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High-temperature effects of oxidation on MgO-SiC composites

Hallum, Gary Wade, Ph.D.
The Ohio State University, 1990
HIGH TEMPERATURE EFFECTS OF OXIDATION ON
MgO-SiC COMPOSITES

A Dissertation

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

by

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* * * * *

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To Lisa and Max
ACKNOWLEDGEMENTS

To everyone that has helped me along the way, I am greatly indebted.
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# TABLE OF CONTENTS

ACKNOWLEDGEMENTS ............................................... iii

VITA ............................................................. iv

TABLE OF CONTENTS .............................................. v

LIST OF TABLES ................................................. vii

LIST OF FIGURES ................................................ viii

CHAPTER PAGE

| I. INTRODUCTION ........................................... | 1 |
| II. LITERATURE REVIEW......................................... | 3 |

2.1 INTRODUCTION ........................................... 3
2.2 OXIDATION OF CERAMIC COMPOSITES ......................... 4
  2.2.1 OXIDATION OF SiC ................................... 4
  2.2.2 OXIDATION OF COMPOSITE CERAMICS ................. 5
  2.2.3 OXIDATION KINETICS ................................ 8
  2.2.4 INTERFACIAL REACTIONS .............................. 12
2.3 TOUGHENING MECHANISMS .................................. 13
  2.3.1 CRACK DEFLECTION .................................. 14
  2.3.2 MICROCRACK TOUGHENING ............................ 19
  2.3.3 CRACK BRIDGING .................................... 21
  2.3.4 CRACK BRANCHING .................................. 24
  2.3.5 CRACK BOWING ...................................... 27

III. THEORY ................................................. 29

  3.1 SYSTEM REQUIREMENTS .................................. 29
  3.2 THERMODYNAMICS ....................................... 29
  3.3 KINETICS ............................................... 30
    3.3.1 REACTION MECHANISMS .............................. 30
    3.3.2 REACTION RATE CONTROLLED ....................... 31
    3.3.3 DIFFUSION REACTION CONTROLLED .................. 34
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.4 Oxidation of MgO containing SiC</td>
<td>37</td>
</tr>
<tr>
<td>IV. Experimental Procedure</td>
<td>41</td>
</tr>
<tr>
<td>4.1 Sample Preparation</td>
<td>41</td>
</tr>
<tr>
<td>4.1.1 MgO/SiC Powder Composite</td>
<td>41</td>
</tr>
<tr>
<td>4.1.2 MgO/SiC Whisker Composite</td>
<td>44</td>
</tr>
<tr>
<td>4.1.3 Composite Consolidation</td>
<td>44</td>
</tr>
<tr>
<td>4.2 Mechanical Testing</td>
<td>48</td>
</tr>
<tr>
<td>4.3 Experimental Apparatus</td>
<td>57</td>
</tr>
<tr>
<td>4.3.1 TGA Experiments</td>
<td>57</td>
</tr>
<tr>
<td>4.3.2 Oxidation Experiments</td>
<td>58</td>
</tr>
<tr>
<td>4.3.3 Dilatometer Experiments</td>
<td>58</td>
</tr>
<tr>
<td>4.4 Microstructural Analysis</td>
<td>59</td>
</tr>
<tr>
<td>4.5 Data Reduction</td>
<td>60</td>
</tr>
<tr>
<td>V. Results</td>
<td>61</td>
</tr>
<tr>
<td>5.1 Introduction</td>
<td>61</td>
</tr>
<tr>
<td>5.2 Microstructural Effects</td>
<td>61</td>
</tr>
<tr>
<td>5.2.1 Thermal Expansion</td>
<td>61</td>
</tr>
<tr>
<td>5.2.2 Oxidation Expansion</td>
<td>63</td>
</tr>
<tr>
<td>5.3 Fracture Mechanics</td>
<td>66</td>
</tr>
<tr>
<td>5.3.1 Fracture Toughness</td>
<td>66</td>
</tr>
<tr>
<td>5.3.2 Fracture Strength</td>
<td>70</td>
</tr>
<tr>
<td>5.4 Oxidation Behavior</td>
<td>74</td>
</tr>
<tr>
<td>5.4.1 Oxidation Effects On Strength</td>
<td>74</td>
</tr>
<tr>
<td>5.4.2 Oxidation Effects On Microstructure</td>
<td>83</td>
</tr>
<tr>
<td>5.4.3 Fractography</td>
<td>91</td>
</tr>
<tr>
<td>5.4.4 Oxidation Kinetics</td>
<td>96</td>
</tr>
<tr>
<td>VI. Discussion</td>
<td>110</td>
</tr>
<tr>
<td>6.1 Oxidation Effects On Microstructure</td>
<td>110</td>
</tr>
<tr>
<td>6.1.1 Effect On Surface</td>
<td>110</td>
</tr>
<tr>
<td>6.1.2 Effect On Composite Interior</td>
<td>111</td>
</tr>
<tr>
<td>6.2 Oxidation Effect On Strength</td>
<td>116</td>
</tr>
<tr>
<td>6.3 Oxidation Kinetics</td>
<td>127</td>
</tr>
<tr>
<td>6.3.1 Volume Expansion And SiO2</td>
<td>127</td>
</tr>
<tr>
<td>6.3.2 Effect Of Composition On Rate</td>
<td>130</td>
</tr>
<tr>
<td>6.3.3 Parabolic Kinetics</td>
<td>132</td>
</tr>
<tr>
<td>6.3.4 Comparison With Diffusion Models</td>
<td>138</td>
</tr>
</tbody>
</table>
APPENDICES

A. DENSITY CALCULATIONS .................................. 146
B. CALCULATION OF OXIDATION THICKNESS FROM TGA DATA ... 148
C. INDEXING OF Mg$_2$SiO$_4$ ................................... 150

LIST OF REFERENCES .............................................. 153
LIST OF TABLES

<table>
<thead>
<tr>
<th>TABLE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Chemical Lot Analysis of MgO Powder</td>
<td>42</td>
</tr>
<tr>
<td>2. Chemical Lot Analysis of SiC Whiskers</td>
<td>42</td>
</tr>
<tr>
<td>3. Hot-Pressing Times, Temperatures and Pressures</td>
<td>44</td>
</tr>
<tr>
<td>4. Data From Fracture Toughness Measurements</td>
<td>72</td>
</tr>
<tr>
<td>5. Retained Room Temperature Strengths for MgO/SiC Powder Composites</td>
<td>79</td>
</tr>
<tr>
<td>6. Retained Room Temperature Strengths for MgO/SiC Whisker Composites</td>
<td>84</td>
</tr>
<tr>
<td>7. Flaw Sizes Calculated from Equations 2 and 56 as compared to Oxidation Depth</td>
<td>126</td>
</tr>
<tr>
<td>8. Experimentally Determined Parabolic Rate Constants</td>
<td>133</td>
</tr>
<tr>
<td>9. Experimental Activation Energies for the Oxidation of MgO-SiC Composites</td>
<td>135</td>
</tr>
<tr>
<td>10. Tabulated Lattice and Grain Boundary Activation Energies and Diffusion Constants</td>
<td>136</td>
</tr>
</tbody>
</table>
**LIST OF FIGURES**

<table>
<thead>
<tr>
<th>FIGURES</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Oxidation depth as a function of time for alumina with SiC whiskers (From Lin)</td>
<td>10</td>
</tr>
<tr>
<td>2. Mass gain per unit area during the oxidation of Al₂O₃/SiC composites (From Luthra)</td>
<td>11</td>
</tr>
<tr>
<td>3. Deflection of a crack by a second-phase particle (From Faber)</td>
<td>15</td>
</tr>
<tr>
<td>4. Stress intensity, K, modes on a crack: (A) Mode I opening; (B) Mode II, sliding; (C) Mode III tearing</td>
<td>16</td>
</tr>
<tr>
<td>5. Effect of second phase particle shape and volume fraction on toughening due to crack deflection</td>
<td>18</td>
</tr>
<tr>
<td>6. Effect of whisker bridging on overall toughness of composite (From Becher)</td>
<td>22</td>
</tr>
<tr>
<td>7. K_p/K_1c as a function of the materials brittleness, H/K_1c (From Kirchner)</td>
<td>26</td>
</tr>
<tr>
<td>8. Determination of grain boundary area</td>
<td>36</td>
</tr>
<tr>
<td>9. Phase diagram for the MgO-SiO₂ system</td>
<td>39</td>
</tr>
<tr>
<td>10. SEM micrograph of as-received A) MgO Powder; and B) SiC Whiskers</td>
<td>43</td>
</tr>
<tr>
<td>11. SEM micrograph of polished and etched surface of MgO/SiC whisker composite: A) 5; B) 10; and C) 15 volume percent</td>
<td>46</td>
</tr>
</tbody>
</table>
12. SEM micrograph of polished and etched surface of MgO/SiC powder composite: A) 5; B) 10; and C) 15 volume percent. 47

13. SEM micrograph of fractured surfaces of MgO/SiC whisker composites: A) 5; B) 10; and C) 15 volume percent. 49

14. SEM micrograph of fractured and etched surface showing alignment of whiskers. 50

15. TEM micrograph of SiC whiskers in MgO matrix. 51

16. SEM micrograph of fractured surfaces of MgO/SiC powder composites: A) 5; B) 10; and C) 15 volume percent. 52

17. Orientation of test bars cut from hot-pressed MgO/SiC composite. 53

18. Placement of Vicker's indentation on tensile surface of test bar. 55

19. Experimental and calculated coefficients of thermal expansion for MgO/SiC composites. 62

20. Volume expansion of (A) MgO/SiC whisker and (B) MgO/SiC powder composites after oxidation at 1500°C. 64

21. Linear expansion of MgO/SiC composites oxidized between 1300 and 1500°C. 65

22. SEM micrograph of Vicker's indentation on the polished and etched surface of MgO/SiC whisker composite. 67

23. SEM micrograph of crack bridging in (A) MgO/SiC whisker and (B) MgO/SiC powder composites. 68

24. Fracture strength of pure MgO as a function of indentation load. 69

25. Measured fracture toughness of MgO/SiC composites... 71
26. Fracture strengths of unindented and unoxidized MgO and MgO/SiC composites ......................... 73

27. SEM micrograph of fracture origins in A) Pure MgO; and; B) MgO/SiC composites ....................... 74

28. Room temperature strengths of oxidized MgO containing 5 volume percent SiC whiskers .............. 75

29. Room temperature strengths of oxidized MgO containing 10 volume percent SiC whiskers ............. 76

30. Room temperature strengths of oxidized MgO containing 15 volume percent SiC whiskers .......... 77

31. Room temperature strengths of oxidized MgO containing 5 volume percent SiC powder ............... 80

32. Room temperature strengths of oxidized MgO containing 10 volume percent SiC powder .......... 81

33. Room temperature strengths of oxidized MgO containing 15 volume percent SiC powder ............. 82

34. Pore formation in MgO sample containing 5 volume percent SiC whiskers oxidized at 1500°C for 1.5 hours ........................................... 85

35. Optical micrograph of polished cross section observed of MgO through polarized light containing 5 volume percent SiC whiskers oxidized at 1400°C for 1.5 hours.............................................. 86

36. Effect of oxidation time on the as-ground surface of MgO containing 5 volume percent SiC whiskers oxidized at 1300°C for: A) 0; B) 0.5; C) 1.5 and D) 3 hours .......................................... 87

37. Effect of oxidation temperature on as-ground surface of MgO containing 5 v/o SiC whiskers oxidized at: A) 1100°C; B) 1200°C; C) 1300°C; D) 1400°C for 1 hour .................................................. 88

38. X-ray diffraction data of surface of MgO/15 v/o SiC whiskers oxidized (A) 0 hours and (B) 2 hours... 89
39. TEM micrograph of oxidized surface of MgO/15 v/o whiskers indicating position of Mg$_2$SiO$_4$ particles and SAD pattern oxidized at 1500°C for 20 hours.

40. Columnar grain growth on MgO/15 v/o SiC whisker sample oxidized at 1500°C for 1.5 hours.

41. X-ray diffraction indicating orientation of (110) grains on oxidized surface of composite.

42. Whisker pullout in MgO/SiC composite oxidized at 1200°C for 0.5 hours.

43. SEM micrograph of partially oxidized SiC whisker in MgO matrix.

44. TEM micrograph of oxidized composite showing possible pore formation between the whisker and matrix.

45. TGA trace of percentage weight gain as a function of time for MgO containing 5 v/o: A) SiC Whiskers B) SiC Powder.

46. TGA trace of percentage weight gain as a function of time for MgO containing 10 v/o: A) SiC Whiskers B) SiC Powder.

47. TGA trace of percentage weight gain as a function of time for MgO containing 15 v/o: A) SiC Whiskers B) SiC Powder.

48. Log-log plot of percentage weight gain as a function of time for MgO containing 5 v/o: A) SiC whiskers and B) SiC powder.

49. Log-log plot of percentage weight gain as a function of time for MgO containing 10 v/o: A) SiC whiskers and B) SiC powder.

50. Log-log plot of percentage weight gain as a function of time for MgO containing 15 v/o: A) SiC whiskers and B) SiC powder.

51. Oxidation depths calculated from TGA as a function of time for MgO containing 5 v/o: A) SiC Whiskers and B) SiC Powder.
52. Oxidation depths calculated from TGA as a function of time for MgO containing 10 v/o: A) SiC Whiskers and B) SiC Powder............................................. 105

53. Oxidation depths calculated from TGA as a function of time for MgO containing 15 v/o: A) SiC Whiskers and B) SiC Powder............................................. 106

54. Comparison of oxidation depths calculated from thermogravimetric analysis and measured from polished cross sections of partially oxidized samples............................................. 107

55. Effect of SiC concentration on the calculated oxidation depths at 1200°C............................................. 108

56. Polarized optical micrograph of MgO composite oxidized at 1400°C for 1.5 hours showing different reaction regions............................................. 112

57. TEM micrograph of porous reaction layer of oxidized composite (oxidized at 1400°C, 2 hours). Arrows indicate pores............................................. 114

58. SEM micrograph of polished cross section of composite partially oxidized at 1500°C for 10 hours............ 115

59. SEM micrograph of sputtered platinum on surface of composite oxidized at 1500°C for 20 hours............ 117

60. Plot of standard deviations of fracture studies as a function of oxidation time............................................. 119

61. SEM micrograph of: A) crack in columnar grain growth layer; B) larger view of inset............................................. 123

62. SEM micrograph of crack formation on surface of composite oxidized at 1200°C for 30 minutes............ 124

63. SiC-SiO₂-O stability diagram at 1700°C. Partial pressures of CO are also shown................................. 129

64. Calculated oxidation depths as a function inverse square root of volume fraction. Data for Alumina taken from Lin............................................. 131
65. Parabolic rate constant, $K_w$, plotted as a function of inverse temperature: A) MgO/SiC whiskers; and B) MgO/SiC powder.

66. The product $\delta D_b$ plotted as a function of inverse temperature for: A) MgO/SiC whiskers; and B) MgO/SiC powder obtained from experimental data.

67. The coefficient $D_L$ plotted as a function of inverse temperature for: A) MgO/SiC whiskers; and B) MgO/SiC powder obtained from experimental data.

68. Comparison of tabulated oxygen lattice diffusion coefficients and experimental lattice diffusion coefficients.

69. Comparison of reported oxygen grain boundary coefficients and calculated experimental grain boundary diffusion coefficients.

