td>3.995</td>
</tr>
<tr>
<td>D085A</td>
<td>1425</td>
<td>1.170</td>
<td>222.78</td>
<td>4.9</td>
<td>0.9991</td>
<td>0.662</td>
</tr>
<tr>
<td>D086A</td>
<td>1450</td>
<td>1.384</td>
<td>242.87</td>
<td>6.5</td>
<td>0.9986</td>
<td>1.708</td>
</tr>
<tr>
<td>D087A</td>
<td>1450</td>
<td>5.537</td>
<td>99.32</td>
<td>3.9</td>
<td>0.9986</td>
<td>3.716</td>
</tr>
<tr>
<td>D090A</td>
<td>1490</td>
<td>3.600</td>
<td>232.17</td>
<td>4.6</td>
<td>0.9988</td>
<td>8.668</td>
</tr>
<tr>
<td>D098A</td>
<td>1490</td>
<td>1.063</td>
<td>495.21</td>
<td>11.9</td>
<td>0.9989</td>
<td>1.846</td>
</tr>
<tr>
<td>D098D</td>
<td>1490</td>
<td>0.629</td>
<td>599.48</td>
<td>9.2</td>
<td>0.9994</td>
<td>1.987</td>
</tr>
<tr>
<td>D101D</td>
<td>1475</td>
<td>28.79</td>
<td>62.35</td>
<td>1.3</td>
<td>0.9967</td>
<td>1.549</td>
</tr>
<tr>
<td>D102A</td>
<td>1475</td>
<td>14.40</td>
<td>79.12</td>
<td>7.6</td>
<td>0.9574</td>
<td>25.911</td>
</tr>
<tr>
<td>D102B</td>
<td>1425</td>
<td>6.091</td>
<td>83.40</td>
<td>0.6</td>
<td>0.9999</td>
<td>3.864</td>
</tr>
<tr>
<td>D113A</td>
<td>1450</td>
<td>34.03</td>
<td>31.65</td>
<td>0.4</td>
<td>0.9991</td>
<td>13.341</td>
</tr>
<tr>
<td>D114A</td>
<td>1426</td>
<td>18.71</td>
<td>34.55</td>
<td>0.3</td>
<td>0.9996</td>
<td>10.197</td>
</tr>
<tr>
<td>D116A</td>
<td>1475</td>
<td>26.17</td>
<td>48.59</td>
<td>0.7</td>
<td>0.9991</td>
<td>29.504</td>
</tr>
<tr>
<td>D116B</td>
<td>1453</td>
<td>14.44</td>
<td>58.59</td>
<td>0.7</td>
<td>0.9995</td>
<td>7.026</td>
</tr>
<tr>
<td>D116C</td>
<td>1427</td>
<td>9.370</td>
<td>52.28</td>
<td>0.8</td>
<td>0.9990</td>
<td>3.021</td>
</tr>
<tr>
<td>D119A</td>
<td>1401</td>
<td>3.599</td>
<td>81.54</td>
<td>1.2</td>
<td>0.9987</td>
<td>3.470</td>
</tr>
<tr>
<td>D119B</td>
<td>1377</td>
<td>5.034</td>
<td>48.84</td>
<td>0.8</td>
<td>0.9988</td>
<td>1.565</td>
</tr>
</tbody>
</table>
(i) Impurities on the surface acting as poisons for the reduction or impurities at the apex of the holes acting as catalysts for the reduction.

(ii) Presence of lattice defects such as dislocations and sub-grain boundaries.

(iii) Temperature gradients in the sample.

(iv) Perturbation in the boundary layer.

A detailed discussion of each of these follows.

(i) Impurities

The analysis of reduced and as cleaved samples (Tables 1 and 7) shows that the concentration levels of Ca and Al are higher on the reduced sample surface (The analysis was done by arc-emission spectroscopy and therefore reflects surface compositions). Since the specimen were cleaved from bigger crystals, all starting (unreduced) surface compositions are representative of the bulk compositions. The rise in the concentration levels of Ca and Al must occur because these oxides are reduced to a lesser extent than MgO and are left behind at the reaction site. EDAX analysis (Table 11) also shows that the concentration levels of Al are higher on the surface indicating that Al is left behind in the reduction. If these materials act as poisons for the reaction, then the holes can not grow because Al accumulates as the reduction occurs and poisons the local area. On the other hand, when the impurities act as catalysts, there is no reason for the
formation of the holes (because EDAX shows high Al concentration on the surface). Therefore, there is no evidence that the impurities (mainly alumina) lead to the formation and growth of the holes on the surface.

