WETTING OF CERAMIC PARTICULATES WITH LIQUID ALUMINUM ALLOYS

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Archives
WETTING OF CERAMIC PARTICULATES
WITH LIQUID ALUMINUM ALLOYS

BY

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ABSTRACTS

Wetting phenomena in ceramic particulate/liquid Al-alloy systems were investigated experimentally. Uniformly packed powder specimens were prepared with a tamping device specially made for the present experiment and wetting tests were conducted by pressure infiltration of liquid Al-alloys through the powder specimens. The threshold pressure for infiltration was used as a measure of wettability. The threshold pressure was converted to wetting angle by a modified capillary pressure equation. With this technique, wettabilities were measured for SiC and B₄C particulates with pure Al, and Al-Cu, Al-Si, and Al-Mg alloys with nominal alloying elements additions of 2 and 4.5%.

Five major variables tested to study wetting phenomena in ceramic/Al-alloy systems were holding time, melt temperature, alloying element, gas atmosphere, and particulate. The metal/ceramic interfaces were investigated with optical microscopy, SEM, EPMA, and Auger Electron Spectroscopy in order to better understand the wetting process.

The threshold pressure decreased with temperature as well as with time for all the ceramic/metal system. The good relationship was found between the alloying effect in the threshold pressure and the free energy of formation of oxide phase of alloying elements. More reactive alloying elements were more effective in improving wettability. In air atmospheres, the threshold pressure usually increased markedly as a result of thick oxide layer formation on the liquid front. B₄C particulates showed lower threshold pressure than SiC particulates.

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# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Chapter</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>TITLE PAGE</td>
<td>1</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>2</td>
</tr>
<tr>
<td>TABLE OF CONTENTS</td>
<td>3</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>6</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>12</td>
</tr>
<tr>
<td>ACKNOWLEDGEMENTS</td>
<td>13</td>
</tr>
<tr>
<td>1. INTRODUCTION</td>
<td>14</td>
</tr>
<tr>
<td>2. BACKGROUND</td>
<td></td>
</tr>
<tr>
<td>2.1. Basic Concepts in Wetting</td>
<td>17</td>
</tr>
<tr>
<td>2.2. Variables in Wetting</td>
<td>19</td>
</tr>
<tr>
<td>2.3. Measurements of Surface Energies and Wetting Angle</td>
<td></td>
</tr>
<tr>
<td>2.3.1. Surface energy of liquids</td>
<td>22</td>
</tr>
<tr>
<td>2.3.2. Surface energy of solids</td>
<td>25</td>
</tr>
<tr>
<td>2.3.3. Solid-liquid interfacial energy</td>
<td>26</td>
</tr>
<tr>
<td>2.3.4. Wetting angle on particulates</td>
<td>27</td>
</tr>
<tr>
<td>2.4. Theoretical Estimation of Surface Energy</td>
<td>29</td>
</tr>
<tr>
<td>2.4.1. Miedema's approach</td>
<td>30</td>
</tr>
<tr>
<td>2.4.2. Warren's approach</td>
<td>34</td>
</tr>
<tr>
<td>2.5. Wetting of Ceramic Materials with Liquid Aluminum Alloys</td>
<td></td>
</tr>
<tr>
<td>2.5.1. Wetting experiment</td>
<td>36</td>
</tr>
<tr>
<td>2.5.2. Approaches to improve wettability</td>
<td>38</td>
</tr>
<tr>
<td>2.6. Metal:Ceramic Interfaces</td>
<td></td>
</tr>
<tr>
<td>2.6.1. Physics and chemistry of interfaces</td>
<td>40</td>
</tr>
<tr>
<td>2.6.2. Metal:ceramic interaction</td>
<td>42</td>
</tr>
</tbody>
</table>
3. EXPERIMENTAL METHODS

3.1. Materials
  3.1.1. Ceramic particulates 45
  3.1.2. Alloy preparation 47
3.2. Powder Specimen Preparation 47
3.3. Pressure Infiltration 48
3.4. Calculation of Wettability 50
3.5. Microstructural Analysis 51
3.6. Auger Electron Spectroscopy Analysis 52

4. CHARACTERIZATION OF INFILTRATED SPECIMEN

4.1. Surface Characterization of Ceramic Particulates 53
4.2. Microstructure of Infiltrated Powder Specimen 54
4.3. Fracture Morphology 56

5. WETTING OF CERAMIC PARTICULATES

5.1. Energetic Considerations 59
5.2. Estimation of wetting angle 62
5.3. Effect of Time 63
5.4. Effect of Temperature 65
5.5. Effect of Alloying Elements 67
5.6. Effect of Gas Atmosphere 69
5.7. Effect of Surface Chemistry of Particulates 70
5.8. Infiltration Behavior 72

6. INTERFACE PHENOMENA

6.1. Gas-solid Reaction of Particulates 78
6.2. Liquid Metal:Gas Interface 81
6.3. Metal:Ceramic Interface
   6.3.1. Dissolution 84
   6.3.2. Chemical reaction 86

7. SUMMARY

    7.1. Summary and Conclusion 89
    7.2. Suggestions for Further Work 91

FIGURES 93

TABLES 191

BIBLIOGRAPHY 201
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Schematic diagram of a liquid drop on the solid surface showing the interfacial forces and wetting angle for (a) wetting and (b) non-wetting systems, respectively.</td>
<td>93</td>
</tr>
<tr>
<td>2.2</td>
<td>Equilibrium at (a) wetting and (b) non-wetting capillary systems.</td>
<td>94</td>
</tr>
<tr>
<td>2.3</td>
<td>Three fundamental types of wetting: (a) adhesional wetting, (b) spreading wetting, and (c) immersional wetting.</td>
<td>95</td>
</tr>
<tr>
<td>2.4</td>
<td>Parameters used in the calculation of the surface energy of liquid.</td>
<td>96</td>
</tr>
<tr>
<td>2.5</td>
<td>Surface energy and dihedral angles in solid:liquid:vapor equilibrium.</td>
<td>97</td>
</tr>
<tr>
<td>2.6</td>
<td>Free energy vs. composition diagram for the solid and liquid pseudo-binary system.</td>
<td>98</td>
</tr>
<tr>
<td>2.7</td>
<td>Wetting angle vs. temperature for Al$_2$O$_3$/Al system.</td>
<td>99</td>
</tr>
<tr>
<td>3.1</td>
<td>SEM photographs of (a) SiC and (b) B$_4$C particulates used for the present study.</td>
<td>100</td>
</tr>
<tr>
<td>3.2</td>
<td>Size distribution of SiC particulates.</td>
<td>101</td>
</tr>
<tr>
<td>3.3</td>
<td>Size distribution of B$_4$C particulates.</td>
<td>102</td>
</tr>
<tr>
<td>3.4</td>
<td>Sketch of tamping device.</td>
<td>103</td>
</tr>
<tr>
<td>3.5</td>
<td>SEM photographs of (a) packed SiC particulates and (b) Saffil paper used as filter.</td>
<td>104</td>
</tr>
<tr>
<td>3.6</td>
<td>Sketch of the pressure chamber used for pressure infiltration.</td>
<td>105</td>
</tr>
<tr>
<td>3.7</td>
<td>Array of equipments in (a) heating system and (b) pressure system.</td>
<td>106</td>
</tr>
<tr>
<td>3.8</td>
<td>Sequence of infiltration of liquid metal through powder specimen under pressure.</td>
<td>107</td>
</tr>
<tr>
<td>4.1</td>
<td>AES spectrum taken from the as-received SiC particulates.</td>
<td>108</td>
</tr>
<tr>
<td>4.2</td>
<td>AES spectrum taken from the as-received B$_4$C particulates.</td>
<td>109</td>
</tr>
<tr>
<td>Section</td>
<td>Description</td>
<td></td>
</tr>
<tr>
<td>---------</td>
<td>-------------</td>
<td></td>
</tr>
<tr>
<td>4.3</td>
<td>AES element profile as a function of sputtering time for as-received SiC particle.</td>
<td></td>
</tr>
<tr>
<td>4.4</td>
<td>AES element profile as a function of sputtering time for as-received B$_4$C particle.</td>
<td></td>
</tr>
<tr>
<td>4.5</td>
<td>AES spectrum obtained from the oxidized SiC particulate.</td>
<td></td>
</tr>
<tr>
<td>4.6</td>
<td>AES element profile for uninfilitrated SiC particulate after wetting experiment.</td>
<td></td>
</tr>
<tr>
<td>4.7</td>
<td>AES element profile for uninfilitrated B$_4$C particulate after wetting experiment.</td>
<td></td>
</tr>
<tr>
<td>4.8</td>
<td>Microstructure of Al-2% Cu alloy solidified inside the quartz tube after pressure infiltration.</td>
<td></td>
</tr>
<tr>
<td>4.9</td>
<td>Microstructure of Al-2% Si alloy solidified inside the quartz tube after infiltration test.</td>
<td></td>
</tr>
<tr>
<td>4.10</td>
<td>Microstructure of Al-2% Mg alloy solidified inside the quartz tube after infiltration test.</td>
<td></td>
</tr>
<tr>
<td>4.11</td>
<td>Al-Cu binary phase diagram.</td>
<td></td>
</tr>
<tr>
<td>4.12</td>
<td>Al-Si binary phase diagram.</td>
<td></td>
</tr>
<tr>
<td>4.13</td>
<td>Al-Mg binary phase diagram.</td>
<td></td>
</tr>
<tr>
<td>4.14</td>
<td>Microstructure of SiC powder specimen infiltrated with Al-2% Cu at (a) matrix:Saffil paper boundary and (b) Saffil paper: powder compact boundary.</td>
<td></td>
</tr>
<tr>
<td>4.15</td>
<td>Typical microstructure of SiC/pure Al system infiltrated at 800 °C.</td>
<td></td>
</tr>
<tr>
<td>4.16</td>
<td>Typical microstructure of SiC/Al-2% Cu system infiltrated at 800 °C.</td>
<td></td>
</tr>
<tr>
<td>4.17</td>
<td>Typical microstructure of SiC/Al-2% Si system infiltrated at 800 °C.</td>
<td></td>
</tr>
<tr>
<td>4.18</td>
<td>Typical microstructure of SiC/Al-2% Mg system infiltrated at 800 °C.</td>
<td></td>
</tr>
<tr>
<td>4.19</td>
<td>SEM micrographs of deep-etched SiC/pure Al system infiltrated at 800°C.</td>
<td></td>
</tr>
<tr>
<td>4.20</td>
<td>Microstructure of SiC/Al-2% Si system (a) at the top and (b) at the bottom portion of the specimen infiltrated at 800 °C.</td>
<td></td>
</tr>
<tr>
<td>4.21</td>
<td>Microstructure of SiC/pure Al system infiltrated (a) at 700 °C and (b) 900 °C.</td>
<td></td>
</tr>
<tr>
<td>4.22</td>
<td>Typical microstructure of B$_4$C/pure Al system infiltrated at 800 °C.</td>
<td></td>
</tr>
</tbody>
</table>
4.23 Typical microstructure of B₄C/Al-2% Cu system infiltrated at 800 °C.
4.24 Typical microstructure of B₄C/Al-2% Si system infiltrated at 800 °C.
4.25 Typical microstructure of B₄C/Al-2% Mg system infiltrated at 800 °C.
4.26 Al-B binary phase diagram.
4.27 SEM photograph of deep-etched B₄C/Al-2% Mg specimen infiltrated at 800 °C.
4.28 EDX peaks obtained (a) from the matrix and (b) from the second phase shown in Fig. 4.34 (b).
4.29 Fracture surface of SiC powder specimen infiltrated with pure Al with 724 kPa at 800 °C.
4.30 Fracture surface of SiC powder specimen infiltrated with Al-2% Cu alloy with 827 kPa at 800 °C.
4.31 Fracture surface of SiC powder specimen infiltrated with Al-2% Si alloy with 765 kPa at 800 °C.
4.32 Fracture surface of SiC powder specimen infiltrated with Al-2% Mg alloy with 621 kPa at 800 °C.
4.33 Fracture surface of B₄C powder specimen infiltrated with pure Al alloy with 758 kPa at 800 °C.
4.34 Fracture surface of B₄C powder specimen infiltrated with Al-2% Cu alloy with 758 kPa at 800 °C.
4.35 Fracture surface of B₄C powder specimen infiltrated with Al-2% Si alloy with 731 kPa at 800 °C.
4.36 Fracture surface of B₄C powder specimen infiltrated with Al-2% Mg alloy with 724 kPa at 800 °C.
4.37 AES spectrum obtained from the surface of fractured B₄C/Al-2% Mg specimen.