70. Comparison of reported magnesium lattice diffusion coefficients and experimental lattice diffusion coefficients.
CHAPTER I

INTRODUCTION

The majority of ceramics exhibit brittle behavior due either to defects within the matrix and/or their low resistance to fracture, or fracture toughness. Processing has reduced the size of most strength controlling flaws to the point that they are now difficult to detect by most modern methods. Therefore, increasing effort has been put into improving the fracture toughness of ceramics so that the material is more resistant to flaws within the matrix material. The method of increasing toughness of importance in this study is the addition of second-phase particulates, typically whiskers, to an oxide, MgO, matrix. SiC whiskers are chosen for their incredible strength and high elastic modulus\(^1\) as well as their ability to be processed within the matrix material easier than SiC fibers. The target use for most oxide ceramics containing SiC whiskers are in high temperature structural applications. Oxides previously studied for matrix materials include alumina\(^2\), zirconia\(^3\), mullite\(^4\) and magnesia\(^5\). These oxides were chosen because of their stability in high temperature oxidizing atmospheres. Similarly, SiC alone is also stable in an oxidizing atmosphere protected by an SiO\(_2\) product layer on the surface. However, recent investigations have shown
that there may be problems associated with the combination of SiC and the matrix oxide in high temperature oxidizing atmospheres. Alumina\textsuperscript{6} and mullite\textsuperscript{7} containing whiskers have been studied in oxidizing environments and several effects have been observed. The strengths of these materials degrade with temperature, a result of cavity formation and coalescence under creep conditions\textsuperscript{8-10}. Oxidation of these materials also results in weight gain that follows a parabolic rate law\textsuperscript{6,7}. Although activation energies have been obtained for the reactions, it is still unclear what mechanisms may be controlling the overall oxidation reaction. Therefore, it is the purpose of this study to examine the effects of oxidation on the microstructure and retained room temperature strength of MgO containing SiC whiskers or particulates. MgO has been chosen for several reasons: 1) the material can be easily fabricated into a dense composite microstructure; 2) MgO does not form a low temperature eutectic glass with SiO\textsubscript{2} keeping the grain boundaries free of glass; and finally, 3) the diffusional processes in MgO have been well studied allowing the possible determination of the reaction controlling mechanism during oxidation. Several areas that will be examined will be the effect that the volume percentage of SiC in the MgO matrix will have on the microstructure and on the oxidation resistance of the composite. Also of importance are the kinetics of the oxidation reaction and the products formed in the matrix from the oxidation reaction.
CHAPTER II

LITERATURE REVIEW

2.1 INTRODUCTION

The interest in whisker reinforced ceramics has grown considerably in the last five years. The possible increase in fracture toughness has lead to the potential use of ceramics in several structural applications. The systems that have been developed typically have single crystal silicon carbide whiskers embedded in a ceramic matrix on the order of five to sixty volume percent. Matrices range from Si₃N₄ to Al₂O₃ with each matrix chosen for a specific application. Currently, oxide matrices such as Al₂O₃, ZrO₂ and mullite have been studied because of the ability to produce strong, dense and tough ceramic composites from these oxide materials. The microstructure, crack behavior, and mechanical behavior at room and elevated temperatures, of several systems have been studied. However, few of these studies examine the effects that high temperature oxidation has on the microstructure and the oxidation mechanisms and kinetics. Therefore, it is the purpose of this investigation to understand the relationship between strength, composition, time, temperature and the mechanisms and kinetics of the oxidation reaction.
2.2 OXIDATION OF CERAMIC COMPOSITES

2.2.1 Oxidation of Silicon Carbide

The oxidation of SiC can occur by two processes: 1) active oxidation occurs at low partial pressures of oxygen resulting in weight loss from SiO and carbonaceous gases being formed; 2) passive oxidation occurs at higher oxygen partial pressures and results in the formation of an SiO_2 product layer and carbonaceous gases. In this study, it is likely that the oxidation of SiC will occur at low oxygen pressures, however, because the SiC will be within an MgO matrix, SiO formation will be limited because of its low partial pressure and SiO_2 will be formed. Therefore, the passive oxidation of SiC will be discussed. Studies\textsuperscript{28,29} have been done on the passive oxidation of SiC in which SiC reacts with oxygen according to:

\[
\text{SiC}_\text{(s)} + \frac{3}{2} \text{O}_\text{2(g)} = \text{SiO}_2\text{(s)} + \text{CO(g)} \tag{1}
\]

with SiO_2 and CO being formed at the SiO_2/SiC reaction interface. The oxidation of SiC is similar to the passive oxidation of pure silicon which can be modeled by a linear-parabolic rate law developed by Deal and Grove\textsuperscript{30}. In the early stages of silicon oxidation, the reaction can be modeled by a linear rate law. As the oxide product layer increases on the surface, the oxidation reaction begins to be controlled by diffusion of the oxidant through the product layer to the reaction interface. It is the diffusion of the oxidant through the product layer.
that results in classic parabolic oxidation kinetics where the oxide thickness is proportional to the square root of time. Similarly, SiC shows parabolic reaction rate oxidation\textsuperscript{28-30}, although it is slower than silicon oxidation because the carbon also reacts with the oxygen.

A primary artifact in the oxidation of polycrystalline SiC, is the formation of bubbles at the SiO$_2$/SiC interface that have been attributed to CO evolution\textsuperscript{30}. This assumption is based on the premise that CO can not readily diffuse out through the oxide scale and can only be released to the atmosphere via bubbles. Meiskowski et al.\textsuperscript{31}, however, attributed bubble formation in the oxide scale to carbon inclusions within the polycrystalline SiC. This was supported by the fact that the oxidation of single crystal SiC did not produce bubbles in the oxide scale. Even for CO bubbles to form in polycrystalline SiC, it has been suggested that a critical SiO$_2$ product layer thickness ($\approx 0.3 \, \mu$m) must be reached. Most commercially available SiC whiskers have diameters in this range\textsuperscript{32}. The critical thickness for bubble formation is controlled by the permeation of CO through the oxide scale. The diffusion of CO away from the reaction interface has been suggested as the mechanism that controls the overall oxidation of SiC\textsuperscript{29,31}.

2.2.2 Oxidation of Composite Ceramics

Oxide ceramics are typically stable in high temperature oxidizing atmospheres. However, if oxidizable second-phase particles are present in the matrix material either at the grain boundaries or within the
grains, oxidation can result in material degradation. Carbon contamination in dense oxide materials can result in pore formation due to the formation of carbonaceous gasses at high temperatures. Bennison and Harmer\textsuperscript{33} observed such pore formation in hot-pressed alumina and attributed it to the oxidation of carbon contamination at the grain boundaries. Sambell\textsuperscript{5} conducted high temperature strength studies in air on MgO containing carbon whiskers. A reduction in strength above 400°C was the result of crack formation due to the progressive oxidation of the carbon whiskers. The mechanisms of the reaction were not determined but it was found that the cracks in the matrix may have resulted in a faster oxidation rate. Hallum\textsuperscript{34} studied the oxidation kinetics of MgO containing one volume percent carbon particles and found that material degradation occurred due to pore formation from product gases. The oxidation rate was linear with time and had an activation energy of 298 kJ/mole. This activation energy is similar to reported activation energies\textsuperscript{35-39} for oxygen transport along the grain boundaries and indicates a possible diffusion controlling mechanism.

Oxidation studies of ceramic oxides containing SiC whiskers or particles are very few. The majority of high temperature studies on oxides containing SiC whiskers have been to examine creep\textsuperscript{9,21,22,40} or high temperature strength\textsuperscript{3,9}. In creep studies of alumina containing SiC whiskers from 1200° to 1450°C for times up to 1000 hours, the mechanisms of failure were creep cavitation and coalescence of cavities along the grain boundaries. A glass phase was found at the oxide-
whisker interface but no mention of gas bubbles within the matrix was made. A variety of high temperature strength studies were done on oxide-whisker composites. MgO containing carbon whiskers showed a decrease in strength above 400°C due to crack formation, possibly due to CO formation in the matrix\textsuperscript{5}. The strength of tetragonal ZrO\textsubscript{2} polycrystals with SiC whiskers also degraded with increasing temperature but remained stronger than the matrix material at 1000°C\textsuperscript{3}. The overall strength decrease in the oxidizing environment was due to oxidation of the whiskers creating a glass interface and possibly CO pressure build-up. Becher\textsuperscript{8} studied the retained strength of alumina containing SiC whiskers after the composite had been oxidized between 200° to 1200°C from 1 to 250 hours. Samples were subjected to loads of up to \( \frac{1}{4} \) the fracture strength at the desired oxidation temperature. After a specified time the load was rapidly increased until the samples fractured. Becher found that the strengths of composites oxidized below 1100°C increased or remained unchanged with exposure time. Formation of a glass phase during oxidation was suggested as a mechanism of blunting surface cracks resulting in a retained strength or an improvement in strength. Above 1100°C, strength degradation occurred rapidly due to creep processes such as crack nucleation and growth along the grain boundaries. Cavitation was further enhanced by the presence of a product glass found along the grain boundaries. Similar marked decreases in fracture strengths were observed by Niihara\textsuperscript{9} who found that the fracture strength of alumina-SiC particle composites abruptly
degraded above 1000°C. The fracture strength reduction was again the result of creep cavitation along the grain boundaries. It is interesting to note that in each of the studies noted above, an improvement in the high temperature fracture toughness was observed, a result of glass formation at the matrix-whisker interface which softens at high temperature allowing debonding of the whiskers from the matrix.

2.2.3 Oxidation Kinetics of Composite Ceramics

The overall oxidation reaction can be controlled by several factors such as oxygen diffusion in, CO diffusion out, mixed diffusion of either, or, the actual oxidation reaction. The oxidation kinetics of ceramic oxides containing SiC whiskers has received very little attention. Borom studied the oxidation of alumina and mullite matrices containing dispersed phases of either MoSi2 or SiC41,42. Oxidation of these composites resulted in a scale that increased linearly with the square root of time. Activation energies calculated for the oxidation reactions were dependent on the type of matrix, either alumina or mullite41, and the amount of alkali and/or alkaline impurities present in the starting materials. Composites with larger amounts of impurities showed overall lower oxidation resistance. Expansion of the composite during oxidation was attributed to volume expansion due to solid product formation and product gas formation creating bubbles in the matrix. In both alumina and mullite, the oxidation reaction was determined to be controlled by oxygen diffusion through the oxidation product. The oxidation product was typically SiO2 that would react with the alumina
to form mullite. Lin\textsuperscript{6} studied the oxidation behavior of SiC whiskers dispersed in an alumina matrix. Oxidation resulted in similar parabolic oxidation kinetics along with mullite and glass formation. The oxidation depths as a function of time for the oxidation of SiC in alumina as reported by Lin\textsuperscript{6} are shown in Figure 1. These results indicate that the oxidation depth is strongly influenced by the amount of SiC present in the matrix. Oxygen diffusion was considered to be the most likely rate controlling mechanism for composite materials containing less than 25 volume percent SiC. At higher SiC contents, the reaction is assumed to be controlled concurrently by diffusion of oxygen through the silica product layer and by the escape of CO product gas. The increasing amounts of silica formed during oxidation was attributed to slowing down the oxidation reaction as seen in Figure 1. Graphitic carbon was found as a reaction by-product during the oxidation of SiC into SiO\textsubscript{2}. Lin mentioned that the carbon was possibly protecting the SiC whiskers by reacting with incoming oxygen. Luthra also studied the oxidation kinetics of alumina and mullite containing SiC particles\textsuperscript{27,43}. Oxidation of these materials resulted in mass gain that increased linearly with the square root of time. Luthra showed that the mass gain per unit area was dependent on the amount of SiC in the matrix shown in Figure 2. However, unlike Lin\textsuperscript{6}, Luthra indicated that the oxidation depth was independent on the amount of SiC present in the matrix. Reaction products were determined to be mullite, aluminosilicate glass and CO gas, the latter leading to bubbles in the matrix. Activation
Figure 1. Oxidation depth as a function of time for alumina with SiC whiskers (From Lin\textsuperscript{6}).
Figure 2. Mass gain per unit area during the oxidation of Al₂O₃/SiC composites (From Luthra²⁷).
and CO gas, the latter leading to bubbles in the matrix. Activation energies were determined for alumina containing 8 to 50 volume percent SiC and all were found to be similar and in the range of 422 to 472 kJ/mole. The overall oxidation of the composites was determined to be controlled by diffusion of oxygen through polycrystalline alumina.

2.2.4 Interfacial Reactions

The interface between the whisker and the matrix is important and can greatly effect the toughness of the material. The optimum condition is when the whisker can debond from the matrix when a crack front passes through the matrix. Typically, vacuum hot-pressed samples of alumina-SiC whisker composites show no visible compound formation or interfacial reactions between the whisker and the alumina using transmission electron microscopy (TEM). Whisker debonding is typically limited in these materials by high frictional stresses between the matrix and whisker resulting from a combination of different thermal expansion coefficients between the matrix and the whisker and morphological irregularities of the whisker surface. Oxidation of the whiskers may even increase the bonding between the matrix and whisker. In most of the oxidation reactions described, the SiC whiskers react with oxygen to form SiO2. In an alumina matrix, the SiO2 may then react with the matrix to form mullite or a glassy interface resulting in a strong chemical bond between the whisker and the matrix. When a continuous SiO2 layer between the matrix and the whisker exists, crack extension through the matrix will also occur through the whisker without
the whisker debonding from the matrix\textsuperscript{44}. Although an SiO\textsubscript{2} layer around the whisker may be detrimental to strength and toughness at room temperature it may actually decrease the amount of mechanical degradation at higher temperatures. ZrO\textsubscript{2} reinforced with SiC whiskers was found to have a higher strength and toughness as compared to the monolithic material\textsuperscript{3}. The glassy interface results in better load transfer to the whisker at higher temperatures because of the softening of the glass allowing debonding of the whisker from the matrix and subsequent whisker pullout.

2.3 TOUGHENING MECHANISMS

Ceramics are well known for their brittle behavior, typically resulting in catastrophic failure from the growth of a single crack or defect. The effect of flaws on the fracture strength of brittle materials is exemplified by the following relation:\textsuperscript{45}

\[ \sigma = \frac{K_c}{\sqrt{Y c}} \]  

(2)

where \( K_c \) is the critical fracture toughness, \( c \) is the dimensions of the largest crack and, \( Y \) is a geometric factor describing the configuration of the crack. Since ceramics have low fracture toughnesses, a possible method of increasing strength is by reducing the size of strength controlling flaw. However, controlling flaw population and their size, or detecting their presence, are difficult in ceramics. Recently, the trend in ceramics has been to design the microstructure so that it is
resistant to fracture by increasing the fracture toughness. The method that is of importance in this investigation is the introduction of second-phase particulates in to the matrix. The particulates are added to increase the fracture toughness of the ceramic, sometimes at the expense of the fracture strength.

Rice lists several methods in which the fracture toughness in ceramic particulate composites can be increased. The mechanisms of interest here are: 1) Crack Deflection, 2) Microcracking, 3) Crack Bridging, 4) Crack Branching, and 5) Crack Bowing.

2.3.1 Crack Deflection

Crack deflection is typically the most predominant toughening mechanism mentioned for ceramics containing low aspect ratio second-phase particulates. Crack deflection toughening can be described as the interaction of the crack front with a second-phase particle so that the crack deviates from the its original crack plane. The reorientation of the crack plane away from the original plane (Figure 3) results in a lower stress intensity at the crack tip and a diminished crack driving force, $G$. Further extension of the crack may cause it to twist between particles also reducing $G$. Tilting and twisting of the crack is known as mixed-mode local loading. When a crack deflects an angle $\Theta$ (Figure 3), the crack experiences mode I(opening) and mode II(sliding) contributions to the stress intensity (see Figure 4). Likewise, when the crack twists between particles at an angle $\Phi$, the crack experiences
Figure 3. Deflection of a crack by a second-phase particle (From Faber).
Figure 4. Stress intensity, K, modes on a crack: (A) Mode I opening; (B) Mode II, sliding; (C) Mode III (tearing).
mode I and mode III (tearing) contributions to the stress intensity. Mixed-mode loading results in a reduced crack driving force which is always less than $G_{\text{planar}}$ for a mode I crack.