(ii) Dislocations and Sub-grain Boundaries

From the micrographs in Figures 28 and 29 it is evident that the holes do not necessarily form at the dislocation sites. The single crystal samples used usually have sub-grain boundaries which would be outlined if the holes form at the dislocation sites. No sub-grain boundaries can be seen on the surface of the crystals that were reduced (but not etched).

(iii) Temperature Gradients in the Sample

The predominant mode of heat transfer to the specimen is radiation because the conductivity of the gas is very low and because the heat radiated is proportional to the fourth power of the temperature. The specimen and the thermocouple (used to measure the temperature of the specimen) are surrounded by an alumina tube which is the source of the radiation. However, there may not be enough heat transfer to the gas (by conduction, convection and radiation) to raise the temperature of the gas to that of the sample. The following calculations elucidate the points made above.
(a) Heat Transfer from Alumina Tube to Hydrogen Gas.

Because of the lack of exact solutions to the heat transfer equations involved the following assumptions are necessary.

Throughout the length of the tube (till the gas reaches the hot zone) the heat flux from the tube to gas is constant.

The properties of the gas do not vary.

Under these conditions the Nusselt number is given by the following equation (26).

\[
N_{ud} = 4.36 + \frac{0.0360 \cdot (d/L) \cdot Re_d \cdot Pr}{1 + 0.0011[(d/L) \cdot Re_d \cdot Pr]} \tag{47}
\]

where:

the subscript d means that the dimensionless number is calculated using the diameter of the tube.

\( L \) is the length of the tube

\[
Pr = \frac{\text{viscosity} \cdot \text{heat capacity}}{\text{thermal conductivity}} \quad = 0.614
\]

\[
Re_d = 0.38
\]

\[
N_{ud} = \frac{h \cdot d}{k}
\]

\( h \) = heat transfer coefficient

\( k \) = thermal conductivity

Substituting the numbers,
The heat flux from the tube to the gas, \( Q \), is given by:

\[
Q = \text{area} \cdot h \cdot (T_t - T_g)
\]

\[
Q = 1.05(T_t - T_g)
\]

The average flow rate of gas is 2400 cc/min. The energy required to heat the gas from room temperature to the hot zone temperature is 0.0143\( T_g \) cal/sec.

From these calculations at the tube temperature, \( T_t \), of 1500°C, the average temperature of the gas is about 1480°C. Since the Reynolds number is low the actual temperature of the gas at the center of the tube would be much lower.

(b) Heat transfer to the Sample by Radiation

The heat flux from the tube to the sample is given by

\[
Q = A_s \cdot F' \cdot C \cdot (T_t^4 - T_s^4)
\]

where

\[
F' = \frac{1}{\left( \frac{1}{F} \right) + \left( \frac{1}{E_1} - 1 \right) + \frac{A_s}{A_t} \cdot \left( \frac{1}{E_2} - 1 \right)}
\]

where \( A_s = \) area of the sample

\( A_t = \) area of the tube
\[ F = \text{geometric factor and is equal to unity for a small object totally surrounded by the larger object} \]

\[ \sigma = \text{Stefan-Boltzmann constant} \]

\[ \varepsilon_2 = \text{Emissivity of the radiating surface} \]

\[ \varepsilon_1 = \text{absorptivity of the sample}. \]

Magnesium oxide crystals are transparent to infrared radiation up to 6 microns wavelength (33). The transmission decreases from >95\% at 6.5 microns (for a MgO plate 0.91 mm thick (33)) to very low values at 10 microns. The 50\% transmission wavelength is about 9 microns (33,34). In the above equation, the integrated absorptivity in the wavelength range of 6 to 10 microns should be used. The integrated absorptivity calculated from the published data (33) is 0.25 in the wavelength range of 6 to 10 microns.

From a black body at 1500°C, the total intensity of radiation above 6 microns wavelength is about 7\%.

The integrated emissivity of alumina in the wavelength range of 1 to 10 microns is 0.62 (35). At wavelengths exceeding 5 microns, the emissivity of alumina is close to 1.

The heat absorbed by the sample can be calculated by substituting,
\[ F^\prime = \varepsilon_1 = 0.25 \]
\[ \varepsilon_2 = 1 \]
\[ T_t = 1773^\circ K \]
\[ T_s = 1723^\circ K \]
\[ A_s = 1 \]

\[ Q = A_s \cdot F^\prime \cdot \sigma \cdot (T_t^4 - T_s^4) \times 0.07 \]

Q, the heat absorbed by the specimen is 0.02 cal/sec. With this rate of energy absorption, the time required to increase the temperature of 0.5 mg specimen by 1°C is about 6 seconds. If the temperature difference is only 10°C, then the time required would be 0.5 minutes.