5.1 Infiltration of liquid between particulates. Top and side views for (a) wetting system, and (b) non-wetting system.
5.2 Sketch of liquid front valancing with surface energy and wetting angle at (a) initial, (b) after time (t).
5.3 Schematic dependence of the threshold pressure on time. Infiltration begins at time (t).
5.4 Effect of shape factor on the wetting angle for SiC/Al system.
5.5 Effect of shape factor on the wetting angle for $B_4C/Al$ system.

5.6 Change in wetting angle with time for SiC/Al-alloy system at 800 °C.

5.7 Change in wetting angle with time for $B_4C/Al$-alloy system at 800 °C.

5.8 Change in wetting angle with temperature for SiC/Al-alloy system.

5.9 Change in wetting angle with temperature for $B_4C/Al$-alloy system.

5.10 Change in wetting angle with alloying element in SiC/Al-alloy system at 800 °C.

5.11 Change in wetting angle with alloying element in $B_4C/Al$-alloy system at 800 °C.

5.12 Change in threshold pressure with time for SiC/Al-alloy systems.

5.13 Change in threshold pressure with time for $B_4C/Al$-alloy systems.

5.14 Comparison of time dependence of calculated and experimental values of threshold pressure for SiC and $B_4C$ specimen infiltrated with Al-2% Si alloy at 800 °C.

5.15 Change in threshold pressure with temperature for SiC/Al-alloy systems.

5.16 Change in threshold pressure with temperature for $B_4C/Al$-alloy systems.

5.17 The relationship between $\cos \theta$ and temperature for SiC/Al-alloy systems.

5.18 The relationship between $\cos \theta$ and temperature for $B_4C/Al$-alloy systems.

5.19 Plot of $\log P_{th}$ (kPa) vs. $1/T$ (K) for SiC/Al-alloy systems.

5.20 Plot of $\log P_{th}$ (kPa) vs. $1/T$ (K) for $B_4C/Al$-alloy systems.

5.21 Change in threshold pressure with alloying element for SiC/Al-alloy system at 800 °C.

5.22 Change in threshold pressure with alloying element for $B_4C/Al$-alloy system at 800 °C.

5.23 Relationship between the threshold pressure and the free energy of formation of oxide of each alloying element in SiC/Al-alloy system.
5.24 Relationship between the threshold pressure and the free energy of formation of oxide of each alloying element in B₄C/Al-alloy system.

5.25 Infiltration behavior in Ar and in air atmosphere for B₄C/Al-4.5% Cu system at 800 °C.

5.26 Infiltration behavior in Ar and in air atmosphere for SiC/Al-4.5% Cu system at 800 °C.

5.27 Infiltration behavior in Ar and in air atmosphere for B₄C/Al-2% Mg system at 800 °C.

5.28 Variation of infiltration distance as a function of applied pressure for untreated SiC and oxidized SiC powder specimen tested with Al-2% Mg alloy at 800 °C.

5.29 Microstructure of oxidized-SiC powder specimen infiltrated with Al-2% Mg alloy at 800 °C.

5.30 Variation of the infiltration distance as a function of the applied pressure for SiC/Al-2% Cu system at 900 °C.

5.31 Variation of the infiltration distance with the applied pressure for SiC and B₄C powder specimen infiltrated with Al-2% Mg alloy at 800 °C.

5.32 Variation of the infiltration distance as a function of the applied pressure for SiC/Al-2% Cu system at different melt temperatures.

5.33 Variation of the infiltration distance as a function of the applied pressure for SiC/Al-2% Cu system at different holding times at 800 °C.

5.34 Variation of the infiltration distance as a function of the applied pressure for B₄C/Al-2% Si system at different holding times at 800 °C.

5.35 Infiltration distance as a function of time for B₄C/Al-2% Si system at 800 °C.

5.36 Comparison of the time dependence of calculated and experimental values of infiltration distance for B₄C/Al-2% Si system infiltrated with 724 kPa at 800 °C.

5.37 Comparison of pressure dependence of calculated and experimental values of infiltration distance for B₄C/Al-2% Si system infiltrated at 800 °C for 5 min.

5.38 Sketch of changes in wetting angle with velocity of moving liquid.

5.39 Contribution of reaction-assisted infiltration to the total infiltration distance.
5.40 Infiltration distance vs. applied pressure for $B_4C$/Al-alloy systems at 800 °C for 5 min.

6.1 Free energy change of carbides as a function of temperature.

6.2 Free energy change of oxides as a function of temperature.

6.3 AES element profile on a $B_4C$ particulate after vacuum cleaning at 220 °C for 30 min.

6.4 Sketch of oxide layer formation on the particulates during the infiltration.

6.5 AES element profile for matrix-side from the fracture surface of SiC/pure Al specimen.

6.6 AES element profile for particle-side from the fracture surface of SiC/pure Al specimen.

6.7 AES element profile for particle-side from the fracture surface of SiC/Al-2% Mg specimen.

6.8 AES peak-to-peak profile for particle-side from the fracture surface of SiC/pure Al specimen.

6.9 AES peak-to-peak profile for particle-side from the fracture surface of SiC/Al-2% Mg specimen.

6.10 AES element profile for matrix-side from the fracture surface of $B_4C$/pure Al specimen.

6.11 AES element profile for particle-side from the fracture surface of $B_4C$/pure Al specimen.

6.12 AES peak-to-peak profile for matrix-side from the fracture surface of $B_4C$/pure Al specimen.

6.13 AES peak-to-peak profile for particle-side from the fracture surface of $B_4C$/pure Al specimen.

6.14 (a) Al-Si-C phase diagram at 800 °C.
    (b) Al-B-C phase diagram at 900 °C.

6.15 Schematic description of wetting processes for (a) SiC and (b) $B_4C$ particulates with liquid aluminum alloys.
# LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Surface energy of liquid aluminum.</td>
<td>191</td>
</tr>
<tr>
<td>2.2</td>
<td>Wetting angles of ceramic materials with liquid aluminum alloys.</td>
<td>192</td>
</tr>
<tr>
<td>3.1</td>
<td>Chemical analysis of particulates.</td>
<td>193</td>
</tr>
<tr>
<td>3.2</td>
<td>Chemical analysis of alloys.</td>
<td>194</td>
</tr>
<tr>
<td>4.1</td>
<td>Infiltred specimens used for metallography, fractography, and AES analysis.</td>
<td>195</td>
</tr>
<tr>
<td>5.1</td>
<td>Values of the coefficients $c$ and $d$ in eq. (5.7) for SiC and $B_4C$</td>
<td>196</td>
</tr>
<tr>
<td></td>
<td>particulates systems at $800,^\circ$C.</td>
<td></td>
</tr>
<tr>
<td>5.2</td>
<td>Threshold pressure, surface energy, and wetting angle for SiC/Al-alloy</td>
<td>197</td>
</tr>
<tr>
<td></td>
<td>systems.</td>
<td></td>
</tr>
<tr>
<td>5.3</td>
<td>Threshold pressure, surface energy, and wetting angle for $B_4C$/Al-alloy</td>
<td>198</td>
</tr>
<tr>
<td></td>
<td>systems.</td>
<td></td>
</tr>
<tr>
<td>5.4</td>
<td>Threshold pressure for SiC and $B_4C$ particulates in Ar and in air</td>
<td>199</td>
</tr>
<tr>
<td></td>
<td>atmosphere at $800,^\circ$C.</td>
<td></td>
</tr>
<tr>
<td>5.5</td>
<td>Threshold pressure and slope of infiltration distance vs. pressure for SiC/Al alloy and $B_4C$/Al alloy systems.</td>
<td>200</td>
</tr>
</tbody>
</table>
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1. INTRODUCTION

There have been many efforts in materials technology to provide high performance materials. Metal matrix composites are a family of advanced materials which may have attractive properties including high axial strength, high-temperature properties, low coefficient of thermal expansion, good wear resistance, decreased life cycle cost, and insensitivity to environment. Composite materials also offer the opportunity to develop new materials with a unique set of properties that are not available with conventional materials. However, the development of metal matrix composites had received only limited attention because of either their high cost or limited service experience. Recently higher performance requirements and new applications for the aerospace and automobile industries renewed activity.