Deflection of the crack can be the result of stresses that exist between the matrix and the second-phase particle produced by differences in the thermal expansion coefficients or elastic moduli. For example, if the second-phase has a higher thermal expansion or elastic modulus than the matrix, then the matrix produces a tangential compressive strain near the interface that deflects the crack around the particle. If the second-phase has a lower thermal expansion or elastic modulus than the matrix, then the matrix induces a tangential tensile strain which diverts the crack towards the particle$^{47,48}$.

Original crack deflection studies used glass matrices with second phase inclusions$^{47-49}$. This allowed the actual deflection due to the particles to be studied. Faber$^{47}$ determined that the toughening from second-phase particles depends only on the volume fraction and the shape of the particles. Particles with high aspect ratios (Figure 5) such as whiskers impart maximum toughening because of their influence on the deflection of the crack. The toughening increases with the volume fraction of the whiskers (Figure 5). It is for this reason that whiskers are more effective in toughening matrices.

Single crystal SiC whiskers are the most studied whisker added to ceramic matrices. They have been added to a variety of matrices such as MoSi$_2$$^{50}$, ZrO$_2$$^{3,19}$, Si$_3$N$_4$$^{19}$, mullite$^{7,11,17}$, and alumina$^{2,6,11,25,40}$ with
Figure 5. Effect of second phase particle shape and volume fraction on toughening due to crack deflection.
several of these materials exhibiting crack deflection toughening¹¹,¹⁹,⁵⁰. Wei et al.¹¹ has also shown that the amount of crack deflection increases when the crack plane is parallel to the hot-pressing axis or normal to the plane the whiskers lie in. The volume fraction of whiskers in the matrix has been shown to have a significant influence on the toughness of the composite supporting Faber's calculations. Both alumina¹¹,⁵¹ and zirconia²⁴ have shown a large increase in fracture toughness with up to 30 volume percent whiskers. How much of this fracture toughness increase is due to crack deflection is difficult to determine since other toughening mechanisms are apparently present as well.

2.3.2 Microcrack Toughening

Materials containing second-phase particles with thermal expansion coefficients or elastic moduli different from the matrix material will produce residual stresses within the material. Evans and Faber⁵² modeled the effects of microcracks produced by these stresses and their effect on toughening. The amount of toughening in the composite is dependent on the size and distribution of the second-phase particles that may be inducing the microcracks. In addition, microcracking should be within the zone of high stress concentration near a large crack. This results in a crack shielding process where the stress at the major crack tip is reduced by the lower elastic modulus of the microcracked material within the zone and by dilation in this zone induced by microcracking. However, if microcracking is to occur, the second-phase
particles must be of a critical size or larger. If the particles are smaller than the critical size, then microcracks can only be induced by the application of an external tensile stress. Lange\textsuperscript{53} developed a relation to determine the critical particle size based on an energy balance concept. The critical size ($d_c$) at which microcracks can occur is defined by the following relation:

$$d_c \beta^2 \geq \text{constant}$$  \hspace{1cm} (3)

where the constant depends upon the given composite system and $\beta$ describes the stress caused by the particle in the matrix. The stress, $\beta$, was determined by Selsing\textsuperscript{54} where:

$$\beta = \frac{[(\alpha_m - \alpha_p)\delta T]}{(1+\nu_m)/2E_m + (1-2\nu_p)/E_p}$$  \hspace{1cm} (4)

where $\alpha$ is the thermal expansion coefficient, $\delta T$ is the temperature cooling range, $E$ is the elastic modulus and, $\nu$ is Poisson's ratio. The subscripts m and p stand for the matrix and particle, respectively.

Sambell et al.\textsuperscript{5} attributed a decrease in strength in MgO containing carbon whiskers to cracking between the whiskers and MgO matrix due to thermal expansion mismatch, however, this same material showed an increase in the work of fracture up to 15 volume carbon whiskers. Part of this increase in work of fracture was attributed to microcracking within the matrix. Cracking between the matrix and second-phase particles has been observed in other systems\textsuperscript{9,49}, however,
the amount microcracking contributes to the total toughening process is yet to be determined.

2.3.3 Crack Bridging

Most crack toughening mechanisms described so far occur near the crack tip, however, experiments with Al₂O₃ have shown that a major part of toughening can occur far behind the crack tip by crack bridging. Crack bridging can be described as the interlocking of protruding grains on a rough fracture surface or the bridging of a crack by whiskers or fibers. The locked grains or bridging whiskers cause a closure force on the crack surfaces resulting in a decrease in the stress intensity at the crack tip. Estimating quantitatively the amount of toughening from this mechanism is difficult. Greater success in modeling bridging with whiskers or fibers has been achieved by Becher and Evans who analytically described the toughening behavior due to whisker bridging behind the crack tip. Theoretical solutions were based on the reduction of the stress intensity or change in strain energy due to the bridging of whiskers. It was found that toughness increases as the fracture strength, volume fraction, and radius of the whiskers decrease. The toughness also increases as the ratio of the elastic modulus of the composite to that of the whisker increases. For bridging to occur, a certain amount of debonding of the whisker from the matrix is necessary. The toughening contribution to a crack zone that is bridged by whiskers (Figure 6) a length $D_b$ behind the crack tip was determined by Becher.
Figure 6. Effect of whisker bridging on overall toughness of composite (From Becher\textsuperscript{2}).
and is

$$dK = 2\sigma_c (2D_b/\pi)^{1/2}$$  \hspace{1cm} (5)$$

where $dK$ is the increase in fracture toughness, and $\sigma_c$ is the closure stress on the crack. This assumes that the total crack length $c \approx D_b$, and the closure stress is constant along the length $D_b$. The closure force, $F_c$, on the crack by the whiskers is

$$F_c = \sigma_1 A_1$$  \hspace{1cm} (6)$$

where $\sigma_1$ is the stress imposed by each whisker and $A_1$ is the cross sectional area of a whisker. If $\sigma_c$ is assumed to be a uniform line stress between $x=0$ and $x=D_b$, then $\sigma_c$ becomes

$$\sigma_c = F_c N$$  \hspace{1cm} (7)$$

where $N$ is the number of bridging whiskers per unit area and can be described as

$$N = V_f / \pi r^2$$  \hspace{1cm} (8)$$

where $V_f$ is the volume fraction of whiskers in the matrix, and $r$ is the whisker radius. This is the simplest model assuming a square array of aligned whiskers. Debonding and sliding of the whisker in the matrix is controlled by the frictional shear stress $\tau$, where

$$\tau = \mu q$$  \hspace{1cm} (9)$$

where $\mu$ is the friction coefficient and $q$ the nominal residual compression normal to the interface. The value of $q$ is dependent on the misfit strain or the differences in the elastic moduli between the
whisker and matrix. Debonding and subsequent whisker pull-out has been experimentally observed on the fracture surfaces of whisker composites along with whisker bridging \(^4,5,11,14\).

2.3.4 Crack Branching

Crack branching has been considered one of the most prevalent mechanisms of toughening \(^1\) and commonly occurs in combination with crack deflection and microcracking in two phase materials. Branching mechanisms are expected to increase the fracture toughness two-fold or more due to the formation of additional crack surfaces. Crack branching in brittle materials is very unpredictable due to variations in microstructure, anisotropic grains, grain boundaries and second-phase particles. Wu \(^57\) showed crack branching is common in second-phase particulate composites. Crack branching as described by Wu is the formation of two or more cracks deviating from an original crack plane. Several criteria have been postulated to be necessary for toughening by crack branching: crack velocity \(^58\); that the strain energy near the tip of the crack must be enough to produce two cracks (four surfaces) \(^59\); a critical stress intensity factor \(^60\) for crack branching; and a critical strain criterion for crack branching \(^61\). Other possible mechanisms include the linking of microcracks or flaws ahead of the crack tip \(^60\). Congleton \(^60\) was first to develop the idea that crack branching occurred when a critical stress intensity, \(K_b\), was reached near the tip of the crack where:
\[ K_b = Y \sigma_f \frac{h}{C_b} \] = constant \hspace{1cm} (10)

where \( Y \) is a geometrical factor appropriate for a semicircular crack, and \( C_b \) is the radius of the fracture surface where crack branching has not occurred. Kirchner later developed the strain intensity criterion model that enabled \( K_b \) to be determined from the elastic modulus of the material. This model examined the critical strain in the vicinity of the crack tip. Kirchner later adapted his model to take into account the total strain of the material and assumed that crack branching occurs when the total strain near the crack tip is a constant such that:

\[ \frac{K_b}{E} = Y \epsilon_f C_b \] \hspace{1cm} (11)

where \( E \) is the elastic modulus and \( \epsilon_f \) the strain at failure. Kirchner found a linear correlation between the stress intensity factor for crack branching, \( K_b \), and the elastic modulus so that it may be applied to other ceramics. By taking the ratio of \( K_b/K_{Ic} \) and relating it to the brittleness of the material, it was possible to get a measure of the amount of overloading that was occurring at the crack tip before crack branching. The ratio of \( K_b \) to \( K_{Ic} \) was found to increase linearly with the brittleness of the material (Figure 7). In this case, brittleness is described by \( H/K_{Ic} \) where \( H \) is the hardness of the material. When \( H/K_{Ic} = 0 \), ideal plastic behavior is assumed and \( K_b/K_{Ic} = 1/2 \). At this point crack branching occurs when the energy available for fracture is
Figure 7. $K_b/K_{IC}$ as a function of the materials brittleness, $H/K_{IC}$ (From Kirchner).
double the amount to form one crack\textsuperscript{62}. This observation supports earlier investigations\textsuperscript{64} that crack branching occurs in soft materials when there is enough energy to form two cracks. As a material becomes more brittle, other factors begin to control crack branching since $K_{b}/K_{IC} > \sqrt{2}$.

Crack branching in monolithic materials can result in an increase in the toughness of the material\textsuperscript{1} just by the formation of two cracks. If crack branching occurs in a matrix with a second-phase particulate, not only is energy dissipated by the formation of two new cracks but each of those cracks must go through crack deflection processes around second-phase particles further increasing the toughness of the composite.

2.3.5 Crack Bowing

Crack bowing was described by Lange\textsuperscript{65} as the bowing out of the crack front between second-phase particles while still remaining pinned at all positions where the crack encounters the particles. This bowing effect can increase the strength\textsuperscript{66,67} of the material and also the fracture toughness\textsuperscript{61,68,69}. It was found that the fracture energy had an inverse relationship with the particle spacing\textsuperscript{61,66,68}. Later it was determined\textsuperscript{61} that the fracture energy was also dependent on the size of the second-phase inclusions with the larger inclusions giving a higher fracture energy. The increase in strength is due to the increase in surface energy and the extended length of the crack due to the bowing\textsuperscript{65,67}. The extra crack length due to bowing has a line tension
energy associated with it which requires additional energy to increase the length of the crack front. In matrices with brittle obstacles, the line tension was found to be the major contributor to the observed increases in strength. In addition, for crack pinning by second-phase particles to occur, the crack must remain planar and not fracture the second-phase particles when reaching them. Lange also showed that the flexural strength increases as the volume fraction of second-phase particles increases. This is due to the elastic modulus component of the second-phase particles (assuming that $E_{\text{second-phase}} > E_{\text{matrix}}$). Finally, the thermal expansion coefficient between the particles and the matrix must be similar or $\alpha_{\text{matrix}}$ must be $> \alpha_{\text{second-phase}}$ so that the crack front will intersect the particles and create pinning.
CHAPTER III

THEORY

3.1 SYSTEM REQUIREMENTS

MgO was chosen as a model matrix for several reasons: (1). MgO can be easily hot-pressed into a dense composite system; (2). MgO does not form a glass with SiO₂ at temperatures below 1500°C therefore eliminating any possible glass phase along the grain boundaries; (3). MgO represents a model system in which the diffusion, both grain boundary and lattice, has been well studied and documented; and finally, (4), presently, MgO is not known to form any intermediate compounds with SiC possibly eliminating any chemical bonding during fabrication.

3.2 THERMODYNAMICS

The presence of SiC within the MgO matrix may create a reducing atmosphere in the vicinity of the SiC particle through the reactions:

\[
C(s) + \frac{1}{2}O_2(g) = CO(g) ; \quad K = \frac{v_{CO}/v_{O_2}}{12}
\]

and
\[
\text{Si}(s) + \text{O}_2(g) \rightarrow \text{SiO}_2(s); \quad K = e^{\Delta \text{SiO}_2/\text{PO}_2} (13)
\]

For these reactions to proceed in an inert or reducing environment, MgO must decompose according to:

\[
\text{MgO}(s) \rightarrow \text{Mg}(s) + \frac{1}{2} \text{O}_2(g); \quad K = P_{\text{O}_2}^{\frac{1}{2}} (14)
\]
such that the overall reaction may be described as:

\[
3 \text{MgO}(s) + \text{SiC}(s) \rightarrow \text{SiO}_2 + 3 \text{Mg}(s) + \text{CO}(g) (15)
\]

Calculations with tabulated thermodynamic data\textsuperscript{70} in the temperature range 1500°K to 1800°K indicate that Reaction 15 is thermodynamically unfavorable with CO pressures below 10\textsuperscript{-20} atm at 1700°K. It is therefore unlikely that carbon or silicon will reduce MgO. If SiC is to oxidize, oxygen must be supplied from an external source such as an oxidizing environment.

3.3 KINETICS

3.3.1 Reaction Mechanisms

The oxidation of SiC located within a dense matrix of MgO is likely to occur by several steps:

(I) Mass transfer of the gaseous reactant from the bulk gas stream to the external surface of the solid.

(II) Diffusion of the reactant through a dense or porous matrix.

(III) Chemical reaction between the reactant and the unreacted solid.
(IV) Diffusion of the gaseous product through the dense or porous matrix.

Since these mechanisms must occur in series, the rate of the overall reaction is controlled by the slowest step. If the overall reaction is controlled by steps (I), (II), or (IV), then the reaction is called a transport or diffusion controlled reaction. If the rate of reaction is controlled by step (III), the reaction rate is surface reaction controlled. To be able to compare model and experiment, the experimental conditions should be chosen carefully so that only a single mechanism dominates.

3.3.2 Reaction Rate Controlled

The following is the assumed overall oxidation reaction for the oxidation of SiC in MgO:

$$\text{SiC}(s) + \frac{3}{2} \text{O}_2(g) \rightarrow \text{SiO}_2(s) + \text{CO}(g) \quad (16)$$

this reaction may occur in several steps such as:

$$\text{SiC}(s) + \frac{1}{2} \text{O}_2(g) \rightarrow \text{SiO}(g) + \text{CO}(g) \quad (17)$$
$$\text{SiC}(s) + \text{O}_2(g) \rightarrow \text{SiO}_2(s) + \text{CO}(g) \quad (18)$$
$$\text{SiC}(s) + \text{O}_2(g) \rightarrow \text{SiO}_2(s) + \text{C}(s) \quad (19)$$

If the overall reaction is controlled by the oxidation of SiC, then the rate of SiC oxidizing can be described by:

$$J_r(\text{moles/cm}^2\text{sec}) = \frac{k_o}{RT} \left[ p_o^o - \frac{e}{p_o^e} \right] \quad (20)$$
where \( J_r \) = Rate of oxidation of SiC in moles/cm\(^2\)-sec.

\[ k_s = \text{Reaction rate constant.} \]

\[ P_{O_2}^o = \text{Pressure of oxygen in bulk gas.} \]

\[ P_{O_2}^e = \text{Equilibrium oxygen pressure at reaction interface.} \]

The amount of SiC being oxidized is equal to the amount of SiO\(_2\) being formed such that:

\[ J_r = J_{SiO_2} \quad (21) \]

\[ J_{SiO_2} = V_f \frac{\rho}{MA} \frac{dv}{dt} \quad (22) \]

and

\[ J_{SiO_2} = V_f \frac{o}{M} \frac{dx}{dt} \quad (23) \]

where \( \rho \) = Density of SiO\(_2\) in g/cc.