From these observations, it is clear that the temperature of the specimen is almost equal to that of the alumina tube (under steady state conditions). The temperature of the gas, on the other hand, is lower. Also unlike the case of opaque materials, the radiation absorption in the MgO specimen occurs not just at the surface but throughout the bulk of the specimen. This phenomenon, together with the cooling of the surface of the sample by the gas (which is at a lower temperature) lead to temperature gradients in the sample (with the interior of the sample being hotter than the surface). A simplified
Figure 34. Temperature profile through flowing gas and magnesium oxide sample.
schematic of the temperature profile in the sample and the
gas is shown in Figure 34.

Under the circumstances, any depression on the surface
of the crystal would be unstable and tends to grow into the
bulk of the specimen. The partial pressures of the reaction
products at the bottom of the hole (because of higher
temperatures) would be higher than those at the surface and
a significant portion of the weight loss occurs from the
bulk of the sample.

(iv) Perturbation in the Boundary Layer

In some instances during vapor growth of crystals
similar surface instability has been observed. Reed and
LaFleur (27,28) were able to explain the growth of
dendrites during the growth of iodine and camphor crystals
from vapor phase on the basis of supersaturation of the
vapor in the boundary layer. The supersaturation occurs
when the temperatures in the boundary layer are not high
enough. Extending this treatment to the reduction of
magnesium oxide, a perturbation which causes a temporary
decrease in the partial pressures of the products at some
random location on the sample surface may lead to the
surface instability observed experimentally. For the
benefit of the doubt, imagine that such a disturbance occurs
close to the surface. In this case, the depletion in the
partial pressures may be countered with (i) diffusion
(gaseous) from the adjacent areas so as to damp out the
perturbation or (ii) with additional reaction at the local area or with both of the above mentioned processes. The first option does not lead to any topological unevenness whereas the second one leads to a depression or a hole on an otherwise smooth surface. This happens only when the diffusion is extremely slow and the rate of the (forward) reaction is high. If this were to continue, the depression on the surface would also continue to grow. But the width to depth ratio of the depression should be equal to, or more than, one. This makes the depression a shallow pit or, at the most, semispherical. This model is not consistent with observations (because the surface contains holes that are many times deeper than they are wide and they are too numerous). This model also assumes that the perturbation persists in the same location for extended periods for which there is no justification.
6. CONCLUSIONS AND SUGGESTIONS FOR FURTHER RESEARCH

6.1 Conclusions

1. The reduction of magnesium oxide in hydrogen occurs by the formation of Mg vapor and water vapor when the ambient water vapor pressure is low. At higher ambient water vapor pressures the magnesium lost is in the form of magnesium monohydroxide and magnesium vapor.

2. The rate controlling step in the reduction of magnesium oxide is the diffusion of the products through the gaseous boundary layer.

3. The standard enthalpy of reduction is 108.7 Kcal/mole (456.4 KJ/mole) with a standard deviation of 16 Kcal/mole (67.2 KJ/mole).

4. For polycrystalline MgO the reduction occurs almost entirely at the grain boundaries. The apparent standard enthalpy of reaction for this process is 87.7 Kcal/mole (368.3 Kcal/mole) with a standard deviation of 20 Kcal/mole (84.6 Kcal/mole).

5. The standard free energy of the reduction to Mg vapor and water vapor is 60.5 Kcal/mole (254.1 KJ/mole) at 1450°C for Type 1 MgO (obtained from Oak Ridge National Laboratory). For Type 2 crystals the standard free energy of reduction is 52.8 Kcal/mole (221.8 KJ/mole) at 1450°C.
6. Surfaces of reduced single crystals of magnesium oxide are not smooth (as the starting surfaces were) but are full of holes. The holes grow into the crystal as the reduction proceeds. The reason for the formation of these holes is the temperature gradient in the crystal. The temperature gradient arises because the crystal is mainly heated by radiation.

7. Aluminum oxide, present as an impurity, is left over as a reaction product and accumulates at the site of reaction.

6.2 Suggestions for Further Research

1. Studies of polycrystalline magnesium oxide should prove helpful in the assessment of the performance of magnesia refractories under reducing environments. Since the grain boundary phase plays an important role in the gaseous corrosion of magnesia refractories its characterization is important.

2. Analysis of the reduction products with a mass spectrometer would shed further light on the reduction process.

3. Reduction studies done at lower temperatures might be surface reaction controlled and the kinetics may give information about the surface process. Since the rates are very low fine powdered material may have to be used.
REFERENCES