Emphasis in the metal matrix composites field has been focused in the area of light metal matrices, especially on aluminum alloys. Continuous elastic mono-filaments, such as boron and SiC, and multi-fiber yarns, such as graphite and aluminum oxide, are being used as reinforcing materials. Discontinuous particulates or whiskers, such as SiC, B_4C, and Al_2O_3, are being used to reinforce aluminum alloys for low-cost, isotropically loaded structures.

Discontinuous particulate or whisker reinforced aluminum alloy composites have a unique combination of high specific modulus and strength as well as good thermal stability. Compared with continuous fiber reinforced composites, discontinuous second phase reinforced composites provide improved ductility and reduced anisotropy in mechanical properties. Furthermore, the latter can be subjected to secondary working with conventional equipments. Extrusions may be carried out or may be worked further by rolling or forging. Recently, particulates are being added to be distributed among continuous fibers in fiber-reinforced aluminum alloys to improve both longitudinal and
transverse strength.

The potentials of metal matrix composites can be fully exploited only after the development of suitable processing techniques. Fabrication techniques for organic matrix composites are now well defined. However, the translation of this technology to metal matrix composites has been difficult mainly due to high chemical reactivity and poor wettability between solid reinforcements and liquid matrix. Therefore, the process technology of metal matrix composites is still immature in spite of its 20-year history.

The fabrication of metal matrix composites by casting is an attractive processing method since this process offers a wide selection of materials and processing conditions. Good wetting is an essential condition for the generation of a satisfactory bond between solid ceramic phase and liquid metal matrix during the fabrication of composites. In spite of the importance of wettability in the manufacture of composites, relatively few studies have been conducted and many fundamental questions remains unanswered.

In metal matrix composites, the primary function of the reinforcements is to support most of the applied load, while that of the matrix is to bind the reinforcements together and to transmit and distribute the external loads to the individual reinforcements. Since transfer of loads require a bonding between the constituents, the nature of interface is critical to the property of composites. Generally, it is desirable to have a strong enough interface to allow transfer and distribution of load from the matrix to the reinforcements without failure. The ideal interface may be a mechanic continuum involving coherency on the atomic surfaces, and chemical discontinuum having no mass transports between constituents.

For non-wetting systems, application of pressure alone can not overcome poor wettability in practical sense due to debonding during solidification and void formation in the small channels. Therefore, good wettability is one of the most important parameters for successful fabrication of composites by casting.
The main objective of this thesis work is to establish a basic understanding of wetting phenomena in ceramic/liquid aluminum alloy system. Since the wettability of fine ceramic particulates with liquid metal cannot be measured by conventional method, such as sessile-drop test or multiphase equilibrium method, the first step of this research work was to develop a reliable experimental technique for evaluation of wettability of solid particulates with liquid metal.

The new technique includes uniform packing of ceramic powder followed by pressure infiltration of liquid metal through the powder specimen. The threshold pressure for infiltration was either used as a measure of wettability or converted to a wetting angle by using the modified capillary force equation.

Metal-ceramic interface phenomena were studied to investigate the relationship between the interfacial reactions and wetting. A qualitative analysis was made on the reaction-assisted wetting with experimental results.

Two commonly used ceramic particulates, SiC and B$_4$C, and seven different aluminum alloys, pure Al, Al-2% Cu, Al-4.5% Cu, Al-2% Si, Al-4.5% Si, Al-2% Mg, and Al-4.5% Mg, were employed in this study.
2. BACKGROUND

2.1. Basic Concepts in Wetting

In a system consisting of a liquid and a solid phase, the former will wet the latter to a degree dictated by the surface energies of the system. If a liquid drop rests on a solid substrate, as shown in Fig. 2.1, the wetting angle, \( \theta \), characterizes the wetting of solid by liquid. The fundamental relationship between wetting angle and surface energy in equilibrium is given by

\[
\gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cos \theta
\]

(2.1)

where \( \gamma_{sv} \) is the surface energy of solid, \( \gamma_{sl} \) is the solid-liquid interfacial energy, \( \gamma_{lv} \) is the surface energy of liquid, and \( \theta \) is the wetting angle. This equation was first derived by Young [1], but is often referred as the Young - Dupré equation [2].

The surface energy of any liquid may be viewed as a force existing through the surface, arising from a combined effect of attractive forces and repulsive forces between atoms or molecules. In a nonmetallic liquid, such as water, the intermolecular forces consist of a number of intermolecular attractive forces and overlapping electron repulsion classified as primary (chemical) bonds, and secondary (physical) bonds. The surface energies of liquid metals or alloys, however, arise primarily by metallic interatomic interactions.

Capillary rise is another phenomenon which is directly related to wetting. It is a simple wetting process in a vertical direction, and is eventually equilibrated by the gravity force acting on the raised or depressed liquid. When a capillary tube is immersed into liquid, as shown in Fig. 2.2, the curved meniscus can either rise or depressed depending on the wetting angle. Considering the equilibrium of the liquid column, capillary pressure, \( P_c \), is given by
\[ P_c = \frac{2 \gamma_v \cos \theta}{r} \]  \hspace{1cm} (2.2)

where \( P_c \) may be from an applied pressure or from the hydrostatic pressure in the capillary of:

\[ P_c = \rho g h \]  \hspace{1cm} (2.3)

where \( r \) is the radius of the tube, \( \rho \) is the density of liquid, \( g \) is the gravity force, and \( h \) is the height of the liquid column.

Wettability is often defined as "the ability of a liquid to wet a solid surface, i.e., to give an even, continuous film over the solid surface ....." [3]. In general, a system is called "wetting" when its wetting angle is less than 90°, and called "non-wetting" when the wetting angle is greater than 90°.

The type of wetting is characterized by the kind of free energy change which occurs in the system. From this standpoint, there are three different types of wetting: adhesional wetting, spreading wetting, and immersional wetting [3].

When a solid surface is lowered toward a liquid until contact is made, as shown in Fig. 2.3 (a), adhesional wetting occurs. The expression for the change in free energy or the work necessary to restore the initial conditions, \( W_a \), can be formulated by

\[ W_a = \gamma_{sv} + \gamma_{lv} - \gamma_{sl}. \]  \hspace{1cm} (2.4)

The spread of liquid on the solid surface gives a case of spreading wetting, as shown in Fig. 2.3 (b). During this process a certain area of solid surface dissappear, while equivalent area of liquid surface and solid-liquid interface are created. The change in free energy of system or the work involved in this process is expressed by

\[ W_s = \gamma_{sv} + \gamma_{sl} - \gamma_{lv}. \]  \hspace{1cm} (2.5)
Unless the quantity of $W_s$ is positive, liquid will not form a adhering film, but will draw up into drops.

Immersional wetting occurs when a solid is immersed into liquid. In this process a solid surface exchanges a gas for a liquid environment, without change in liquid-gas interface. Fig. 2.3 (c) shows this type of wetting. The free energy change or the work performed, $W_i$, is given by

$$W_i = \gamma_{sv} - \gamma_{sl} \quad (2.6)$$

Capillary rise is a practical example of immersional wetting.

Sometimes, wettability is expressed by the total amount of free energy change or work performed during the wetting process, i.e., $W_a$, $W_s$, or $W_i$.

The wetting coefficient, which is defined as [4]:

$$k = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}} \quad (2.7)$$

is also used as a measure of wettability. If $k \leq -1$, the solid is not wetted. If $k \geq 1$, the solid is completely wetted. If $-1 < k < 1$, $k = \cos \theta$ and the solid is only partially wetted.

2.2. Variables in Wetting

Solid:liquid wetting properties are governed by several variables, including heat of formation, stoichiometry, electronic configuration, valence electron concentration, surface geometry, interfacial reactions, temperature, and time.

Heat of formation is the chemical measure on the stability of the solid phase and thus
indirectly a measure of its bond strength. Ramqvist [5] established a relationship between wetting angles or work of adhesion and heats of formation of the carbides. He found that the work of adhesion decreases with increasing heat of formation (-ΔH) of the carbides. The high energy of a stable carbide should imply strong interatomic bonds that show only a slight tendency to break; interaction with other phases would then be correspondingly weak. This leads to a high interfacial energy and a small work of adhesion, i.e., poor wetting.

Goretzki et al. [6] also concluded the more stable the carbide, the less the wetting, by varying the stoichiometry of the carbides of the group IV A and V A metals. The wetting angles of copper and the carbides of the group IV A metals (Ti and Zr carbides) were found to decrease monotonically with decreasing carbon content. The group V A metal carbides (Nb and Ta carbides), in contrast, show a maximum wetting angle at 44 at.% carbon.

Samsonov [7] explained the good wetting properties of the iron group metals by their functioning as electron acceptors, owing to an unfulfilled d band. He showed that metals of group III B - V B hardly wet carbides of refractory metals, while transition metals wet them more or less well. This difference in the character of the interaction was explained by the difference in the electronic configurations of wetting metals. Since the atoms of the nonwetting metals have completely vacant d shells and transition metals which wet carbides have partially-filled d shells, the decisive factor may be their interaction with sharing of the partially-filled d shells.

Ramqvist [8,9] showed by the electron spectroscopy method (ESCA) that a linear relationship exists between the work of adhesion and the energy shift of the carbon 1s electron. Since an increasing energy shift indicates increasing ionic bonding, Ramqvist relates wetting to the stability of the carbides; the more stable the carbide, the smaller the wetting tendency.

Samsonov [7] also showed a systematic dependence of wetting angle on the valence electron concentration (VEC). It is also known that the stability of carbides decreases with increasing VEC.