\( M \) = Molecular weight of SiO\(_2\) in g/mole.

\( A \) = Area.

\( v \) = Volume reacted.

\( t \) = Time.

\( V_f \) = Volume fraction of SiC in MgO.

\( x \) = Oxidation Depth

Assuming a flat plate geometry and equating Equations (20) and (23) results in:
Rearranging Equation (24) gives

\[
\frac{dx}{dt} = \frac{Mk_s}{\rho V_f RT} [P_{O_2}^0 - P_{O_2}^e]
\] (25)

Integration of Equation (25) yields:

\[
x = \frac{Mk_s}{\rho V_f RT} \int [P_{O_2}^0 - P_{O_2}^e] \, dt
\] (26)

Equation (26) shows that for a chemical reaction controlled process, a plot of the reacted layer thickness as a function of time will result in a linear dependence with the slope equal to the reaction rate, \( K_r \), where \( K_r \) equals:

\[
K_r = \frac{Mk_s}{\rho V_f RT} [P_{O_2}^0 - P_{O_2}^e]
\] (27)

In addition, by plotting the log of the reaction rate, \( K_r \), as a function of reciprocal temperature, the activation energy for the reaction can be determined from the slope of the plot by:

\[
\log K_r = (-Q/2.303R) \frac{1}{T}
\] (28)
where \( Q \) is the activation energy and \(-Q/2.303R\) is the slope of the line.

### 3.3.3 Diffusion Reaction Controlled

Assuming steady state diffusion within the MgO matrix, the flux of oxygen into the system is governed by Fick's first law:

\[
J_0 = -C_0 \frac{D_o \Delta G}{RT}
\]

(29)

where \( D_o \) is the apparent diffusion coefficient, \( C_0 \) the concentration of oxygen in the structure, and \( \Delta G \) the gradient of the oxygen chemical potential. The driving force for oxygen diffusion is the difference in the oxygen chemical potential between the ambient atmosphere and the reaction interface in which Equation (29) can be rewritten as:

\[
J_0 = -\frac{D_o C_0}{xRT} \left[ \ln p_0^e - \ln p_0^o \right]
\]

(30)

Canceling the RT term and substituting \( h \) for \( \mu_0 \) results in

\[
J_0 = -\frac{D_o C_0}{2x} \left[ \ln p_{02}^e - \ln p_{02}^o \right]
\]

(31)

The majority of oxygen entering the MgO matrix reacts with the SiC to form SiO\(_2\) according to and SiC is present in the MgO a percentage, \( V_f \):

\[
J_{SiO_2} = \frac{\rho V_f}{MA} \frac{dv}{dt} = \frac{\rho V_f}{M} \frac{dx}{dt}
\]

(32)
The amount of oxygen entering the matrix is therefore equal to the amount of \( \text{SiO}_2 \) being formed such that:

\[
J_{\text{SiO}_2} = \frac{2}{3} J_0 \quad (33)
\]

The factor 2/3 represents that some of the oxygen entering the system reacts to form CO. Substituting into Equation (33) gives:

\[
\frac{\Delta V_f}{M} \frac{dx}{dt} = -2D_a \frac{C_o}{3x} \left[ \ln \frac{p_{O_2}^e}{p_{O_2}^0} - \ln \frac{p_{O_2}^e}{p_{O_2}^0} \right] \quad (34)
\]

where

\[
G_{\text{SiO}_2} = \rho_{\text{SiO}_2}/M_{\text{SiO}_2} = \gamma_{\text{SiO}_2} \quad (35)
\]

and

\[
x \frac{dx}{dt} = -4D_a \frac{3V_f}{3V_f} \left[ \ln \frac{p_{O_2}^e}{p_{O_2}^0} - \ln \frac{p_{O_2}^e}{p_{O_2}^0} \right] \quad (36)
\]

Integration of Equation (36) gives the parabolic rate equation:

\[
x^2 = K_d t \quad (37)
\]

where

\[
K_d = \frac{-8D_a}{3V_f} \left[ \ln \frac{p_{O_2}^e}{p_{O_2}^0} - \ln \frac{p_{O_2}^e}{p_{O_2}^0} \right] \quad (38)
\]
By plotting the oxidation depth as a function of the square root of time, the slope of this line will give the parabolic rate constant, $K_d$. Plotting $K_d$ as a function of reciprocal temperature should result in a linear dependence with the slope equal to $-Q/2.303R$ where $Q$ is the activation energy of the reaction. The slope can also be used to determine the apparent diffusion coefficient for the reaction since the partial pressures of oxygen can be estimated from thermodynamic data\(^{70}\).

When grain boundary diffusion is occurring, the grain boundary dimensions must be considered in Equation (32) where now $A$ is the area of the grain boundaries. If diffusion is assumed to enter through the grain boundaries, then area would be the total grain boundary area on the surface of the sample. This is indicated in Figure 8.

\[ \delta = \text{grain boundary width} \]
\[ L = \text{sample dimensions} \]
\[ d = \text{grain size} \]

![Figure 8. Determination of grain boundary area](image)

The total grain boundary area is $2\delta(L^2/d)$ resulting in:

\[ J_{SiO_2} = \frac{\rho dV_f}{2\delta L^2 M} \frac{dV}{dt} \]  

(39)
Equating Equation (40) with (31) results in:

\[
\frac{\partial V_f}{\partial t} - \frac{dx}{dt} = \frac{2qD_a}{3M_x} \left[ \ln p_0^e - \ln p_0^o \right] \quad (41)
\]

rearranging yields

\[
x \frac{dx}{dt} = -\frac{4qD_a}{3V_f d} \left[ \ln p_0^e - \ln p_0^o \right] \quad (42)
\]

integration yields

\[
x^2 = -\frac{8qD_a}{3V_f d} \left[ \ln p_0^e - \ln p_0^o \right] t \quad (43)
\]

and

\[
x^2 = K_d t \quad (45)
\]

where

\[
K_d = -\frac{8qD_a}{3V_f d} \left[ \ln p_0^e - \ln p_0^o \right] \quad (46)
\]

It can now be seen that the oxidation depth is inversely proportional to the grain size. The parabolic rate constant can be determined from the slope of a plot of \(x^2\) as a function of time.

3.4 OXIDATION OF MgO CONTAINING SiC

The reaction mechanisms discussed in the previous section are typically applied to single phase reactions. The oxidation models for reaction and diffusion control can be used for the oxidation of discrete
second-phase particles within a oxide matrix by incorporating the volume fraction of the second-phase into the equations as seen in Equations (22), (32), and (39). MgO is stable in an oxidizing atmosphere in the temperature range from 1000°C to 1500°C. The fact that SiC forms a protective SiO$_2$ layer in an oxidizing environment also makes it somewhat stable. It was mentioned previously that the oxidation reaction of pure SiC may be controlled by the diffusion of the product gas, CO, out$^{29,31}$. Such a mechanism may control the oxidation of SiC in MgO. If the reaction is diffusion controlled, three possible situations may exist:

1) the diffusion of CO out of the matrix is much faster than the diffusion of oxygen into the system, $D_{CO} > D_{O}$,

2) the diffusion of oxygen into the matrix is much faster than the diffusion of CO out, $D_{O} > D_{CO}$, and

3) the diffusion of oxygen and CO are approximately the same, $D_{O} \approx D_{CO}$. What further complicates this diffusion model is the fact that SiO$_2$ may form on the surface of the SiC and the SiO$_2$ may react with MgO to form MgSiO$_3$ or Mg$_2$SiO$_4$ as illustrated by the MgO-SiO$_2$ phase diagram in Figure 9$^{72}$. Therefore the diffusing species may also have to diffuse through these reaction products. For now, only diffusion through the MgO matrix will be considered for simplicity.

If the diffusion of CO through the oxide materials is much faster than the diffusion of oxygen, then the build up of product gases within the matrix is avoided and the oxidation reaction can continue. This situation would then result in a reaction controlled by the diffusion of oxygen into the matrix. Since CO is a large linear molecule, its
Figure 9. Phase diagram for the MgO-SiO₂ system\textsuperscript{71}.
diffusion is most likely much slower than diffusion of ionic oxygen.

If the diffusion of oxygen is much faster than the diffusion of CO through the matrix, then two conditions can exist. First, if the CO pressure in the matrix increases to the equilibrium partial pressure of CO for the oxidation reaction, then the reaction is suppressed until the CO can diffuse out and is therefore controlled by the diffusion of CO. Alternatively, if the CO partial pressure for the oxidation reaction of SiC is high, then oxidation and bubble formation can occur as long as oxygen is present. This situation would then result in a reaction controlled by oxygen diffusion into the matrix.

For bubble growth to occur in the matrix, the pressure must be great enough to overcome surface tension forces of the MgO, \( \tau_s \), the ambient pressure, \( P_{\text{atm}} \), and the movement of dislocations and defects within the matrix, \( \delta_d \).

\[
P_{\text{internal}} = \frac{2\tau_s}{r} + P_{\text{atm}} + \delta_d \quad (47)
\]

where \( r \) is the radius of the bubble. Above 1100°C, MgO is fairly plastic and the contributions from \( P_{\text{atm}} \) and \( \delta_d \) are most likely minimal. Taking the surface tension to be approximately 1.4 J/m\(^2\) and bubble radii from 0.5 \( \mu \)m to 10 \( \mu \)m results in internal pressures ranging from 0.24 MPa to 6 MPa.
CHAPTER IV

EXPERIMENTAL PROCEDURE

4.1 SAMPLE PREPARATION

The samples in this study were made with high purity magnesium oxide powder (Fisher M-51) with the actual lot analysis shown in Table 1. The as-received MgO powder consisted of primary particles ranging in sizes from 0.5 to 5 \( \mu \text{m} \) as shown in Figure 10a. The MgO composites were made by adding either SiC particles or SiC single crystal whiskers. The SiC powder (Superior Graphite Co.) had a cubic structure and a mean particle size between 1 and 5 \( \mu \text{m} \). The as-received SiC whiskers (Tateho Chemical Ind.) were single crystal \( \beta \)-SiC with a nominal diameter of 0.5 \( \mu \text{m} \) and lengths of 10 to 40 \( \mu \text{m} \) shown in Figure 10b. The lot analysis for the SiC whiskers is shown in Table 2. The lengths of the whiskers showed an irregular surface. The as-received whiskers were typically grouped in intertwined agglomerates.

4.1.1 MgO/SiC Powder Preparation

SiC powder was added to MgO powder in amounts of five, ten or fifteen volume percent. Percentages were calculated using a density of 3.21 g/cc for the SiC and 3.58 g/cc for the MgO. The MgO/SiC powder mixtures were milled in polyethylene bottles using zirconia milling
### TABLE 1
CHEMICAL LOT ANALYSIS OF MgO POWDER

<table>
<thead>
<tr>
<th>Impurity</th>
<th>Weight Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Barium (Ba)</td>
<td>0.005 %</td>
</tr>
<tr>
<td>Iron (Fe)</td>
<td>0.003 %</td>
</tr>
<tr>
<td>Chloride (Cl)</td>
<td>0.001 %</td>
</tr>
<tr>
<td>Calcium (Ca)</td>
<td>0.001 %</td>
</tr>
<tr>
<td>Manganese (Mn)</td>
<td>3 ppm</td>
</tr>
<tr>
<td>Potassium (K)</td>
<td>0.001 %</td>
</tr>
<tr>
<td>Sodium (Na)</td>
<td>0.1 %</td>
</tr>
<tr>
<td>Strontium (Sr)</td>
<td>0.001 %</td>
</tr>
<tr>
<td>Sulfate (SO₄)</td>
<td>0.01 %</td>
</tr>
</tbody>
</table>

### TABLE 2
CHEMICAL LOT ANALYSIS OF SiC WHISKERS

<table>
<thead>
<tr>
<th>Impurity</th>
<th>Weight Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnesium (Mg)</td>
<td>0.090 %</td>
</tr>
<tr>
<td>Iron (Fe)</td>
<td>0.020 %</td>
</tr>
<tr>
<td>Calcium (Ca)</td>
<td>0.130 %</td>
</tr>
<tr>
<td>Aluminum (Al)</td>
<td>0.180 %</td>
</tr>
<tr>
<td>Oxygen (O)</td>
<td>0.430 %</td>
</tr>
<tr>
<td>Free Carbon (C)</td>
<td>0.570 %</td>
</tr>
</tbody>
</table>
Figure 10. SEM micrograph of as-received A) MgO Powder; and B) SiC Whiskers.
media (Toso, Inc.) in isopropyl alcohol. The powders were milled for 24 hours and the resulting slurry was dried at 65°C while being agitated.

4.1.2 MgO/SiC Whisker Preparation

The as-received SiC whiskers were dispersed ultrasonically in isopropyl alcohol (1% by volume) and then allowed to agglomerate and settle. The supernatant was removed and the above procedure was repeated. The whiskers were then dried and added to MgO powder that had been previously milled for 20 hours. The whiskers were added to the MgO powder in amounts of five, ten or fifteen volume percent. The MgO/SiC whisker mixtures were then milled for an additional four hours. The powder whisker mixture was then dried at 65°C while being agitated.

4.1.3 Composite Consolidation and Characterization

The composite mixtures were vacuum hot-pressed in graphite dies with Grafoil (Union Carbide Corp.) as a liner between the powder and the graphite die. A pressure of 27.7 MPa (4000 psi) was applied to the powder at 1000°C with the pressure held constant throughout the hold temperature. After densification was complete, the furnace was cooled to 1100°C before the pressure was released. Heating and cooling rates were 25°C/minute. Hot-pressing times and temperatures are shown in Table 3. The hot-pressed composite disks were approximately 0.6 cm thick and 7.6 cm in diameter. The outer edges and faces of the disks were ground down with 120 grit SiC paper to remove any residual grafoil
lining. Densities of hot-pressed composites are also shown in Table 3. Densities were measured by Archimedes' principle in isopropyl alcohol as shown in Appendix A.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pressure</th>
<th>Time</th>
<th>Temp(°C)</th>
<th>% Th.Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure MgO</td>
<td>41.3MPa</td>
<td>30min</td>
<td>1300</td>
<td>&gt; 99.3</td>
</tr>
<tr>
<td>SiC Powder</td>
<td>27.6</td>
<td>90</td>
<td>1610</td>
<td>&gt; 99.8</td>
</tr>
<tr>
<td>5 v/o SiC</td>
<td>27.6</td>
<td>150</td>
<td>1635</td>
<td>&gt; 98.3</td>
</tr>
<tr>
<td>10 v/o SiC</td>
<td>27.6</td>
<td>180</td>
<td>1625</td>
<td>&gt; 98.0</td>
</tr>
<tr>
<td>15 v/o SiC</td>
<td>27.6</td>
<td>90</td>
<td>1750</td>
<td>&gt; 98.0</td>
</tr>
<tr>
<td>SiC Whisker</td>
<td>27.6</td>
<td>60</td>
<td>1530</td>
<td>&gt; 99.8</td>
</tr>
<tr>
<td>5 v/o SiC</td>
<td>27.6</td>
<td>120</td>
<td>1680</td>
<td>&gt; 98.1</td>
</tr>
<tr>
<td>10 v/o SiC</td>
<td>27.6</td>
<td>90</td>
<td>1750</td>
<td>&gt; 98.0</td>
</tr>
<tr>
<td>15 v/o SiC</td>
<td>27.6</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The pure hot-pressed MgO was translucent, while the MgO/SiC whisker was light green and the MgO/SiC powder was black. Polished and etched (50/50 Nitric Acid/H₂O at 50°C) surfaces of the MgO/SiC whisker and MgO/SiC powder composites are shown in Figures 11 and 12, respectively. The average grain size of all the composites was approximately 5 μm which was kept constant by altering hot-pressing conditions. The
Figure 11. SEM micrograph of polished and etched surface of MgO/SiC whisker composite: A) 5; B) 10; and C) 15 volume percent.
Figure 12. SEM micrograph of polished and etched surface of MgO/SiC powder composite: A) 5; B) 10; and C) 15 volume percent.
smallest grain size achieved for pure, dense MgO was 7 μm. The fracture surfaces of the MgO/SiC whisker composites are shown in Figure 13. Fracture was completely transgranular with the SiC whiskers found primarily at the grain boundaries. The majority of whiskers were oriented perpendicular to the hot-pressing direction. Whisker orientation was determined by etching the fractured surface (Figure 14) with nitric acid. Whisker orientation has been commonly found for hot-pressed samples by other investigators\(^3,23,45\). No indication of whisker pullout was observed on any of the MgO/SiC whisker composite fracture surfaces. At 15 volume percent whiskers, TEM (Figure 15) reveals that voids between the whisker and matrix are common and typically found in areas where the concentration of whiskers are high.