Wenzel [10] attempted to explain the effect of surface geometry on wetting by
developing an expression between the macroscopic roughness of the solid surface, \( r \), the observed wetting angle, \( \phi \), and the true wetting angle, \( \theta \):

\[
\cos \phi = r \cos \theta \tag{2.8}
\]

where \( r \) is defined as the ratio of the true wetted area of the solid to the apparent area. The roughness is one of the factors which cause hysteresis in wetting angle.

In principle, the interfacial energy and adsorption properties of solid-vapor and solid-liquid interfaces depend on the crystallographic orientation of the interface. The anisotropy of surface energy on clean metals has been measured by a number of techniques. In the case of solid-vapor surfaces, Mycova [11] developed a sensitive technique based on the measurement of the dihedral angles found at the intersection of an annealing twin boundary with the free surface of the metal. With this approach, McLean and Gale [12] showed that in a typical fcc metal, such as copper, some low index orientation have low values of the surface energy which differ by the order of a percent. Generally selective adsorption of impurities on particular crystallographic planes induces a large decrease in solid-vapor surface energy. For example, adsorption of oxygen on the surface of copper caused the decrease of surface energy by about 45% [13]. As expected the anisotropy of adsorption increases with decrease in temperature.

In general, whenever interfacial reactions occur, the wetting tendency and work of adhesion are increased. Details of the relationship between wetting and interfacial reactions will be discussed in a later section.

Brennan and Pask [14] investigated the effect of temperature on the wetting angle of molten aluminum with \( \text{Al}_2\text{O}_3 \). For this system wetting was initially poor; wetting angles were greater than 90° up to about 900 °C then decreased rapidly to indicate reasonable good wetting above 1,100 °C. Rhee [15] found that \( \cos \theta \) increased linearly with temperature, using wetting angle data reported in the literature.
In carbide-metal systems the wetting angle usually decreases markedly with time, though complete wetting is not always achieved. Time dependence of the wetting angles in metal-carbide systems was observed by Ramqvist [5], who found that for Ni/TiC system, equilibrium was reached within 5 to 10 minutes. In the Fe/TiC system, an equilibrium angle was never obtained at 1,490 °C since iron evaporated rapidly. Brennan and Pask [14] investigated the change in wetting angle with time for Al/Al$_2$O$_3$ system at different temperatures. Their results showed that equilibrium was reached after several hours even though at the beginning there were rapid drops in wetting angles.

2.3. Measurement of Surface Energy and Wetting Angle

2.3.1. Surface energy of liquids

Several techniques were developed over the past century to measure the surface energies and wetting angles of liquids at room temperature. In principle, all the room temperature techniques devised for surface energy measurements can be employed in the studies of liquid metals and alloys. However, some of the techniques are not practical for use with liquid metals because of their high melting point and chemical reactivity.

To date the most satisfactory and accurate methods for measuring the surface energies of liquid metals are the sessile drop, the maximum bubble pressure, and the pendant drop methods. Generally, the sessile drop technique is used in the temperature range from 400 to 2,000 °C, and the maximum bubble pressure technique is employed in the temperature range from room temperature up to 1,000 °C. The pendant drop technique is particularly suitable for refractory metals.

The sessile drop technique is based on an analysis of the shape of a drop resting on a flat, non-wetting solid substrate. The shape is determined by a balance between gravitational and surface energies, and therefore is a function of the size of a liquid drop as well as the
density and surface energy of the liquid. Wetting angles can be measured from the photographs of liquid drops. Equilibrium force equations [16-18] have been used for calculating the surface energy of liquid. To evaluate the surface energy of liquid, Bashforth and Adams [16] used the equation:

\[ 2 + \beta \left( \frac{z}{b} \right) = \left( \frac{b}{R} + \frac{b \sin \phi}{x} \right) \quad (2.9) \]

where \( \beta = b^2 \rho g \gamma_{lv} \), \( b \) is the radius of curvature at the pole of the liquid drop, \( Z \) is the ordinate of the point M, \( R \) is the radius of curvature at point M, \( \phi \) is the angle made by the normal at point M with the axis of revolution, and \( x \) is the horizontal coordinate of the point M. Fig. 2.4 shows these parameters. Surface condition and the gas atmosphere have a strong influence on the values of surface energy, and must be carefully controlled. Although independent of the wetting angle, the sessile drop method requires large values of wetting angle (\( \theta > 90 \)) for accurate determination of surface energy. For wetting liquid drops, the surface energy may be calculated from the particular modifications of conventional methods as those proposed by Staicopolus [19,20].

In the maximum bubble pressure technique, a capillary tube is immersed in the liquid metal and by slowly increasing the pressure of an inert gas, a bubble is formed at the tip of the tube. If the diameter of the capillary is small enough, the bubble will be hemispherical. In this case, the maximum pressure required to detach the bubble is given by

\[ P_h + P_\gamma = \rho g h + \frac{2 \gamma_{lv}}{r} \quad (2.10) \]

where \( P_h \) is the hydrostatic pressure, \( P_\gamma \) is the pressure required to create a new surface, \( h \) is the depth of immersion of the tube, and \( r \) is the capillary radius. Many approximate relations
have been proposed, among which the best known is that of Schrödinger [21]:

\[ \gamma_{lv} = \left( \frac{r}{2} \frac{P}{\gamma} \right) \left[ 1 - \frac{2}{3} \left( \frac{r}{P} \frac{\rho}{\gamma} \right) \right] + \frac{1}{6} \left( \frac{r}{P} \frac{\rho}{\gamma} \right)^2 \]  \hspace{1cm} (2.11)

Although the maximum bubble pressure method is the only technique of direct measurement of surface energy of liquid, it has several disadvantages, such as difficulties in measuring the precise immersion depth or effective capillary diameter due to thermal expansion, chemical reaction, and wetting between solid and liquid at the tip of pipe.

In the pendant drop technique, the surface energy of a liquid is calculated from the measured values of the shape parameters on a liquid drop. Even though the meniscus of pendant drop can be described by the equation of Bashford and Adams [16], Andreas et al. [22] showed that the surface energy of liquid can be derived from the simple construction lines applied to a pendant drop as:

\[ \gamma_{lv} = J g \rho \frac{d_m}{d_s} \]  \hspace{1cm} (2.12)

where \( J \) is the drop shape factor, and is tabulated as a function of \( d_s/d_m \); \( d_s \) is the diameter in a horizontal plane located at a distance \( d_m \) from the base of a drop, \( d_m \) is the maximum drop diameter, \( g \) is the gravity force, and \( \rho \) is the density of liquid. A significant advantage of this technique is that liquid drop can be formed from a pure rod of the test materials, thereby eliminating possible contamination from reactions.

Experimental values for the surface energy of liquid aluminum are summarized in Table 2.1. As can be seen in Table 2.1, the surface energy of liquid aluminum is about 860 mJ/m\(^2\) at the melting point. However, there has been an argument [27] that surface energy about 860 mJ/m\(^2\) corresponds to oxidized aluminum whereas unoxidized aluminum has a surface energy about 1,100 mJ/m\(^2\).
2.3.2. Surface energy of solids

Of the various techniques which have been introduced to measure the surface energy of solids, the zero-creep technique and multiphase equilibrium technique are considered the most reliable.

The zero-creep method is based on the observation that metal specimens with a large surface-to-volume ratio, such as thin wires or foils, contract when heated to near the melting point. If a load is applied to the specimen, the critical force which prevents any contraction can be evaluated and related to the surface energy. In the case of a wire of radius \( r \), the equilibrium is given by [28]

\[
\gamma_{sv} = \frac{w}{\pi r} \left( 1 - \frac{r \gamma_{gb}}{a \gamma_{sv}} \right) \tag{2.13}
\]

where \( w \) is the zero-creep load, \( \gamma_{gb} \) is the surface energy of grain boundary, and \( a \) is the average length of grains. Under the conditions of zero creep, the grain boundaries align themselves normal to the loading direction forming a so-called bamboo structure. The ratio \( \gamma_{gb}/\gamma_{sv} \) can be obtained by measuring the dihedral angle of the grain boundary grooves formed at the intersection with free surfaces. This method is limited to high temperature (\( T/T_m > 0.75 \)) where the atomic mobility is high enough to make the surface tension equal to the specific surface free energy. The high experimental uncertainty due to the different orientation of grains and the segregation of surface active elements, and the temperature limitation make the measure of surface energy less accurate than that of liquid metals. Details of this method have been reviewed by Inman and Tipler [28], and by Hondros [29].

The principle of the multiphase equilibrium method consists of placing a liquid drop of a metal on a large-grain solid substrate. At equilibrium, as shown in Fig. 2.5, three dihedral
angles are formed; $\theta$ at the solid-liquid-vapor line, $\phi_{ls}$ at the grain boundary groove in contact with liquid, and $\phi_{vs}$ at the groove in contact with vapor phase. From the measured value of the angles with known surface energy of liquid, the three unknown surface energies of the system, $\gamma_{sv}$, $\gamma_{sl}$, and $\gamma_{gb}$, can be obtained by using the force equilibrium relations;

\[
\begin{align*}
\gamma_{sv} &= \gamma_{sl} + \gamma_{lv} \cos \theta \quad (2.14 \text{ a}) \\
\gamma_{gb} &= 2 \gamma_{sv} \cos (1/2 \phi_{sv}) \quad (2.14 \text{ b}) \\
\gamma_{gb} &= 2 \gamma_{sl} \cos (1/2 \phi_{sl}) \quad (2.14 \text{ c})
\end{align*}
\]

The wetting angle is measured by photographs. For the measurement of dihedral angles, the system is rapidly cooled in order to freeze the equilibrium shapes. The dihedral angles are then measured by metallographic sectioning [30], interferometry [31], or electron microscopy [28]. This method is used frequently because it allows measurements of the solid surface energy to be made as low as $T \equiv 0.45 T_m$.

Unlike solid metals and some other ceramic materials, such as oxides, there are only a few data on the surface energy of SiC, and none for $B_4C$. Allen and Kingery [32] estimated the surface energy of SiC as 840 mJ/m² at 1,200 °C from the results of their sissile drop tests with some pure metals. Yupko and Gnesin [33] reported the surface energy of SiC as 830 mJ/m² in their experiment on a SiC/Si(l) system in a He atmosphere at 1,415 °C.

2.3.3. Solid-liquid interfacial energy

In contrast to the surface energy of liquid or solid, the experimental measurement of solid-liquid interfacial energy, $\gamma_{sl}$, is not easy even for pure materials. Major problems which hinder the progress in the experimental evaluation are the dependence of $\gamma_{sl}$ to the dimension of solid-liquid interfacial region and adsorbed layer of minor elements on the interface. Due to these problems, it seems almost impossible to evaluate the accurate value
of $\gamma_{sl}$. The rough experimental determination of solid-liquid interfacial energies of pure metals and alloys has been performed by using one of the two methods [34]; multiphase equilibrium method or a method based on the Gibbs-Thomson equation.

For a pure spherical solid particle of radius $r$ in a liquid, the equilibrium equation is given by

$$T_m - T = \frac{2 \gamma_{sl} T_m}{r L \rho_s}$$

(2.15)

where $T_m$ is the normal melting point, $T$ is the melting point of the solid particle, $L$ is the latent heat of fusion per unit mass, and $\rho_s$ is the density of the solid phase. Thus, if the appropriate physical constants are known, measurements of $\Delta T (= T_m - T)$ for known values of $r$ for a system at equilibrium will yield values of $\gamma_{sl}$ directly. However, there is a practical difficulty associated with using the Gibbs-Thomson equation. In fact, a single crystal of solid surrounded by its melt at the equilibrium temperature is in a condition of highly unstable equilibrium; a small fluctuation will lead either to complete melting or complete solidification, and the attainment of equilibrium is thus difficult. Eq.(2.15) is also used as a basic equation for the solid-liquid interfacial energy measurements by other experimental techniques, such as homogeneous nucleation [35-37] or depression of melting point experiments [38-40].

2.3.4. Measurement of wetting angle on particulates

Even though the wetting angle on particulates is often of great technical importance, its measurement is quite difficult. Due to the difficulty in qualitative wetting angle measurements, an ordinal (or ranking) scale was proposed [41] as a measure of wettability of particulates with liquids. A variety of experimental procedures has been described in the literature which in one way or another lead to an ordinal scale of wettabilities. Those
procedures either consist of the numerical measurement of certain quantities which can then be used as an indication of an ordinal wettability score of the system, or compare two cases and yield the relative order of these two cases. A repetition of the latter type of test with many pairs of cases will then also provide an ordinal scale. In all these tests the problem of standardization is of utmost importance so that one arrives in every case at a meaningful wettability score.

The work of Bartell et al. [42-44] gives quantitative measures of wetting angles. They measured the pressure exerted by the liquid entering through a compacted powder. They obtained the radius of the equivalent cylindrical capillary tube, \( r \), by measuring the pressure set up by a liquid known to wet the particulates completely, i.e., \( \theta \) is zero. From the displacement pressure to force liquid into a powder compact, the wetting angle was evaluated by using the capillary force equation, eq. (2.2). The value of pressure was reported as quite reproducible.

Another approach to measure the wetting angle of particulates with liquid was introduced by Hackett [45] and others [43]. This method is based on the measurement of the rate of fluid flow through the powder compact, and applying Poiseuille's type of equations to the experimental results. However, different researchers derived different fluid flow equations with different physical constants.

The concept of the hydraulic radius, introduced by Carman [46], made the calculation of wetting angle simple. The hydraulic radius, \( r_h \), is defined as

\[
\frac{r_h}{= \frac{\text{volume of column of liquid in capillary}}{\text{area of wetted surface of capillary}}}.
\]

For a compacted powder,

\[
\frac{r_h}{= \frac{D_w}{6 \lambda (1 - w)}}
\]
where \( D \) is the average diameter of particulate, \( w \) is the void fraction of powder compact, and \( \lambda \) is a geometry factor which depends on the geometry of both particulate and capillary channel. For non-spherical, blocky particulates, the value of the geometry factor was determined in experiments with perfect wetting liquids as \( 8.5/6 \), and showed very good fit over a hundredfold variation in particle size.

The methods discussed above have been used mostly for wetting organics at room temperature. For liquid metals, only a few experiments \([47]\) have been conducted and these were on large particulates with wetting liquid metals. Thus it is necessary to develop a new experimental technique which is accurate at small particle sizes for non-wetting solid/liquid metal systems.

2.4. Theoretical Estimation of Surface Energy

Energies of interfaces involving only fluid phases are readily measured to a high degree of accuracy. However, measurement of interfacial energy involving solid phases is difficult and inaccurate, which makes a theoretical model for the energies of such interfaces highly desirable.

Surface energy is the work needed to expand surface area and as such is inherently related to interatomic forces. Consequently, such material parameters as the heat of fusion or evaporation, hardness, elastic modulus, and melting temperature may provide a rough gauge of the surface energy \([48,49]\).

Even though there is no accurate model, several theoretical approaches have been introduced for the calculation of the solid-vacuum \([50-53]\), liquid-vacuum \([54-55]\), and solid-liquid \([56-61]\) interfacial energies.

In some cases, theoretical values of surface energies show good agreement with experimental values. However, almost all the models dealt with pure metal systems. So far only a few models have been presented for alloy liquid-solid compound systems. In this
section, the models of Miedema and Warren are reviewed briefly for solid-liquid metal, and solid compound-liquid metal systems, respectively.

2.4.1. Miedema's approach

The lack of thermodynamic measurements and an accurate model has for years impeded theoretical studies of alloy stabilities, nucleation, growth, spinodal decomposition, and coarsening, as well as wetting and other interfacial phenomena. A "macroscopic atom" model developed over the past decade by Miedema and co-workers [54,60] provided for the first time an accurate energetic model based on atomic properties only which may be used to calculate surface energies for liquid, solid, and solid-liquid pure metals.

Miedema's original approach gave mixing enthalpies of binary liquids or enthalpies of formation of binary compounds to an accuracy comparable to that of calorimetry. Mixing enthalpies of solid solutions were obtained to a lower accuracy.

Miedema's "macroscopic atom" approach depicts elemental A and B to be separated into Wigner-Seitz atomic cells, and then reassembled into the liquid or solid solution or intermetallic compound.

In the case of liquid solutions or intermetallic compounds the enthalpy of mixing is given by

\[
\Delta H \propto P (\Delta \phi^*)^2 + Q (\Delta n_{ws1/3})^2 - R + \Delta H_{trans} \quad (2.18)
\]

where

\[
\Delta \phi^* = \text{difference in electron potentials of the elements},
\]

\[
\Delta n_{ws} = \text{difference between electron densities of the elements at the Wigner-Seitz cell boundary.}
\]

Unequal electron densities at the Wigner-Seitz boundary \((n_{ws})\) give a positive contribution
to the enthalpy, and unequal electron potentials ($\phi^*$) cause charge transfer and a negative enthalpy contribution. The constant $R$ is from electron hybridization which occurs when $d$-valence electrons of transition metals hybridize with $s$ or $p$ valence electrons of polyvalent non-transition elements. The calculation works only for metallic elements; $\Delta H_{\text{trans}}$ is the enthalpy required to transform a non-metallic component (e.g. silicon) to a metal.

Miedema's approach was very successful in calculating the enthalpies of formation of liquid solutions, and of intermetallic compounds, and of other compounds, in particular, oxides, carbides, and borides.

Miedema then utilized his model in the calculation of liquid:vapor, and solid:vapor surface energies of pure metals and of solid:liquid and solid:solid surface energies of one component and two component systems. These calculations are therefore highly relevant to the wetting phenomena of interest in this study.

The liquid:vapor surface energy, $\gamma_1$, is sometimes taken as proportional to the enthalpy of vaporization of the liquid, $\Delta H_{\text{vap}}$. In some cases, a roughly linear relationship has been found to exist between $\gamma_1$ and $\Delta H_{\text{vap}}$. Miedema noted, however, that $\Delta H_{\text{vap}}$ depends in part on the properties of the free atoms in the gaseous state. Certain gaseous atoms, in particular Hg, have very stable electron configurations which lead to anomalously low $\Delta H_{\text{vap}}$. Atoms at the liquid:vapor interface do not have this low energy electron configuration, so the proportionality between $\Delta H_{\text{vap}}$ and $\gamma_1$ is destroyed. The value of $n_{ws}$ is a much more accurate measure of the disruption in the electron gas on creating a surface. Miedema found a significantly better proportionalities exist between $\gamma_1$ and $n_{ws}$ than with $\Delta H_{\text{vap}}$.

Subsequently, Miedema showed that there was little difference between solid:vapor and liquid:vapor surface energies, and that in fact $\gamma_s / \gamma_1 = 1.13$ for all pure metals. He refined his surface energy model to better account for the number of valence electrons per atom to obtain:

$$\gamma_s = \text{const} \cdot n_{ws}^{5/3} / (\phi^* - 0.6 \text{ eV})^2.$$  \hspace{1cm} (2.19)
Eq.(2.19) can then be used with confidence to obtain γ_s or γ_l for any metallic element. It may be possible to adapt Miedema's model to give surface energies of compound phases.

Finally, Miedema and den Broeder [60] calculated solid:liquid and solid:solid surface energies for one or two component metallic systems. The calculation is predictably more complex than it was for liquid:vapor and solid:vapor surface energies.

For a one component system, the enthalpy of the atom in the first atomic layer in contact with the melt are increased by a fixed fraction of the enthalpy of fusion so that

\[
γ_{sl}^I = 2.5 \times 10^{-9} \Delta H_f / V_m^{2/3}
\]  

(2.20)

where \( V_m \) is the molar atomic volume of the solid. To this an entropic term, \( S^* \), due to the added disorder in the surface layer is added:

\[
γ_{sl}^{II} = S^* T_m / V_m^{2/3}
\]  

(2.21)

where \( S^* = 0.52 \times 10^{-7} \text{ J/K} \).