The fracture surfaces of the MgO/SiC particle composites are shown in Figure 16. Fracture was entirely transgranular with the fracture surface appearing to intersect the SiC particles but not fracture them.

4.2 MECHANICAL TESTING

Mechanical test bars of 2.25mm x 3mm x 22.5mm were machined\(^73\) from the hot-pressed disks with the 3mm length parallel to the pressing direction (Figure 17). This configuration was chosen so that the majority of whiskers would lie in a plane perpendicular to the hot-pressing direction. All faces were ground flat and parallel with a 320 grit finish. The edges were beveled to avoid any stress concentrations at sharp corners.

Fracture strengths were determined using a four-point bending
Figure 13. SEM micrograph of fractured surfaces of MgO/SiC whisker composites: A) 5; B) 10; and C) 15 volume percent.
Figure 14. SEM micrograph of fractured and etched surface showing alignment of whiskers.
Figure 15. TEM micrograph of SiC whiskers in MgO matrix.
Figure 16. SEM micrograph of fractured surfaces of MgO/SiC powder composites: A) 5; B) 10; and C) 15 volume percent.
Figure 17. Orientation of test bars cut from hot-pressed MgO/SiC composite.
fixture with a 20mm outer span and a 10mm inner span. Loading rates (Instron 4201) were adjusted to give a strain rate of $10^{-4}$/sec which translates into a crosshead speed of 0.18 mm/second. The standard equation for determining fracture stress is given in Equation 48\textsuperscript{74} where:

$$
\sigma_f = \frac{3P(L-a)}{2bd^2}
$$

(48)

where $\sigma_f$ is the fracture stress, $P$ is the fracture load, $L$ is the distance between the outer supports, $a$ is the distance between the inner supports, $b$ is the width of the bar, and $d$ is the depth of the bar. A total of five bars were used to determine unoxidized room temperature strength. The load versus deflection curve showed typical elastic behavior until failure had occurred.

Fracture toughness was determined by the indentation-strength-in-bending (ISB)\textsuperscript{75} technique. The ISB technique involves measuring the failure stress of a rectangular bend bar that has a Vicker's indentation of load $P_I$ on the tensile side of the bend bar (Figure 18). Indentations were made with a Zwick 3212 microhardness tester. The indentations loads were chosen by indenting polished surfaces and observing which loads produced indentation cracks with no lateral chipping. A load of 21.6 N was found to produce optimal cracks. The indentation was placed in the center of the tensile face such that one set of orthogonal cracks was perpendicular to the tensile axis. The bend bar was then loaded in a four-point bend fixture with the indentation in the exact center of the
Figure 18. Placement of Vicker's indentation on tensile surface of test bar.
fixture. A total of six bars were tested per indentation load with the
time of loading approximately fifteen seconds. This test was done only
on unoxidized samples. Each bar was examined to make sure failure
occurred at the indentation. The failure stress (Equation 48) was then
used to calculate the fracture toughness from

\[ K_{IC} = 0.59 \left( \frac{E}{H} \right)^{1/8} \left( \frac{P_c}{3\sigma_f} \right)^{3/4} \] (49)

where \( E \) is the elastic modulus and \( H \) is the hardness of the composite.
The factor 0.59 is a geometric factor based on the half penny shaped
crack produced by the indentation. The hardness-to-modulus ratio \( H/E \)
was determined by two separate methods. The first method for evaluating
\( H/E \), developed by Marshall et al.\(^{76}\), is from Knoop indentations on a
polished surface. This technique is based upon the elastic recovery of
a Knoop impression upon unloading. The amount of elastic recovery can
be related to the ratio \( E/H \). The ratio of the major and minor axes of
the Knoop impression is measured and calculated. This ratio is then
fitted to a curve generated by Marshall allowing a hardness-to-modulus
ratio to be determined. This method gave a rough estimate of \( H/E \) but
was unable to distinguish between different volume percentages of SiC
because of indentation chipping even at low indentation loads. The
second method of determining the \( H/E \) ratio was by measuring the hardness
of the composite and the elastic modulus separately. The hardness was
determined with a Vicker's indentation on a polished surface and
measuring the impression dimensions. The hardness was then calculated
with Equation 50:

\[ H = 0.47 \frac{P}{a^2} \]  

where \( P \) is the indentation load (26.5 N) and, \( a \) the diagonal dimensions of the impression. The elastic modulus was measured by using the resonant frequency technique on a Grindo-sonic where the elastic modulus is determined by measuring the resonant frequency, mass and dimensions of a rectangular bar. This method was found sensitive enough to distinguish between various amounts of SiC.

4.3 EXPERIMENTAL APPARATUS

4.3.1 TGA Experiments

Initial oxidation studies were done with thermogravimetric analysis (TGA) on a Cahn 2000 microbalance connected to a strip chart recorder that continuously monitored the weight change due to oxidation. Recorder sensitivity was limited to 1 milligram full scale due to building vibrations and furnace convection currents. A platinum chain was used to lower two 12 inch segments of alumina rod (.025 cm in diameter) that were connected end to end into a vertical tube furnace. Hooks were placed on the alumina rods by fusing half inch lengths of similar alumina rods to the ends with an acetylene torch. Samples were lowered to within one-half inch of a type R (Pt-13%Rh/87%Pt) thermocouple placed inside a vertical tube furnace used to control the
The furnace was heated to the desired temperature (between 1100°C and 1500°C) before the samples were lowered into the furnace via the platinum chain. The samples were of known rectangular dimensions and weight and cleaned ultrasonically in acetone before loading into the TGA unit. Oxidation tests in the TGA were done in stagnant air since introducing a gas flow created large oscillations of the hangdown assembly and reduced sensitivity of the balance. Oxidation times ranged from 10 to 24 hours.

4.3.2 Oxidation Experiments

Samples not oxidized in the TGA furnace were oxidized in a horizontal tube furnace. This included all mechanical test bars. Test bars were supported at the ends by platinum wires so they were equally oxidized on all surfaces. The bars were then placed into the furnace at the desired temperature. The samples dimensions and weights were recorded before and after oxidation. Additional samples were also oxidized and fractured in half with one-half mounted and prepared for Scanning Electron Microscopy (SEM) while the other half was mounted in epoxy and polished for optical microscopy.

4.3.3 Dilatometer

One inch samples of the composite materials were placed in a recording dilatometer (Orton Foundation). Samples were heated at approximately 3°C/minute to 900°C to measure the thermal expansion of
the composites. The samples were placed in a high purity alumina tube and kept in a flowing gas atmosphere of argon during heating to prevent expansion due to oxidation.

4.4 MICROSTRUCTURAL ANALYSIS

Fracture surfaces were examined with secondary electron imaging in a scanning electron microscope (SEM) (ISI SX-40 or Hitachi S-510) to determine the mode of fracture. Fracture surfaces were cut from mechanical test bars, mounted on aluminum stubs with conductive carbon paint and sputter coated with Au-Pd for observation in the SEM. The SEM was also used to determine if whisker pullout during fracture had occurred.

The interface between the MgO matrix and the SiC whiskers was examined using Transmission Electron Microscopy (TEM). TEM samples were prepared by cutting 3 mm disks with a Gatan Model 601 ultrasonic disk cutter. Unoxidized samples were ground to a thickness of 100 μm and dimpled 40 μm in on both sides. The samples were then ion milled on both sides until perforated. TEM samples that had been oxidized were dimpled from the back (the unoxidized side) and back thinned with an ion mill until the sample was perforated. Samples were then carbon coated before viewing on the TEM (JOEL-200CX).

Optical microscopy was done on samples polished down to 0.25μm diamond grit. Samples were examined with a reflected light microscopy capable of 1000X magnification. Oxidized samples were observed through polarized light to see the reaction zone on the surface.
4.5 DATA REDUCTION

The oxidation rate in terms of product layer growth rate was obtained by two methods: 1) direct measurement optically of the oxidized region on sectioned and polished samples partially oxidized; and 2) conversion of weight gain versus time data on the TGA, assuming complete oxidation everywhere behind the oxidation interface. These methods were both possible since the reaction interface was uniform and easily identifiable. Since a volume change, (expansion of the oxidized region) does occur during oxidation, data converted from weight gain measurements (the assumption that CO eventually diffuses out was used) is more convenient and reflects the true volume being reacted.

For this particular study, the second method was chosen after comparison to microstructural analysis. The details of the calculation are shown in Appendix B. It was found that the calculation of the oxidized layer thickness from weight change data was accurate up to 150 μm. At this depth, the expansion of the oxidized region produced negligible error (>10% above 200 μm) allowing the kinetic data to be more conveniently obtained from weight-loss measurements.
CHAPTER V

EXPERIMENTAL RESULTS

5.1 INTRODUCTION

The oxidation of MgO containing silicon carbide particles or whiskers results in a variety of microstructural changes and degradation. The effect of oxidation on the microstructure of MgO containing SiC will be presented first followed by the effect that the oxidized microstructure has on the strength of the composites. The kinetics of the oxidation reaction will be presented last.

5.2 MICROSTRUCTURAL EFFECTS

5.2.1 Thermal Expansion

The thermal expansion of MgO and MgO containing SiC with whiskers is shown in Figure 19 as compared to the theoretical thermal expansion calculated from Equation 51.

\[ \alpha_c = \frac{\alpha_1 K_1 V_1/\rho_1 + \alpha_2 K_2 V_2/\rho_2}{K_1 V_1/\rho_1 + K_2 V_2/\rho_2} \]  

(51)

where \( \alpha_c \) = Composite thermal expansion coefficient,
\( \alpha_i \) = Thermal expansion coefficient of phase 1 or 2,
\( \rho_i \) = Density of phase 1 or 2.
Figure 19. Experimental and calculated coefficients of thermal expansion for MgO/SiC composites.
\[ V_i = \text{Volume fraction of phase 1 or 2.} \]
\[ K_i = \text{Bulk modulus of phase 1 or 2.} \]

where

\[ K_i = \frac{E_i}{3(1-2\mu)} \]  \hspace{1cm} (52)

where \( E_i = \text{The elastic modulus of phase 1 or 2.} \)
\( \mu = \text{Poisson's ratio (taken as 0.25).} \)

Pure MgO has the highest thermal expansion coefficient with the coefficient decreasing as the amount of SiC in the MgO increases. The thermal expansion of MgO is reported as \(13.6 \times 10^{-6}\text{in/in°C} \). The expansion coefficient of pure MgO measured in this study was \(14.6 \text{in/in°C} \) and is within experimental error.

5.2.2 Oxidation Expansion

The most notable effect of high temperature air environments on MgO containing SiC whiskers or particles is the volume expansion that occurs during oxidation. The expansion is thought to be due to the formation of product gas trapped in the matrix. Figure 20 illustrates the amount of volume expansion that occurs during oxidation at \(1500°C \) for MgO containing SiC whisker and MgO with SiC particles. It is interesting to note that expansion due to oxidation is dependent on the amount of SiC present in the matrix. Linear expansion of the composite materials is also very dependent on the temperature of oxidation as shown for samples oxidized for 10 hours in Figure 21. Samples
Figure 20. Volume expansion of (A) MgO/SiC whisker and (B) MgO/SiC powder composites after oxidation at 1500°C.
Figure 21. Linear expansion of MgO/SiC composites oxidized between 1300 and 1500°C.
containing 5 volume percent SiC resulted in the greatest amount of expansion followed by 10 and then 15 volume percent SiC. On the larger faces of the samples, expansion resulted in the bowing out of the surface. Therefore, the data presented in Figure 20 does not represent the true expansion of the sample but rather a rough estimate.

5.3 FRACTURE MECHANICS

5.3.1 Fracture Toughness

The fracture toughness was calculated with the indentation strength-in-bending technique (ISB). The fracture toughness of pure hot-pressed MgO was measured at several indentation loads. Loads above 11.7 N were found to produce cracks long enough for valid tests. Indentations on the surface of MgO-SiC composites are shown in Figure 22. Crack bridging is also apparent in both types of MgO-SiC composites as illustrated in Figure 23. When the fracture strength of a material is dependent on the indentation and not the material flaw size, the fracture toughness is said to be in the steady-state region. The fracture strength dependence on indentation load is given by:

\[
\sigma_f = \left[ \frac{3K_{IC}}{4} \right]^{4/3} (FP)^{1/3} \tag{53}
\]

By plotting the fracture stress as a function of indentation load on a log-log plot, a slope of -1/3 should be obtained in the steady state region. The fracture strength of pure MgO as a function of indentation load is shown in Figure 24. The slope of this line is -0.31 ± 0.03
Figure 22. SEM micrographs of Vicker indentation on polished surface of (A) MgO/SiC whisker and (B) MgO/SiC powder composites.
Figure 23. SEM micrograph of crack bridging in (A) MgO/SiC whisker and (B) MgO/SiC powder composites.
Figure 24. Fracture strength of pure MgO as a function of indentation load.
indicating that the fracture toughness is in the steady state region.

The fracture toughnesses determined from the fracture strength of the indented bars of pure MgO and MgO-SiC whisker MgO-SiC particulate composites are shown in Figure 25. Results of these toughness tests are also listed in Table 4. A total of six bars were fractured for each toughness test with the error bars representing the standard deviation, $s$, divided by $\sqrt{n}$, where $n$ is the number of bars in each test.

Indentation loads of 21.6 N were used to measure the toughnesses. It can be seen in the figure that the fracture toughness is increased significantly with the addition of SiC whiskers or SiC particles. The addition of SiC whiskers to the MgO matrix increases the toughness almost 20 percent over the SiC particles at each composition.

5.3.2 Fracture Strength

The fracture strengths of unindented and unoxidized MgO and MgO-SiC whisker and MgO-SiC particulate composites are shown in Figure 26. A total of five bars were tested for each composite with the error bars representing $s/\sqrt{n}$. It can be observed that the composite materials strength is higher than the strength of pure MgO. However, the fracture strength does not increase with volume percent of SiC although the fracture toughness does. This indicates that the strength controlling flaw size increases with volume percent SiC offsetting any strength increases due to increased fracture toughness (see Equation 48).

Fracture was entirely transgranular with no whisker pullout observed and crack branching occurring in some fractures. Fracture origins in pure
Figure 25. Measured fracture toughness of MgO/SiC composites.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Indent Load</th>
<th>Failure Load</th>
<th>Fracture Stress</th>
<th>$K_{IC}$ (MPa $\sqrt{m}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO</td>
<td>1.2 N</td>
<td>14.22 kg</td>
<td>135.2 MPa</td>
<td>2.25</td>
</tr>
<tr>
<td></td>
<td>2.2</td>
<td>11.55</td>
<td>109.8</td>
<td>2.24 (0.07)*</td>
</tr>
<tr>
<td></td>
<td>2.7</td>
<td>11.2</td>
<td>106.5</td>
<td>2.30</td>
</tr>
<tr>
<td>5v/o P</td>
<td>2.2</td>
<td>13.71</td>
<td>130.4 (4.95)</td>
<td>2.50 (0.07)</td>
</tr>
<tr>
<td>10v/o P</td>
<td>2.2</td>
<td>17.25</td>
<td>164.1 (12.6)</td>
<td>2.92 (0.17)</td>
</tr>
<tr>
<td>15v/o P</td>
<td>2.2</td>
<td>19.95</td>
<td>189.8 (7.6)</td>
<td>3.21 (0.10)</td>
</tr>
<tr>
<td>5v/o W</td>
<td>2.2</td>
<td>17.99</td>
<td>171.1 (10.4)</td>
<td>3.06 (0.14)</td>
</tr>
<tr>
<td>10v/o W</td>
<td>2.2</td>
<td>21.11</td>
<td>200.8 (17.3)</td>
<td>3.39 (0.22)</td>
</tr>
<tr>
<td>15v/o W</td>
<td>2.2</td>
<td>24.97</td>
<td>237.3 (4.59)</td>
<td>3.79 (0.05)</td>
</tr>
</tbody>
</table>

*Numbers in parentheses indicate standard deviations.
Figure 26. Fracture strengths of unindented and unoxidized MgO and MgO/SiC composites.
MgO were due mostly to large grains within the matrix (Figure 27a). Obvious fracture origins of MgO-SiC composites were typically areas of agglomerated SiC particles or whiskers (Figure 27b).

5.4 OXIDATION BEHAVIOR

5.4.1 Oxidation Effects on Strength

**MgO-SiC Particles**

The retained room temperature strengths of MgO composites containing 5, 10, and 15 volume percent SiC particles are shown in Figures 28, 29 and, 30, respectively. The most striking feature for MgO containing 5 and 10 volume percent SiC is the sudden drop in strength in the first half-hour of exposure regardless of oxidizing temperature. For 5% SiC, oxidation times longer than a half-hour below 1200°C result in little additional strength degradation. At 1300°C and above, strength degradation occurs at a much slower rate. For 10% SiC, oxidation times longer than a half-hour showed no general decrease in strength. Composites containing 15 volume percent SiC showed a gradual decrease in strength with increased oxidation time. A summary of MgO containing SiC particulates strengths are given in Table 5.

**MgO-SiC Whiskers**

The retained room temperature strengths of MgO containing 5, 10 and, 15 volume percent SiC whiskers are shown in Figures 31, 32, and, 33, respectively. Strength degradation trends similar to those found in
Figure 27. SEM micrograph of fracture origins: (A) in pure MgO; and in (B) MgO/SiC composites.
Figure 28. Room temperature strengths of oxidized MgO containing 5 volume percent SiC whiskers.
Figure 29. Room temperature strengths of oxidized MgO containing 10 volume percent SiC whiskers.
Figure 30. Room temperature strengths of oxidized MgO containing 15 volume percent SiC whiskers.
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* Room Temperature
Figure 31. Room temperature strengths of oxidized MgO containing 5 volume percent SiC powder.
Figure 32. Room temperature strengths of oxidized MgO containing 10 volume percent SiC powder.
Figure 33. Room temperature strengths of oxidized MgO containing 15 volume percent SiC powder.
SiC powder composites are observed here after oxidation. A large drop in room temperature strength is observed in the first half-hour of high temperature exposure. For oxidation times between 1.5 and 3 hours, the strength does not significantly change from the half-hour strength for most of the composites. The exception being 5 volume percent whiskers at 1300 and 1400°C in which the strength continued to decrease with exposure time. A summary of MgO containing SiC whiskers strengths are given in Table 6.

5.4.2 Oxidation Effects on Microstructure

It was shown in Figure 20 that oxidation of MgO containing SiC results in expansion presumably due to trapped product gas. The evidence of this trapped gas can be seen in Figure 34 in which pores are found in the oxidized region of the composite. The oxidized region, or the reaction layer can easily be observed under polarized light with an optical microscope as illustrated for a partially oxidized sample in Figure 35. The reaction interface is very distinct and uniformly deep. The effect of oxidation time on the as-ground surface of test bars is shown in Figure 36. Alternatively, the effect of temperature on the as-ground surface is shown in Figure 37. The most obvious effect is the restructuring of the surface to form new grains. Analysis of the surface with x-ray diffraction (Figure 38) indicates that SiC oxidizes and then reacts with the MgO matrix to form Mg$_2$SiO$_4$. The presence of Mg$_2$SiO$_4$ was further confirmed by TEM, as shown in Figure 39, in which Mg$_2$SiO$_4$ was found along the grain boundaries in oxidized composites.
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Figure 34. Pore formation in MgO sample containing 5 volume percent SiC whiskers oxidized at 1500°C for 1.5 hours.
Figure 35. Optical micrograph of polished cross section observed of MgO through polarized light containing 5 volume percent SiC whiskers oxidized at 1400°C for 1.5 hours.
Figure 36. Effect of oxidation time on the as-ground surface of MgO containing 5 volume percent SiC whiskers oxidized at 1300°C for: A) 0; B) 0.5; C) 1.5 and D) 3 hours.
Figure 37. Effect of oxidation temperature on as-ground surface of MgO containing 5 v/o SiC whiskers oxidized at: A) 1100°C; B) 1200°C; C) 1300°C; D) 1400°C for 1 hour.
Figure 38. X-ray diffraction data of surface of MgO/15 v/o SiC whiskers oxidized (A) 0 hours and (B) 2 hours. M = MgO; S = SiC; and MS = Mg$_2$SiO$_4$. 
Figure 39. TEM micrograph of oxidized surface of MgO/15 v/o whiskers indicating position of Mg$_2$SiO$_4$ particles and SAD pattern oxidized at 1500°C for 20 hours.
Identification of $\text{Mg}_2\text{SiO}_4$ was determined by selected area diffraction. Indexing of the $\text{Mg}_2\text{SiO}_4$ pattern is discussed in Appendix C. Figure 39 also shows no indication of a continuous grain boundary phase existing between the grains in any of the partially oxidized MgO-SiC composites.

5.4.3 Fractography

Determining the location of fracture origins in oxidized composite materials was found to be very difficult. Although the typical mirror region on the fracture surface could be seen, in most cases no identifiable fracture origin could be located within this region.

SEM of the fracture surfaces of the partially oxidized composites showed similar degradation of the microstructure between the SiC whisker and SiC particulate composites. The most notable feature on the fracture surface were the rapid growth of grains on the surface of the bars (Figure 40). This grain growth on the surface of the composite bars occurred between 1100 and 1500°C. X-ray diffraction (shown in Figure 41) of the surface indicates that the majority of the grains were oriented such that the 110 planes were parallel to the as-ground surface. Closer examination of the fracture surfaces in the oxidized regions indicates whisker pullout (Figure 42). Figure 11 earlier showed that no whisker pullout occurred in unoxidized composites. SEM of the whiskers in this region showed a reaction layer around the whiskers (Figure 43) that appears to be degrading the surface of the whisker. TEM of these oxidized samples indicates possible pore formation along
Figure 40. Columnar grain growth on MgO/15 v/o SiC whisker sample oxidized at 1500°C for 3 hours.
Figure 41. X-ray diffraction pattern with strong increase in (110) peak. Oxidized for 92 hours at 1400°C. M = MgO; S = SiC; and MS = Mg$_2$SiO$_4$. 
Figure 42. Whisker pullout in MgO/SiC composite oxidized at 1200°C for 0.5 hours.
Figure 43. SEM micrograph of partially oxidized SiC whisker in MgO matrix.
the length of the whiskers as seen in Figure 44 which could contribute to whisker pullout during fracture.

5.4.4 Oxidation Kinetics

The reaction kinetic data were obtained from thermogravimetric analysis (TGA) by recording weight loss as a function of time. TGA traces are shown in Figures 45, 46 and 47 for 5, 10 and, 15 volume percent SiC whiskers and particles, respectively, oxidized between 1100°C and 1500°C for a total of 24 hours or until complete oxidation. The log percent weight gain was plotted as a function of log time in Figures 48, 49, and 50 and slopes were found to range between 0.5 and 0.7 indicating that the oxidation weight gain follows a t^k dependence for limited oxidations, i.e. oxidation depths less than 15 percent of the sample thickness. Oxidation depths were calculated from the weight gain data (see Appendix B) which also showed a similar parabolic dependence on time for 5, 10 and 15 volume percent SiC whiskers and particles as illustrated in Figures 51, 52, and 53, respectively. The calculated oxidation depth can also be compared to the measured oxidation depth determined from the polished cross sections of partially oxidized samples. The comparison can be seen in Figure 54 showing that the TGA calculated depth is very close to the measured depth. The slight positive deviation towards the measured depth is due to the reaction layer expanding during oxidation. By combining parts of Figures 51, 52, and 53, it can also be seen (Figure 55) that the oxidation depth is a func-
Figure 44. TEM micrograph of oxidized composite showing possible pore formation between the whisker and matrix.
Figure 45. TGA trace of percentage weight gain as a function of time for MgO containing 5 v/o: A) SiC Whiskers B) SiC Powder.
Figure 46. TGA trace of percentage weight gain as a function of time for MgO containing 10 v/o: A) SiC Whiskers B) SiC Powder.
Figure 47. TGA trace of percentage weight gain as a function of time for MgO containing 15 v/o: A) SiC Whiskers B) SiC Powder.
Figure 48. Log-log plot of percentage weight gain as a function of time for MgO containing 5 v/o: A) SiC whiskers and B) SiC powder.
Figure 49. Log-log plot of percentage weight gain as a function of time for MgO containing 10 v/o: A) SiC whiskers and B) SiC powder.
Figure 50. Log-log plot of percentage weight gain as a function of time for MgO containing 15 v/o: A) SiC whiskers and B) SiC powder.
Figure 51. Oxidation depths calculated from TGA as a function of time for MgO containing 5 v/o: A) SiC Whiskers and B) SiC Powder.
Figure 52. Oxidation depths calculated from TGA as a function of time for MgO containing 10 v/o: A) SiC Whiskers and B) SiC Powder.
Figure 53. Oxidation depths calculated from TGA as a function of time for MgO containing 15 v/o: A) SiC Whiskers and B) SiC Powder.
Figure 54. Comparison of oxidation depths calculated from thermogravimetric analysis and measured from polished cross sections of partially oxidized samples.
Figure 55. Effect of SiC concentration on the calculated oxidation depths at 1200°C for: A) MgO/SiC Whisker; and B) MgO/SiC Powder.
tion of the amount of SiC present in the matrix, with the reaction front moving faster in a 5 volume percent sample than the reaction front in a 10 or 15 volume percent.
CHAPTER VI

DISCUSSION

6.1 OXIDATION EFFECTS ON THE MICROSTRUCTURE

6.1.1 Effect on the Surface

It is clear from Figures 36 and 37 that oxidation above 1100°C severely alters the surface of the MgO composites regardless of the amount or type of SiC present in the material. In the first half hour of oxidation, grain growth on the surface is observed. These grains eventually grow to form the columnar grain layer observed on the surface of the oxidized composite as was shown in Figure 40. X-ray analysis (Figure 38) of the surface had shown that the majority of the surface grains were MgO with the presence of Mg$_2$SiO$_4$ as a minor phase. The presence of Mg$_2$SiO$_4$ indicates that SiC is oxidizing to form SiO$_2$. The SiO$_2$ will concurrently react with the MgO matrix according to:

$$\text{SiO}_2(s) + 2\text{MgO}(s) \rightarrow \text{Mg}_2\text{SiO}_4(s) \quad (54)$$

This reaction can only occur if SiC is allowed to oxidize, i.e. it can only occur in an oxidizing environment.

110
6.1.2 Effect on Composite Interior

The microstructure of the MgO containing SiC appears to go through several stages during oxidation: 1) initial oxidation of SiC at or near the surface as illustrated by Figure 43; 2) oxidation of the SiC within the matrix resulting in SiO$_2$ and product gas formation in which the pores disrupt the microstructure (Figure 34); and 3) the SiO$_2$ reacts with the MgO matrix to form Mg$_2$SiO$_4$ as indicated by x-ray diffraction and SAD. These stages can all exist in the same sample since in a partially oxidized composite, the oxidized layer is in different stages of oxidation. Some of these oxidation stages can be observed through polarized light with an optical microscope in the partially oxidized sample shown in Figure 56. The layer closest to the surface (Region A) corresponds to the columnar grain growth layer, observed in Figure 40. The rapid growth of these grains results in a dense surface layer. Further from the surface is a porous reaction layer (Region B), a result of trapped product gases from the oxidation of SiC. The last layer (Region C) represents the reaction interface where the SiC has just begun to oxidize as illustrated by Figure 43.

The layer closest to the unoxidized composite (Region C) is typically 1 to 10 $\mu$m thick. The matrix material was still relatively dense in this region. However, a large amount of whisker pullout was observed (see Figure 42) on the fractured surfaces of these samples. The pullout of these whiskers is attributed to be the separation of the
Figure 56. Polarized optical micrograph of MgO composite oxidized at 1400°C for 1.5 hours showing different reaction regions.
whisker from the MgO matrix as a result of pore formation along the whisker-matrix interface. These pores will reduce the stress necessary to debond the whisker from the matrix during fracture.

In the next oxidized region closer to the surface (Region B), the microstructure is porous and does not contain any sign of SiC as determined by TEM. The pores are a result of trapped gases from the oxidation of SiC. Figure 57 shows a TEM micrograph from this area in which the SiC whiskers have been completely oxidized resulting in a network of pores throughout this oxidized region. The porosity can easily be observed with the SEM in Figure 58 for a polished cross section of MgO containing 5 volume percent SiC whiskers that was partially oxidized at 1300°C for 7.5 hours. The regions A, B, and C are also included in this micrograph.

The layer closest to the surface is the columnar grain layer consisting of MgO and Mg$_2$SiO$_4$ as determined by x-ray and SAD analysis in Figures 38 and 39. Growth of this layer can be the result of either secondary grain growth or Mg$^{2+}$ diffusion to the surface where it would oxidize to form a layer of MgO. Secondary grain growth of the surface MgO grains would be possible if SiC is removed from the grain boundaries. With the SiC removed the MgO can rapidly grow on the surface. As SiC is progressively oxidized further into the sample, the grain growth would also extend into the sample. However, Mg$_2$SiO$_4$ is known to be forming along the grain boundaries of the MgO (Figure 39) and would also result in pinning of the grain boundaries. Grain growth
Figure 57. TEM micrograph of porous reaction layer of oxidized composite (oxidized at 1400°C, 2 hours). Arrows indicate pores.
Figure 58. SEM micrograph of polished cross section of composite partially oxidized at 1500°C for 10 hours.
could occur if the Mg$_2$SiO$_4$ can move along with the grain boundary or the grain boundary can break away from these particles. This is unlikely since most of the Mg$_2$SiO$_4$ phase was found by TEM to be located at the grain boundary. The diffusion of Mg$^{2+}$ out would also result in the formation of MgO grains on the surface where the cations would oxidize. This results in the original surface being buried beneath the surface of the new MgO layer. To test this theory, a porous platinum marker was sputtered on to the surface of an unoxidized sample which was then oxidized at 1500°C for 20 hours. The platinum was found to remain on the surface during oxidation as illustrated in Figure 59. If growth of the layers had occurred by Mg$^{2+}$ diffusion out, and the platinum remains in its original position, the platinum would have been located at the interface between the columnar grain growth layer and the small grain region (pointed out on Figure 59) as a result of MgO formation around the platinum marker. The possibility of Mg$^{2+}$ Diffusion out will discussed in later sections.