Then

\[
γ_{sl} = γ_{sl}^I + γ_{sl}^{II}.
\]  

(2.22)

Somewhat surprisingly, Miedema's and den Broeder's values for \( γ_{sl} \) fit the empirical Skapski [50] relation:

\[
γ_{sl} = γ_s - γ_l
\]  

(2.23)

fairly accurately.
Using Miedema's values for $\gamma_s$ and $\gamma_l$,

$$\gamma_{sl} = 0.13 \gamma_s.$$  \hspace{1cm} (2.24)

For the binary interfaces of solid metal A against liquid metal B,

$$\gamma_{sl}^{AB} = (\gamma_{sl}^I)_A + (\gamma_{sl}^{II})_B + \gamma_{sl}^{III}$$  \hspace{1cm} (2.25)

where $\gamma_{sl}^I$ and $\gamma_{sl}^{II}$ are given by eqs.(2.19) and (2.20), respectively. The first enthalpy term, $\gamma_{sl}^I$, is for the solid A and the other enthalpy term, $\gamma_{sl}^{II}$, is for liquid B. To these two term a chemical term due to interactions between A-B atoms is added:

$$\gamma_{sl}^{III} = 2.5 \times 10^{-9} \Delta H / V_i$$  \hspace{1cm} (2.26)

where $i$ stands for either A or B, and $\Delta H$ is the heat of solution of A in B or of B in A. Since $\Delta H_A/V_A$ and $\Delta H_B/V_B$ are slightly different, an averaged value is used. Heats of solution needed for eq.(2.26) can easily be calculated by eq.(2.18).

Solid:solid surface energies are taken to consist of a structural term and a chemical term:

$$\gamma_{ss}^{AB} = \gamma_{struct} + \gamma_{chem}.$$  \hspace{1cm} (2.27)

High angle grain boundary energies are about 30% that of a solid:vapor interface. The structural part of the A-B grain boundary energy was therefore taken as the average of the A-A and A-B grain boundary energies. Miedema had shown in earlier papers that except for strain energy, energetic interactions between atoms were about the same in liquids and in solids. The chemical contribution to the solid:solid interface was therefore taken to be the same as the binary solid:solid interface. Thus:
\[ \gamma_{ss}^{AB} = 0.15 \left( \gamma_s^A + \gamma_s^B \right) + \gamma_{ss}^{\text{chem}} \quad (2.28) \]

where \( \gamma_s^A \) and \( \gamma_s^B \) can be calculated from eq.(2.19) and \( \gamma_{ss}^{\text{chem}} \) is given by eq.(2.27).

The foregoing shows that the Miedema's approach is powerful and is based only on easily obtained atomic properties. However, the analysis is thus for limited to binary metallic systems. For liquid alloy:solid compound system, it may be possible to treat the alloy:compound systems as a pseudo-binary and to calculate the needed structural and chemical contribution to \( \gamma_{sl} \) and \( \gamma_{ss} \).

2.4.2. Warren's approach

In Warren's model [61], a thermodynamic model of the solid-liquid metallic interface in a binary system is extended to a pseudo-binary system which is composed of a metallic liquid and a stable solid carbide or oxide phase. This model assumes that a finite value of the interfacial energy exists because a region in the neighborhood of the interface is disturbed from the bulk equilibrium states of both solid and liquid. Disturbances in the chemical composition and structure are treated as separate contributions.

The chemical contribution of the interface atoms to the interfacial energy is taken to be the difference between equilibrium molar free energy, \( F_5 \) in Fig. 2.6, of the atoms in an equilibrium two-phase mixture without an interface, and \( F_6 \), their energy when forced to exist together as a liquid of composition \( X' \) in a two atomic-layer interface. Then, the chemical contribution to the interfacial energy per unit area, \( \gamma_{sl(c)} \), becomes

\[ \gamma_{sl(c)} = n \left( F_6 - F_5 \right) / N \quad (2.29) \]

where \( N \) is an Avogadro's number and \( n \) is the number of interface atoms per unit area which is equal to the sum of the solid molecules and liquid atoms at the interface, \( n_s + n_l \). For
simplicity and as a rough approximation, the disturbed region is considered to extend over only two atomic layers. Assuming a simple cubic arrangement of atoms, then

\[ n_s = \left( \frac{N}{V_s} \right)^{2/3} \]  \hspace{1cm} (2.30)

where \( V_s \) is the effective molar volume of atoms in the solid. The effective molar volume, \( V_s \), is given by

\[ V_s = X_2 V_B b^{1/2} + (1 - X_2) V_A \]  \hspace{1cm} (2.31)

where \( V_B \) is the molar volume of the compound B, \( b \) is the number of atoms in the molecules, and \( V_A \) is the molar volume of liquid A. Similarly,

\[ n_1 = \left( \frac{N}{V_1} \right)^{2/3} \]  \hspace{1cm} (2.32)

where \( V_1 \) is the average molar volume of atoms in liquid and given by

\[ V_1 = X_1 V_B b^{1/2} + (1 - X_1) V_A. \]  \hspace{1cm} (2.33)

If the solubility of B in A is low, then \( F_5 \) approaches zero giving

\[ \gamma_{si(c)} = \frac{n F_6}{N} \]  \hspace{1cm} (2.34)

with

\[ F_6 = F_3 (X')^2 + RT [X' \ln X' + (1 - X') \ln(1 - X')] \\
- RT \ln X_1 [X' (1 - X')] \]  \hspace{1cm} (2.35)

where \( F_3 \) is the free energy of fusion of the solid B and to a good approximation can be
written as

$$F_3 = H_B (1 - T/T_B)$$  \hspace{1cm} (2.36)\\

where $H_B$ is the latent heat of fusion and $T_B$ is the melting temperature of B. The heat of fusion, $H_B$, can be estimated by using the following empirical relationship:

$$H_B = 25 T_B$$  \hspace{1cm} (2.37)\\

where $H_B$ is measured in J/mole, and $T_B$ in K. The interfacial composition is given by

$$X' = \left( n_1 X_1 + n_2 X_2 \right) / \left( n_1 + n_2 \right).$$  \hspace{1cm} (2.38)

From eq.(2.35), it can be seen that $X'$ is relatively insensitive to changes in $X_1$, therefore $\gamma_{sl(c)}$ is directly proportional to $-\ln X_1$. The structural contribution to $\gamma_{sl}$ can be calculated from the empirical relationship:

$$\gamma_{sl(B)} = c T_B / b (V_B/b)^{2/3}$$  \hspace{1cm} (2.39)\\

where $c$ is an empirical constant and lies between $5 \times 10^{-4}$ and $8 \times 10^{-4}$. $\gamma_{sl(B)}$ is given in J/m$^2$ when $T_B$ in K.

Unfortunately, adequate thermodynamic data are seldom available for metal-ceramic systems. Therefore the value of $\gamma_{sl}$ calculated from this model might not be sufficiently accurate to be used in the precise studies of interfacial phenomena.

2.5. Wetting of Ceramic Materials with Liquid Aluminum Alloys

2.5.1. Wetting experiment
The wetting of ceramic materials by liquid aluminum alloys has been investigated mainly with the sessile drop method. Since aluminum has extremely high oxygen affinity, atmosphere control is very important in such wetting experiments. The free energy of Al₂O₃ formation is such that at 800 °C the oxygen partial pressure should be kept below 4 x 10⁻⁴⁴ atm. to prevent its formation:

\[
2 \text{ Al (l)} + \frac{3}{2} \text{ O}_2 \text{ (g)} = \text{ Al}_2\text{O}_3 \text{ (s)}
\]

\[
\Delta G_f,1073^\circ K = -1,337.6 \text{ kJ/mole} [62].
\]

This calculation means that oxide formation in liquid aluminum alloy systems can not be avoided without special treatments. Even at 400 °C, a 50 Å thick oxide layer was formed on an aluminum alloy in 4 hours [63]. Therefore it can be said that the apparent wetting angle of molten aluminum with solid system is always higher than the true value due to the oxide layer.

Numerous wetting experiments have been conducted on Al₂O₃/Al-alloy systems [14,64-71]. However, as can be seen in Fig. 2.7 [71], experimental results show significant differences in wetting angles which are probably caused by different experimental conditions mostly time and oxide formation. The influence of different oxygen partial pressures on the wetting behavior was investigated by John and Hausner [71] who showed that a very low wetting angle could be obtained by maintaining a very low oxygen partial pressure in the system.

In addition to the oxygen partial pressure in the system, holding time and size of liquid metal droplet on the solid substrate may affect the value of wetting angle due to changes in kinetics of interfacial reactions, and in the mechanical strength of the oxide layer. Of course, the results can also vary depending on the experimental methods. Therefore, to compare the wettability with minimum error, it is necessary to measure the wetting angles with the same experimental conditions.

The wetting of SiO₂ [69,72], SiC [68,73], B₄C [74,75], TiC [15,76], and TiB₂
[15,76] with molten aluminum alloys were also tested by many researchers. The experimental results on the wetting angles are summarized in Table 2.2. Considering the high stability and different physico-chemical properties of ceramic materials, the high wetting angles of those materials with liquid metals are not surprising.

2.5.2. Approaches to improve wettability

A number of approaches have been used to overcome or improve the poor wettability of ceramic particulate/liquid metal systems. These include mechanical techniques, semi-solid casting, squeeze or pressure casting, fluxes, surface treatments, alloy additions, pre-heating of particles, and superheating of melts.

Rohatgi et al. [77] routinely used an impeller-induced vortex, often in conjunction with other techniques, to introduce particulates into melt. They also discussed the use of centrifugal acceleration, gas injection, and ultrasonics. These techniques may be useful in providing a master alloy for subsequent processing, but probably produce too heterogeneous a product for employment as high performance material.

Beginning in about 1970, Flemings and other workers [78-81] have studied the properties and applications of semi-solid alloy slurries. The basic process involves the addition of the nonmetals to partially solidified, vigorously agitated slurries of alloys. The viscous partially solidified, non-dendritic alloy prevents nonmetallic phases from settling, floating, or agglomerating. With increasing mixing time, the particles or fibers may interact with the liquid to develop bonding.