6.2 OXIDATION EFFECT ON STRENGTH

The fracture surfaces of the unoxidized whisker composites in Figure 13 revealed a critical aspect about the mechanics of the fracture. Whisker pullout was not observed in unoxidized composites indicating that a strong bond, either chemical or frictional, exists between the whisker and the matrix. It is apparent that the SiC whiskers and particles are toughening the composite. However,
Figure 59. SEM micrograph of sputtered platinum on surface of composite oxidized at 1500°C for 20 hours.
the overall contribution of each toughening mechanism, such as crack deflection or crack bridging, is difficult. Because of the large difference in the thermal expansion coefficients between the matrix and whisker, it can be assumed that crack deflection processes are occurring during fracture. Crack bridging is also contributing to the toughness of the material as seen by Figure 23, but again, the relative contributions from each mechanism cannot be determined.

The strength of MgO containing SiC was found to very susceptible to degradation as a result of oxidation. The slightest amount of oxidation above 1100°C resulted in severe fracture strength degradation. In unoxidized samples, strength controlling flaws were typically due to processing flaws found on the tensile surface of the bars. However, once the material was even slightly oxidized, apparent fracture origins on the tensile surface could not be located. Since typical processing flaws are no longer controlling the strength of the oxidized composite, the oxidation process is creating new flaws that are more susceptible to tensile stresses. In addition, these flaws are similar in size between samples oxidized under similar conditions. Comparison of the standard deviations with increasing oxidation time from the fracture results listed in Tables 5 and 6 indicates that the flaw size distribution is becoming narrower. Figure 60 plots the standard deviations from several fracture tests as a function of oxidation time. Each point on this figure represents a total of five bars. The standard deviation decreases very rapidly as a function of oxidation time. Such a decrease
Figure 60. Plot of standard deviations of fracture studies as a function of oxidation time.
in the standard deviation would occur if the flaw size distribution on the surface of the oxidized material is becoming narrower. This results in the oxidation reaction producing flaws on the surface that have a very narrow size range for each oxidation temperature. Since in most oxidation tests longer than 0.5 hours the strength does not decrease (Figures 28-33) as dramatically as in the first half hour of oxidation, it can also be assumed that the size of the flaws are only increasing slightly with oxidation past the first half hour of exposure.

In all cases, typically within 0.5 hours of exposure to temperatures above 1100°C, the strength of the composite material drops below that of pure hot-pressed MgO. For this to occur, flaws in the composite material must be larger than flaws in pure MgO to overcome the larger fracture toughness of the composite. Strength controlling flaws in the composites could be found (Figure 27) but such flaws were not found on the fracture surfaces of the oxidized composites. The absence of obvious flaws may indicate that the fracture is no longer the result of a point flaw. This would indicate possible crack formation is occurring on the surface during oxidation or while loading or unloading the sample from the furnace.

Crack formation on the surface of the composite may result from thermal shock when loading or unloading the sample from the furnace or from differences in thermal expansion between the unoxidized and oxidized composite. Two studies were done to determine if thermal shock was affecting the strength of the oxidized composite. In both tests,
composite bars were heated at 10°C per minute to 1300°C and held for 1.5 hours and then cooled at 10°C per minute. The strength of these bars were then compared to the strength of bars rapidly entered and removed from a furnace after oxidation for 1.5 hours at 1300°C. The average strength of the bars slowly heated and cooled was 165 ± 9 MPa while the strength of the rapidly heated and cooled bars was 161 ± 9 MPa. The differences in the strengths is considered negligible. This test indicated that oxidation produces flaws larger than any flaws produced by thermal shock.

Since thermal shock does not significantly lower the strength of the oxidized samples, surface cracks may be forming due to differences in thermal expansion between the oxidized surface and the unoxidized interior. Figure 19 shows that the thermal expansion of MgO decreases as SiC is added to the matrix. If SiC is removed from the surface by oxidation and reacts to form Mg$_2$SiO$_4$, the surface now has a higher thermal expansion. This may result in high enough stresses during cool down to form tensile cracks on the surface. If the stresses on the surface were calculated with the following relation

\[ \sigma = E(T_0 - T)(\alpha_s - \alpha_i)(1 - 3j + 6j^2) \]  

where \( \sigma \) is the tensile stress acting on the outer layer, \( E \) is the elastic modulus of the composite, \( T_0 - T \) is the cooling range, \( \alpha_s \) and \( \alpha_i \) are the thermal expansion coefficients for the oxidized surface and the interior composite, respectively, and \( j \) is the ratio of the oxidized
layer to the thickness of the sample. Assuming 210 GPa for the elastic modulus, a difference in thermal expansion coefficients of only \(2 \times 10^{-6}/^\circ\text{C}\), and a ratio of 5% or approximately 100 \(\mu\text{m}\), a tensile stress of approximately 400 MPa, high enough to produce tensile cracks in the surface of the oxidized sample. These tensile cracks are evident on samples oxidized for long times (>10 hours) as shown in Figure 61a where cracks were easily observed in the columnar growth layer. Closer examination along the interface between the columnar grain growth and the porous MgO matrix, Figure 61b, reveals that the crack extends several microns further into the microstructure. To reveal cracks that occurred in much shorter oxidation times (<3 hours), the surface was first polished before oxidation. After the sample was oxidized, the surface was chemically etched (nitric acid) to enlarge any cracks on the surface of the composite. Observation of these cracks was then possible with an SEM as shown in Figure 62. The white areas are \(\text{Mg}_2\text{SiO}_4\) that has formed from the reaction of \(\text{SiO}_2\) with MgO. The cracks typically originate in or near these reaction zones. Cracks on the surface, as illustrated by Figure 62, would result in a fracture surface in which an obvious fracture origin would not be found since the fracture no longer emanates from a point source.

Since these cracks are not originating from a point source, the geometry can no longer be described as a half-penny shaped crack. Therefore, a different method for calculating the size of the crack was used other than Equation 2. Assuming the surface cracks are at an even
Figure 61. SEM micrograph of: A) crack in columnar grain growth layer; B) larger view of inset.
Figure 62. SEM micrograph of crack formation on surface of composite oxidized at 1200°C for 30 minutes.
depth into the material (a strong possibility since the observed
columnar grain growth and reaction layers are a uniform depth into the
oxidized material), and combinations of these cracks run the entire
width of the test bar, the stress intensity at the crack tip can be
modeled similar to a single-edge notched beam (SENB) test bar. This
would allow a rough estimate of the crack depth to be determined from
Equation 56\textsuperscript{79}.

\[
K_{IC} = \frac{3(L-a)P_c}{b w^2} \frac{Y}{c} (56)
\]

where \( K_{IC} \) is the critical stress intensity, \( Y \) is a geometric factor, \( P_c \)
is the fracture load, \( b \) is the width of the bar, \( w \) is the thickness, \( c \)
is the depth of the crack, \( L \) is the outer span, and \( a \) is the inner span.
The geometric parameter \( Y \) is defined by\textsuperscript{79}

\[
Y = 1.99 - 2.47\left(\frac{c}{w}\right) + 12.97\left(\frac{c}{w}\right)^2 - 23.17\left(\frac{c}{w}\right)^3 + 24.80\left(\frac{c}{w}\right)^4 (57)
\]

if \( c \) is very small compared to \( w \), then \( Y \approx 1.9-1.95 \). Table 7 lists flaw
sizes, \( c \), calculated for MgO containing SiC whisker oxidized at 1200°
and 1300°C. The flaw sizes in Column A were determined by Equations 2
while those in Column B were calculated from Equation 56. These flaw
sizes are also compared to calculated oxidation depths determined from
TGA for the same MgO composite. It can be seen that the oxidation depth
is relatively independent of either calculated flaw size. This is true
because the oxidation depth continues to increase while the strength and flaw sizes after 0.5 hours remain relatively unchanged. The two different types of crack geometries result in a considerable difference in the calculated flaw sizes seen in Table 7. If fracture origins were as large as those calculated from Equation 2, they would have been easily identified during fractography with the SEM.

**TABLE 7**

**FLAW SIZES CALCULATED FROM EQUATIONS 2 & 56 AS COMPARED TO OXIDATION DEPTH**

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Time (hrs)</th>
<th>Column A (c(μm))</th>
<th>Column B (c(μm))</th>
<th>Oxidation Depth (c(μm))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1200</td>
<td>0.25</td>
<td>83</td>
<td>16</td>
<td>&lt; 3</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>103</td>
<td>20</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>130</td>
<td>26</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>3.0</td>
<td>124</td>
<td>26</td>
<td>10</td>
</tr>
<tr>
<td>1300</td>
<td>0.25</td>
<td>104</td>
<td>20</td>
<td>&lt; 10</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>118</td>
<td>24</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>152</td>
<td>30</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>3.0</td>
<td>148</td>
<td>30</td>
<td>28</td>
</tr>
<tr>
<td>1400</td>
<td>0.25</td>
<td>123</td>
<td>24</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>145</td>
<td>29</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>197</td>
<td>42</td>
<td>38</td>
</tr>
<tr>
<td></td>
<td>3.0</td>
<td>181</td>
<td>40</td>
<td>53</td>
</tr>
</tbody>
</table>

Therefore, it appears that the crack size determined from the SENB geometry results in a more realistic crack depth.
6.3 OXIDATION KINETICS

6.3.1 Volume Expansion and SiO₂ Reaction

Swelling of the MgO/SiC composites can result from several mechanisms: formation of a high pressure product gas; and volumetric changes due to the formation of reaction product solids such as SiO₂ and Mg₂SiO₄ which have larger molar volumes than MgO, 27.7 cc/mole and 43.6 cc/mole, respectively. If expansion was due only to the formation of new phases, an MgO matrix containing 15 volume percent SiC would expand 17 percent if all the SiC was oxidized to form SiO₂ and only 11 percent if SiO₂ reacts with MgO to form Mg₂SiO₄. Furthermore, the amount of expansion would be dependent on the amount of SiC present in the MgO. However, it was found in Figure 20 that oxidation of MgO containing 5 volume percent SiC results in the largest amount of volume expansion. Therefore, the majority of swelling during oxidation is the result of pore formation from trapped product gas. Oxidation of MgO containing 15 volume percent SiC for ten hours at 1500°C results in a total expansion of 6 percent. In this same time, the sample has only oxidized 10 percent, or a tenth of the SiC has been oxidized. This tenth would contribute only 18 percent to the overall volume expansion of the material or 1.1 percent of the total 6 percent. This percentage is even less for MgO containing smaller amounts of SiC.

The fact that samples containing smaller percentages of SiC expand more may be explained by the following reason. The creep resistance of oxides is known to increase with increasing SiC whiskers additions to
If pore growth is the result of product gas formation, material transport around the pore must occur to accommodate the expansion of the pore. This is most likely to occur by creep mechanisms. In MgO containing 15 volume percent SiC, the interparticle spacing between SiC particles is closer than in MgO containing 5 volume percent SiC. A rough estimate of interparticle distance can be determined from

\[ d = \frac{2D(1 - V_f)}{3V_f} \]  

which results in interparticle spacings of 4 and 12 μm for 15 and 5 volume percent SiC, respectively. Therefore, for a single SiC particle oxidizing and producing a pore, creep formation of this pore will be more difficult in MgO containing 15 volume percent SiC than for MgO containing only 5 volume percent SiC because the former has a higher density of SiC particles in the vicinity.

If pore formation is the result of product gas formation, the product gas is most likely CO, as illustrated by Equation 1 for the overall oxidation of SiC. If SiC, SiO₂ and C are considered together in a system, CO pressures are not high enough to form a pore within the MgO matrix. The CO partial pressures are illustrated by the calculated stability diagram in Figure 63. The pressure of CO in equilibrium with SiC-SiO₂-O remains below 1 atm as long as the activity of carbon is
Figure 63. SiC-SiO$_2$-O stability diagram at 1700°K. Partial pressures of CO are also shown.
below unity. Therefore oxidation of SiC will form SiO₂ until carbon begins to precipitate out. This will occur when carbon is in equilibrium with SiO₂ at oxygen partial pressures greater than 10⁻¹⁵ atm. Once carbon reaches unit activity, CO pressures can be high enough to create pores in the MgO matrix (> 6 MPa). The oxidation of carbon by oxygen can produce pressures up to 10 atm at 1400°C at oxygen partial pressures as low as 10⁻¹⁴ atm. Therefore, if internal pore pressures are greater than ≈ 2 atm, thermodynamics require that the carbon reach a unit activity to produce high enough CO pressures within the matrix. Such a situation has been shown⁶ to exist during the oxidation of SiC whiskers in an alumina matrix in which SiO₂ was formed leaving carbon on the surface of the whisker separate from the SiC.

6.3.2 Effect of Composition on the Oxidation Rate

Figure 55 indicated that the oxidation depth has a strong dependence on the amount of SiC present in the material. This has been observed by other investigators in alumina and mullite matrices⁶,⁷. The dependence of the oxidation depth on the amount of SiC in the matrix was determined by Equation 38. The oxidation depth was found to be inversely proportional to the square root of the volume fraction of SiC present in the composite. The calculated oxidation depths from TGA data were plotted as a function $V_f^{-1/2}$ and are shown in Figure 64. The oxidation depth does follow a more or less linear dependence on $V_f^{-1/2}$. Also included in this figure are data from the oxidation of alumina/SiC whisker composites from Lin⁶. It appears that the oxidation of SiC in
Figure 64. Calculated oxidation depths as a function inverse square root of volume fraction. Data for Alumina taken from Lin6.
alumina also has the same dependence. However, the oxidation conditions were different for the alumina composite.