Several studies have used pressure to squeeze a molten alloy into a mass of particulates or fibers. Alloy additions have also been used to improve wetting and further encourage liquid flow into the solid preforms. Quigley et al. [82] used pressure casting along with a graphite impeller to produce 20 μm α-Al₂O₃ fiber reinforced Al-Mg composites. Addition of 23 v/o fiber to Al-4% Mg gave a 50% increase in the elastic modulus and a 40% increase
in the UTS; fracture was through the matrix and not at the interface. A spinel formation at the interface was reported.

Addition of particulates through a suitable flux provides a clean, highly wettable interface between the particle and the melt and also removes the oxide scum on the surface of the liquid alloy. Rocher and co-workers [83] reported a complete and spontaneous infiltration of SiC fiber preform with an Al-7 Si-0.6 Mg alloy when the surface of fibers was coated with K$_2$ZrF$_6$. They suggested several possible mechanisms of improvement of wettability of: (i) a simple effect of fiber surface cleaning, (ii) a dissolution of alumina by the fluoride species in the vicinity of the fiber surface as the liquid front propagates through the preform, (iii) a decrease in the wetting angle due to gaseous fluoride species or due to a local overheating resulting from the exothermic reactions, and (iv) a heterogeneous nucleation of Al$_3$Zr or ZrSi$_2$ on the fibers.

In the case of chemically inert ceramic/liquid metal systems, a clean surface provides better opportunity for melt:particulate interaction, hence better wetting. However, surfaces of some nonmetallic particles simply aren't wet by liquid metal, regardless of cleaning techniques, such as acid washing or ultrasonic cleaning. Wetting has been improved in a number of such cases by coating the particulate surface with a wettable metal. Ni and Cu are wet by many alloys and have been used as particulate coatings to a number of low melting alloys. Abdul-Latief et al. [84] coated Al$_2$O$_3$ particles with fine MgO particles to improve wettability. Addition of 15% MgO to the Al$_2$O$_3$ gave optimum retention of Al$_2$O$_3$ in the Al matrix composites.

Alloy additions to the melt can also promote wetting through lowering $\gamma_{sl}$ either by Gibbsian adsorption or by a solid:liquid interfacial reactions. Rohatgi et al. [77] listed a number of studies where alloy additions improved particle or fiber wettability. Mg seems to be particularly beneficial in dispersing a range of particles in Al alloys. Deonath et al. [85] found that Mg addition was needed to disperse mica in Al to produce a bearing material. Banerji et al. [86] found that Mg increased the amount of zircon which would be dispersed in
Al-Si alloys. A reaction zone high in Mg and Si was formed at the particle:matrix interface.

Rohatgi et al. [87] studied the effect of particle pre-heating on the retention of SiO$_2$ particles in Al and Al-Mg composites. Pre-heating the particles to 700 °C resulted in ca. 25-90% retention in Al and Al-Mg alloys. Addition of the fibers without pre-heating, or preheated then cooled, gave ca. 1% retention in the same alloys. Agarwala and Dixit [88] observed the importance of the pre-heating in the incorporation of graphite particles in Al alloys. There was no retention when the graphite particles were not preheated, whereas the particles were retained when preheated.

Generally, superheating of melts tends to reduce the wetting angle and improve wettability. The effect may well be explained partly by thermodynamics, due to changes in surface energies, and partly by kinetics, due to more rapid reaction and spreading. Agarwala and Dixit [88] showed that graphite particle retention can be increased by superheating the Al melt.

2.6. Metal:Ceramic Interfaces

2.6.1. Physics and chemistry of interfaces

Due to the importance of the function of the interface in composite materials, considerable efforts have been made on the study of interface between two dissimilar materials, matrix and reinforcing second phases. In spite of the importance of the interface, understanding of metal:cerealic interfacial phenomena is still in its infancy.

Because of the extremely complicated nature of the interface, Salkind [89] concluded in 1968 that "a precise definition of the interface is beyond our present knowledge." In 1974, Metcalfe [90] proposed the definition of interface as "the region of significantly changed chemical composition that constitutes the bond between the matrix and reinforcement for transfer of loads between these members of the composite structure." Inclusion of the term
"significantly changed chemical composition" in the definition of an interface is to exclude random fluctuations of composition but include systematic changes caused by thermodynamic equilibrium. Dissolution, adsorption, and chemical reaction are the principal systematic changes.

Metal shows a metallic bonds, while, ceramic phases are bonded with ionic and covalent forces. The interface in a metal/ceramic composites, therefore, provide a transition between structures and bond types.

Since metal matrix composites are often non-equilibrium systems, there may exist a gradient of chemical potential at the metal-ceramic interface. This difference in chemical potential provides the driving force for interfacial reactions during the fabrication or high temperature use. Many investigators [14,65,72,73,91,92] suggested that interfacial reactions can make metal/ceramic system wettable.

The marked stability of ceramic phases in metal/ceramic system permits only very low mutual solubilities between the two phases. However, small amounts of dissolution can decrease solid-liquid interfacial energy significantly. Dissolution also can promote chemical reaction by providing reactants. Dissolution will stop when the solute concentration reaches its solubility limit or stable reaction products are formed at the interface.

Adsorption is a surface reaction which is concentration, temperature, and diffusivity dependent. Initially, adsorption is rapid, followed by a slow aging process which continually changes the surface energy. Adsorption is usually limited to the first few layers of interface. The relationship between the adsorption and temperature, surface energy, and concentration in dilute solutions is given by the Gibbs adsorption equation:

$$\Gamma_B = -\frac{1}{RT} \frac{d \gamma}{d \ln X_B}$$  (2.41)

where, \(\Gamma_B\) is the excess solute concentration at the interface, \(R\) is the gas constant, \(T\) is the
temperature, \( \gamma \) is the surface energy, and \( X_B \) is the solute mole fraction. Thus, the greater the adsorption, the more solute tends to lower the surface energy. In general, adsorption on the crystalline ceramic surfaces involves chemical bonding [93], either ionic or covalent, and is quite similar in principle to the chemical adsorption in solid metals.

Among the chemical reactions at the metal:ceramic interface, reduction-oxidation (redox) reactions are common because metallic phases have elements in their reduced state and ceramic phases are compounds containing cations. The redox reaction can be represented as:

\[
A \text{ (metal)} + B \text{ (cation in compound)} = A \text{ (cation in compound)} + B \text{ (metal)}. \tag{2.42}
\]

This reaction is reversible and governed by the change in total free energy of reaction. The formation of complex compounds, such as spinel or glass, also occurs frequently at the metal:ceramic interface.

In aluminum alloy matrix composites, interface studies have been conducted mainly on oxide systems, such as \( \text{Al}_2\text{O}_3/\text{Al-alloys} \) [65,67,94-97], \( \text{SiO}_2/\text{Al-alloys} \) [72]. Due to its potential, the activity in \( \text{SiC/Al-alloy systems} \) [98-103] has grown rapidly in the past few years.

2.6.2. Metal:ceramic interaction

When a liquid is in contact with the surface of a solid phase, two major types of interaction occur at the interface: (i) physical interaction and (ii) chemical interaction. Besides the origins of forces, the main difference between the two types of interactions is their magnitude. Bonding force due to physical interactions are typically the order of several kJ/mole, but the bonding forces due to chemical interactions are in the range between tens and
thousands kJ/mole [104]. Physical interactions determine the wettability of non-reactive liquid having low surface energy such as water and organic liquids which have tens of mJ/m² as surface energies. However, the chemical interactions are dominant in reactive systems, such as ceramic/metal systems, and provide most of the bonding energy.

Physical or dispersion interaction comes mainly from the dispersion forces. These forces arise from the attraction between an instantaneous dipole and dipoles that induces in its vicinity. The interaction energy from the dispersion forces between two free atoms can be estimated by using the London formula:

$$E_{12} = \frac{3}{2} \frac{\alpha_1 \cdot \alpha_2}{r^6} \left( \frac{I_1 \cdot I_2}{I_1 + I_2} \right)$$  \hspace{1cm} (2.43)

where, \(\alpha_1\) and \(\alpha_2\) are the polarizabilities of the two atoms, \(I_1\) and \(I_2\) are the first polarization potentials, and \(r\) is the distance between two atoms. Neglecting entropy contributions and taking into account only interactions between each pair of atoms, the bonding energy between solid and liquid phase, \(E_b\), will be

$$E_b = n \cdot E_{12}$$  \hspace{1cm} (2.44)

where, \(n\) is the number of atom pairs per unit surface area of interface. Fowkes [105] showed that the interaction between solid and low surface energy liquids can be estimated fairly precisely by assuming dispersion interactions as governing bonding forces.

Chemical interactions arise from interfacial reactions between species in the solid and liquid phases. The interfacial reactions include chemical reaction, dissolution, and adsorption. In spite of its importance, estimation of the magnitude of chemical interaction has not been successful.
Efforts were made to estimate the bonding energy between metal and oxide by Naidich [104]. The chemical contribution to the bonding energy was calculated by considering the following reaction:

\[ \text{Me}^{n} + \text{Me'O} = \text{Me''O} + \text{Me}'. \]  

(2.45)

Assuming that \( n' \) and \( n'' \) are the initial amounts of substances of \( \text{Me}^{n} \) and \( \text{Me'O} \) in moles per unit surface area, and \( \alpha_o \) is the degree of reaction at equilibrium, the bonding energy was estimated by the equation of:

\[ E_b = -RT \left[ n' \ln \left(1 - \frac{\alpha_o}{n'}\right) + n'' \ln \left(1 - \frac{\alpha}{n''}\right) \right]. \]  

(2.46)

The degree of reaction, \( \alpha_o \), was estimated from the chemical equilibrium constant and the isobaric potential change during the reaction:

\[ \Delta G = \Delta G'' - \Delta G' = -RT \ln \frac{\alpha^2_o}{(n' - \alpha_o)(n'' - \alpha_o)} \]  

(2.47)

where, \( \Delta G'' \) and \( \Delta G' \) are the changes of isobaric potentials on oxidizing the \( \text{Me}^{n} \) and \( \text{Me}' \) metals, respectively.