6.3.3 Parabolic Kinetics

Figures 48 through 50 indicated that the oxidation reaction obeys parabolic kinetics in which the weight gain was a function of the square root of time. If the mass gain per unit area is calculated from the TGA curves in Figures 45 through 47 and plotted as a function of time, the parabolic rate constant, $K_w$, can be determined from the slope of the line. The parabolic rate constants determined from this method are listed in Table 8. The rate constants can then be plotted as a function of inverse temperature to obtain an activation energy for the overall reaction. These plots are shown in Figure 65a for MgO containing SiC whiskers and 65b for MgO containing SiC powder. The points all fall on a relatively linear line. Furthermore, the slopes of the plotted lines are similar between compositions and the two different types of SiC particles. The similarity in slopes would indicate similar reaction mechanisms. Table 9 lists the activation energies calculated from the slopes of the lines in Figure 65. The activation energies range from 320 to 410 kJ/mole and show no significant dependence on the amount of SiC present. These activation energies can be compared to activation energies for oxygen and magnesium lattice diffusion and oxygen grain boundary diffusion in MgO listed in Table 10. The experimental activation energies are slightly higher than the activation energies for both
### TABLE 8

**EXPERIMENTALLY DETERMINED PARABOLIC RATE CONSTANTS**

<table>
<thead>
<tr>
<th>Material</th>
<th>$K_w$ (g²/cm⁴ sec)</th>
<th>$K_d$ (cm²/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>15 v/o 10 v/o 5 v/o</td>
<td>15 v/o 10 v/o 5 v/o</td>
</tr>
<tr>
<td>MgO/SiC Whisker</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1500°C</td>
<td>1.9x10⁻⁶ 2.1x10⁻⁶ 3.0x10⁻⁶</td>
<td>2.6x10⁻⁶ 5.6x10⁻⁶ 3.2x10⁻⁶</td>
</tr>
<tr>
<td>1400°C</td>
<td>5.3x10⁻⁷ 5.8x10⁻⁷ 1.3x10⁻⁷</td>
<td>8.6x10⁻⁷ 1.8x10⁻⁶ 1.0x10⁻⁶</td>
</tr>
<tr>
<td>1300°C</td>
<td>1.3x10⁻⁷ 1.2x10⁻⁷ 2.0x10⁻⁷</td>
<td>1.5x10⁻⁷ 2.4x10⁻⁷ 2.3x10⁻⁷</td>
</tr>
<tr>
<td>1200°C</td>
<td>2.4x10⁻⁸ 1.9x10⁻⁸ 1.2x10⁻⁸</td>
<td>2.5x10⁻⁸ 2.1x10⁻⁸ 1.7x10⁻⁸</td>
</tr>
<tr>
<td>1100°C</td>
<td>3.0x10⁻⁹ 1.9x10⁻⁹ 9.3x10⁻⁹</td>
<td>5.8x10⁻⁹ 1.9x10⁻⁹ 4.2x10⁻⁹</td>
</tr>
<tr>
<td>MgO/SiC Powder</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1500°C</td>
<td>2.3x10⁻⁸ 1.7x10⁻⁸ 1.0x10⁻⁸</td>
<td>2.6x10⁻⁸ 1.0x10⁻⁸ 2.6x10⁻⁸</td>
</tr>
<tr>
<td>1400°C</td>
<td>3.1x10⁻⁹ 4.4x10⁻⁹ 7.4x10⁻⁹</td>
<td>5.5x10⁻⁹ 3.0x10⁻⁸ 5.8x10⁻⁸</td>
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<tr>
<td>1300°C</td>
<td>7.1x10⁻¹⁰ 1.7x10⁻⁹ 1.3x10⁻⁸</td>
<td>8.2x10⁻¹⁰ 3.0x10⁻⁹ 1.5x10⁻⁸</td>
</tr>
<tr>
<td>1200°C</td>
<td>1.3x10⁻¹⁰ 2.3x10⁻¹⁰ 5.6x10⁻¹⁰</td>
<td>1.3x10⁻¹⁰ 4.3x10⁻¹⁰ 9.5x10⁻¹⁰</td>
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<tr>
<td>1100°C</td>
<td>1.5x10⁻¹¹ 2.2x10⁻¹¹ 5.6x10⁻¹¹</td>
<td>**** 2.4x10⁻¹¹ 2.4x10⁻¹⁰</td>
</tr>
</tbody>
</table>
Figure 65. Parabolic rate constant, \( K_w \), plotted as a function of inverse temperature: A) MgO/SiC whiskers; and B) MgO/SiC powder.
<table>
<thead>
<tr>
<th>MATERIAL</th>
<th>ACTIVATION ENERGY From $K_w$</th>
<th>ACTIVATION ENERGY From $D$ (kJ/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO/15 Volume % SiC Whisker</td>
<td>311</td>
<td>349</td>
</tr>
<tr>
<td>MgO/10 Volume % SiC Whisker</td>
<td>352</td>
<td>329</td>
</tr>
<tr>
<td>MgO/5 Volume % SiC Whisker</td>
<td>407</td>
<td>334</td>
</tr>
<tr>
<td>* * * *</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MgO/15 Volume % SiC Powder</td>
<td>319</td>
<td>362</td>
</tr>
<tr>
<td>MgO/10 Volume % SiC Powder</td>
<td>410</td>
<td>391</td>
</tr>
<tr>
<td>MgO/5 Volume % SiC Powder</td>
<td>352</td>
<td>358</td>
</tr>
</tbody>
</table>
## TABLE 10

**TABULATED LATTICE AND GRAIN BOUNDARY ACTIVATION ENERGIES AND DIFFUSION COEFFICIENTS**

<table>
<thead>
<tr>
<th>TYPE</th>
<th>TEMP (°K)</th>
<th>$\delta D_0$ cm$^3$/sec</th>
<th>$Q$ (kJ/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_{gb}$ 1380-1800</td>
<td>$2.62 \times 10^{-10}$</td>
<td>24481</td>
<td></td>
</tr>
<tr>
<td>&quot; 1339-1523</td>
<td>$5.00 \times 10^{-10}$</td>
<td>25235</td>
<td></td>
</tr>
<tr>
<td>&quot; 1623</td>
<td>$1.37 \times 10^{-9}$</td>
<td>27738</td>
<td></td>
</tr>
<tr>
<td>&quot; 1623</td>
<td>$1.60 \times 10^{-14}$</td>
<td>82</td>
<td></td>
</tr>
<tr>
<td>Oxygen D$_l$ (cm$^2$/sec)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$D_{lattice}$ 1573-2023</td>
<td>$2.50 \times 10^{-6}$</td>
<td>26183</td>
<td></td>
</tr>
<tr>
<td>&quot; 1323-1711</td>
<td>$4.50 \times 10^{-7}$</td>
<td>25285</td>
<td></td>
</tr>
<tr>
<td>&quot; 1293-1723</td>
<td>$2.40 \times 10^{-7}$</td>
<td>23484</td>
<td></td>
</tr>
<tr>
<td>Magnesium D$_l$ (cm$^2$/sec)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$D_{lattice}$ 1429-1660</td>
<td>0.249</td>
<td>33186</td>
<td></td>
</tr>
<tr>
<td>1405-1773</td>
<td>0.54</td>
<td>30987</td>
<td></td>
</tr>
<tr>
<td>2178-2615</td>
<td>$7.43 \times 10^{-2}$</td>
<td>34088</td>
<td></td>
</tr>
<tr>
<td>1723-2673</td>
<td>$4.19 \times 10^{-4}$</td>
<td>26689</td>
<td></td>
</tr>
</tbody>
</table>
grain boundary and lattice diffusion of oxygen in MgO. The activation energies appear to correlate better with the activation energies for magnesium diffusion. Apparent diffusion coefficients for the oxidation reaction can be calculated from parabolic rate constants, \( K_d \), determined from a plot of the square of the oxidation depth as a function of time. The values for \( K_d \) determined in this manner are also listed in Table 8.

From \( K_d \), the apparent diffusion coefficient can be calculated from Equations 38 or 46, depending on if the reaction is controlled by lattice or grain boundary diffusion, respectively. For grain boundary diffusion, the quantity \( \delta D_g \) was calculated instead of the diffusion coefficient \( D_g \) because of the large range of \( \delta \) values reported for the grain boundary thickness. A grain size of 5 \( \mu m \) was substituted for \( d \) in Equation 46. Partial pressures of oxygen in these equations can be estimated from the free energy of the reaction shown in Equation 1 or estimating it from Figure 63. From Equation 1:

\[
\frac{p_{O_2}}{p_{CO}}^e = \frac{2}{3} \exp \left[ \frac{2 \delta G}{3 RT} \right] \tag{59}
\]

or

\[
\ln \frac{p_{O_2}}{p_{CO}}^e = \frac{2}{3} \ln p_{CO} + \left[ \frac{2 \delta G}{3 RT} \right] \tag{60}
\]

Equation 61 shows that the log of the partial pressure of oxygen at the reaction interface is dominated by the free energy of the reaction and
not so much by the partial pressure of CO. Values for $\delta D_{gb}$ were calculated from $K_d$ assuming that the reaction was grain boundary controlled. The $\delta D_{gb}$ values were plotted as a function of inverse temperature in Figures 66a and 66b for MgO containing SiC whiskers and MgO containing SiC particles, respectively. Alternatively, if the reaction is controlled by lattice diffusion, then the diffusion coefficients would be determined from Equation 38 using the values of $K_d$ listed in Table 8. The experimentally calculated lattice diffusion coefficients were plotted as a function of inverse temperature and are shown in Figures 67a and 67b for MgO containing SiC whiskers and MgO containing SiC particles, respectively.

6.3.4 Comparison with Calculated Diffusion Coefficients

Diffusion coefficients for lattice and $\delta D_{gb}$ can be calculated from data reported in the literature (Table 10) from Equation 61:

$$D = D_0 \exp(-Q/RT)$$  \hspace{1cm} (61)

where $D_0$ is the diffusional constant and Q is the activation energy. By substituting in the appropriate values listed in Table 10 for $D_0$ and Q, the experimentally determined diffusion coefficients from this investigation can be compared to other investigators’ values.

Figure 68 shows the comparison between the calculated lattice diffusion coefficient for oxygen and lattice diffusion coefficients determined from experimental data and calculated from Equation 38. It
Figure 66. The product $\delta D_p$ plotted as a function of inverse temperature for: A) MgO/SiC whiskers; and B) MgO/SiC powder obtained from experimental data.
Figure 67. The coefficient $D_1$ plotted as a function of inverse temperature for: A) MgO/SiC whiskers; and B) MgO/SiC powder obtained from experimental data.
Figure 68. Comparison of tabulated oxygen lattice diffusion coefficients and experimental lattice diffusion coefficients. A) MgO/SiC Whisker; and B) MgO/SiC Powder.
is clear that there is a large discrepancy between literature and experimental values. The experimental values for lattice diffusion are three orders of magnitude too fast. Figure 69 shows the comparison of $\delta D_{gb}$ values for oxygen calculated from literature and from experimental data. Some of the experimental values are in better agreement with reported literature values but still are several orders of magnitudes slower than reported literature values. Figure 70 shows the comparison between diffusion coefficients for magnesium diffusion through MgO and calculated lattice diffusion coefficients from this study. This figure shows a very good agreement between the experimental diffusion coefficients and the diffusion coefficients for lattice diffusion of magnesium through MgO. Furthermore, the reported activation energies match the experimental activation energies much closer than for either grain boundary or lattice diffusion of oxygen. It therefore appears that the diffusion of magnesium to the surface where it may oxidize to form MgO may be controlling the overall reaction. This would explain the overall columnar grain growth on the surface of the oxidized samples and preferential crystal orientation. However, this contradicts the platinum marker experiment. If the reaction is controlled by Mg$^{2+}$ diffusion to the surface than the platinum should remain at the bottom of the columnar layer. It may be possible for the platinum to remain on the surface for the following reasons. The surface energy between the platinum and the MgO may be very high. Therefore, platinum on the surface of the MgO would have an overall lower energy than platinum
Figure 69. Comparison of reported oxygen grain boundary coefficients and calculated experimental grain boundary diffusion coefficients. A) MgO/SiC whisker; and B) MgO/SiC powder.
Figure 70. Comparison of reported magnesium lattice diffusion coefficients and experimental lattice diffusion coefficients. A) MgO/SiC whiskers; and B) MgO/SiC powder.
within an MgO matrix. This would allow the platinum to remain on the surface of the sample during oxidation. It is also possible that the magnesium ions are oxidizing just below the surface of the columnar grain growth layer where the oxygen potential is much higher. This would possibly push the surface MgO up leaving the platinum on the surface. If magnesium diffusion out is occurring, then the pores observed in the matrix could also be the result of Mg\(^{2+}\) removal from the matrix.
APPENDIX A

DENSITY CALCULATIONS
Density calculations were determined by the Archimedes' principle. The weights of the samples were taken then they were placed in vacuum chamber and then back filled with isopropyl alcohol. The following equation gives the apparent density of the samples:

\[ \rho_a = \frac{W_d \rho_{al}}{W_s - W_{ss}} \]  

where
- \( \rho_a \) = Apparent density (g/cc)
- \( W_d \) = Weight of dry sample (g)
- \( \rho_{al} \) = Density of alcohol (g/cc)
- \( W_{ss} \) = Weight of sample suspended in alcohol (g)
- \( W_s \) = Weight of saturated sample (g)
APPENDIX B

CALCULATION OF OXIDATION DEPTHS
FROM TGA DATA
Determination of Oxidation Depth

FRACTION REACTED = \frac{\text{PERCENT WEIGHT GAIN}}{\text{TOTAL POSSIBLE WEIGHT GAIN}} = F

8x^3 - 4x^2(a + b + c) + 2x(ca + bc + ab) - abcF = 0

SOLVE EQUATION FOR x BY ITERATION
APPENDIX C

INDEXING OF Mg$_2$SiO$_4$
Mg$_2$SiO$_4$ - Forsterite

Olivine Structure - Space Group Pbmn (D$_h^16$)$_{2h}$

\[ a = 4.765 \quad \alpha = \beta = \gamma = 90^\circ \]
\[ b = 10.23 \]
\[ c = 5.997 \]

Atom Positions$^9$:

\[
\begin{array}{cccc}
M_{Sl} & 0 & 0 & 0 \\
M_{SII} & -0.01 & 0.281 & 0.25 \\
Si & 0.415 & 0.095 & 0.25 \\
\end{array}
\]
\[
\begin{array}{cccc}
O & -0.229 & 0.083 & 0.25 \\
O_{II} & 0.221 & 0.43 & 0.25 \\
O_{III} & 0.262 & 0.152 & 0.027 \\
\end{array}
\]

Using positions reported by Structurbericht$^9$:

\[
\begin{array}{cccc}
M_{Sl} & 0 & 0 & 0 \\
0.5 & 0 & 0 \\
0.5 & 0.5 & 0.5 \\
0 & 0.5 & 0.5 \\
\end{array}
\]
\[
\begin{array}{cccc}
O & 0.771 & 0.083 & 0.25 \\
0.229 & 0.917 & 0.75 \\
0.729 & 0.917 & 0.75 \\
0.271 & 0.417 & 0.027 \\
\end{array}
\]
\[
\begin{array}{cccc}
M_{SII} & 0.99 & 0.281 & 0.25 \\
0.01 & 0.719 & 0.75 \\
0.51 & 0.781 & 0.25 \\
0.49 & 0.219 & 0.75 \\
\end{array}
\]
\[
\begin{array}{cccc}
O_{II} & 0.221 & 0.43 & 0.25 \\
0.779 & 0.57 & 0.75 \\
0.279 & 0.93 & 0.25 \\
0.721 & 0.07 & 0.75 \\
\end{array}
\]
\[
\begin{array}{cccc}
Si & 0.415 & 0.095 & 0.25 \\
0.585 & 0.905 & 0.75 \\
0.085 & 0.595 & 0.25 \\
0.915 & 0.405 & 0.75 \\
\end{array}
\]
\[
\begin{array}{cccc}
O_{III} & 0.262 & 0.152 & 0.027 \\
0.738 & 0.848 & 0.973 \\
0.738 & 0.848 & 0.527 \\
0.262 & 0.152 & 0.473 \\
0.238 & 0.652 & 0.473 \\
0.762 & 0.348 & 0.527 \\
0.762 & 0.348 & 0.973 \\
0.238 & 0.652 & 0.027 \\
\end{array}
\]
These positions are based on a unit cell of:

The International Tables for X-Ray Crystallography\(^2\) use a different basis:

The transformation matrix is then

\[
\begin{bmatrix}
0 & 1 & 0 \\
0 & 0 & 1 \\
1 & 0 & 0
\end{bmatrix}
\]

Doing the transform results in:

\[
\begin{array}{c|ccc}
\text{Mg I in (a) positions} & x & y & z \\
\hline
\text{Mg II in (c)} & 0.281 & 0.25 & -0.01 \\
\text{Si in (c)} & 0.095 & 0.25 & 0.415 \\
\text{O I in (c)} & 0.083 & 0.25 & -0.229 \\
\text{O II in (c)} & 0.43 & 0.25 & 0.221 \\
\text{O III in (c)} & 0.152 & 0.027 & 0.262 \\
\end{array}
\]
LIST OF REFERENCES


70. JANAF Thermochemical Tables, NBS (1971).


74. J. Jones and M. Berrard, _Ceramics: Industrial Processing and Testing_, Iowa State University, Ames, Iowa (1972).