Even though this model seems to be only one of a kind, accurate information is essential in order to estimate the contribution of chemical reaction to the interaction precisely. Since the interfacial reaction is complicated in alloys, application of relatively simple equation is doubtful for systems other than oxide/metal system.
3. EXPERIMENTAL METHODS

3.1. Materials

3.1.1. Ceramic particulates

Silicon carbide (SiC) and boron carbide (B₄C) particulates were used in wetting experiment. These two ceramic particulates are used most frequently for the production of particulates reinforced light metal matrix composites due to their low cost as well as good physical properties.

The most widely used and thoroughly investigated method of producing SiC particulates is by the reaction of silica with carbon at about 1,400 °C, the so-called Acheson process [106,107]. SiC particulates for this study were also produced by this method. The overall reaction is represented by

\[ \text{SiO}_2(s) + 3 \text{C}(s) = \text{SiC}(s) + 2 \text{CO}(g). \]  

(3.1)

After the reaction, reaction product, SiC, is pulverized and classified.

SiC exists in the form of the cubic β-SiC and the hexagonal α-SiC. The transition temperature from one structure to the other has not been determined, therefore, it has been frequently assumed that β transforms into α at about 2,000 °C. But this seems unlikely, because both phases can be produced over temperature ranges of 1,400 - 2,900 °C [61]. The data on heat of formation and equilibrium indicate that β is more stable than α up to 1,700 °C. However, the properties of the two phases are so similar that they have not been adequately differentiated either physically or thermodynamically.

B₄C particulates are produced by a process similar to that for SiC. Commercially, B₄C is produced by reduction of boron anhydride with carbon in accordance with the reaction
of:
\[ 2 \text{B}_2\text{O}_3(l) + 7 \text{C}(s) = \text{B}_4\text{C}(s) + 6 \text{CO}(g). \]  \hspace{1cm} (3.2)

The reaction takes place in two stages [108]:

\[ \text{B}_2\text{O}_3(l) + 3 \text{CO}(g) = 2 \text{B}(s) + 3 \text{CO}_2(g) \]  \hspace{1cm} (3.3)
\[ 4 \text{B}(s) + \text{C}(s) = \text{B}_4\text{C}(s) \]  \hspace{1cm} (3.4)

The minimum temperature for the onset of boron anhydride reduction with carbon monoxide is about 1,400 °C. Usually, the temperature is increased to 2,000 - 2,500 °C to enhance the reaction rate.

\text{B}_4\text{C} has a rhombohedral structure. The phase diagram [108] shows the existance of \text{B}_4\text{C} with a large homogeneity range, 17.6 - 29.5 \% of C or 16.1 - 27.4 at.\% of C.

Due to the processing nature in the production of SiC and \text{B}_4\text{C} particulates, it seems to be difficult to achieve the exact stoichiometries of carbides, and there may be unreacted oxides and free carbon in the final products. Different colors of carbides sometimes indicate different composition. For example, impure SiC with excess SiO_2 and free C is black, while high-purity SiC with small amount of free Si is green.

The shapes of SiC and \text{B}_4\text{C} particulates are shown in Fig. 3.1. Both of the particulates have irregular, blocky shapes. These powders are provided by Norton Company in Worcester, Massachusetts. The chemical analysis data of each powder are listed in Table 3.1.

The analysis of size distribution was conducted by Coulter Counter TA II in Norton Company. The results of size analysis of SiC and \text{B}_4\text{C} particulates are shown in Fig. 3.2 and Fig.3.3, respectively. The average sizes of SiC and \text{B}_4\text{C} particulates were determined as 9.63 and 8.89 μm by volume.
3.1.2. Alloy preparation

Seven different aluminum alloys were used as metal matrices: pure Al, Al-2% Cu, Al-4.5% Cu, Al-2% Si, Al-4.5% Si, Al-2% Mg, and Al-4.5% Mg.

The 99.99% pure aluminum and 99.9% pure silicon were purchased from Atlantic Equipment Engineers in Bergenfield, New Jersey and Aremco Products, Inc. in Ossining, New York, respectively. Al-4.5% Cu and Al-2.3% Mg alloys were ordered from Reynolds Metals Company in Richmond, Virginia. The metallurgical practice used for both aluminum alloys by Reynolds is as follows:

- Super pure aluminum melted in 100 KW induction unit
- Base metal chemical analysis button taken
- Alloy addition added in the form of hardener
- Melt fluxed with pure chlorine
- Chemical analysis button taken
- Metal cast into 3"x8" CC mold
- Ingots stress relieved overnight at 550 °F
- 3"x8" ingots cut in half through length

Other alloys, Al-2% Cu, Al-2% Si, Al-4.5% Si and Al-4.5% Mg, were made from the above four master alloys by using electrical resistance furnace. The results of chemical analysis of the alloys are listed in Table 3.2.

3.2. Powder Specimen Preparation

The most critical step for the present wetting experiment was to prepare a uniformly-packed powder specimen. The tamping device which was developed for packing the powder
into 0.5 cm I.D., 0.8 cm O.D., 13.5 cm long quartz tubes is shown in Fig. 3.4. Just above the lower punch inside the quartz tube, a Saffil (δ-Al₂O₃, ICI product) paper-wrapped porous alumina block was inserted. The porous block was made of fused aluminum oxide with silica binder in Norton Company (Cat.# P 260). The block has a dimension of 0.5 cm dia., 1 cm long, and average pore size of 179 μm. The Saffil paper was used to close out the gap between filter and quartz tube and to prevent pushing out of powders during compacting and infiltration.

About 0.1 cc of loose powder was placed in the quartz tube; the powder was then subjected to 20 strokes of a 30 g weight from a height of 15 cm. The procedure was iterated until the height of the powder compact reached 3 cm. The measured density of powder compact was within the range of 52 ± 1.5 % of theoretical densities of each compound. After packing, the melt side of compact was plugged with two layers of 1 mm thick an 5 mm dia. alumina paper. Alumina paper, produced by Zircar Products Inc., in Florida, New York (Cat.# APA-2), was made from Saffil fiber without binder and has 3 % of theoretical density of alumina. The bottom (powder compact side) of quartz tube was then capped with aluminum foil, and stored in an Ar gas-filled desicator. Fig. 3.5 shows the SEM images of packed SiC particulates and alumina paper.

Due to the high reactivity between the quartz tube and the Al-Mg alloys, the outsides of the quartz tubes were coated with ceramic cement (Ceramabond® 590, Aremco Products Inc.). Coating procedure included coating, drying and firing. Details are given in the instructions for use of this product.

After placing the powder specimens inside, the desiccator was evacuated for 1 hour and filled slowly with Ar gas up to about 1.1 atmosphere. Before the pressure infiltration test, the desiccator was evacuated one more time for 30 min., then filled with Ar gas until the pressure reached about 1.1 atmosphere to prevent influx of air.

3.3. Pressure Infiltration
The wetting tests were carried out with an apparatus specially designed for this study, shown in Fig. 3.6. The body of the pressure chamber was made of an 18 cm I.D., 19.7 cm O.D., and 27.5 cm long steel cylinder. The cap assembly and bottom portion of the pressure chamber were made of 2024 aluminum alloy. Each component has copper tubing for water cooling. The melting furnace is composed of 2 semi-cylindrical heating elements which have dimension of 10.5 cm I.D., 13.7 cm O.D., and 15.2 cm long. The furnace was operated with 115 V and 1,700 W. The specimen holder was made by modification of a vacuum fitting (Cajon Ultra-Torr male connector, cat.# B-4-UT-1-4). Pressure was monitored with a pressure transducer (Omega, cat.# PX 302) which has an accuracy of ± 0.5 %, and a digital pressure indicator (Omega, cat.# DP 350). Fig. 3.7 shows the array of experimental equipment.

Each powder specimen was inserted into the melt and held 5 minutes to preheat the powder specimen and achieve isothermal conditions. Pressure was then applied with pressurized nitrogen gas at a rate of 20 kpa/sec up to predetermined pressure. After a set period of time, normally 5 min., the pressure chamber was vented at a rate of 40 kpa/sec. After ventilation of the pressure chamber, the powder specimen was taken out and air-cooled.

Fig. 3.8 shows the sequence of infiltration of liquid metal into powder specimen. Due to the force from its hydrostatic head, liquid metal enters the quartz tube and makes advancing wetting angle. During the preheating, the liquid metal picks up oxygen from the argon atmosphere and forms a surface oxide layer. A significant amount of the oxygen in the powder compact may be consumed in this stage. As pressurization begins, however, the oxide layer is torn off and fresh liquid metal passes through the Saffil paper filter and contacts the bottom of powder compact. If the applied pressure is higher than the threshold pressure, liquid metal infiltrates into the powder compact.

Three different temperatures, 700, 800, and 900 °C, and three infiltration times were used as experimental variables. Normally 5 min. was used as the standard infiltration time, and 2 and 10 min. were also used to investigate the time dependence of wetting and infiltration.
To minimize the contamination of melt by dissolved silicon and oxygen from the quartz tube, the maximum infiltration time was limited to 10 min. Melt temperature was controlled by temperature controller (Omega, CN 300 KC) with an accuracy of ± 2 °C.

3.4. Calculation of Wettability

After pressure infiltration, the specimens were mounted in epoxy, sectioned with a diamond saw, polished and the infiltrated distance measured. Then the threshold pressure for infiltration was thereby obtained. Since the pressure measuring device has a minimum reading of 1 psi (6.895 kPa), sometimes, more accurate threshold pressure, up to 0.5 psi (3.448 kPa), was obtained from the plot of applied pressure vs. infiltration distance. The threshold pressure was either used as a measure of wettability or converted to the wetting angle by using the modified capillary pressure equation which is obtained by combining eq. (2.2) and (2.17):

\[
P_{th} = \frac{6 \lambda \gamma_v \cos \theta (1 - w)}{D \cdot w}
\]  

(3.5)

where, \( P_{th} \) is the threshold pressure, \( \lambda \) is the shape factor, \( \gamma_v \) is the surface energy of liquid metal, \( \theta \) is the wetting angle, \( w \) is the void fraction, and \( D \) is the particle size. By inserting appropriate parameters into eq. 3.1, the wetting angle can be obtained from the simple formulae:

\[
\cos \theta = -0.37 \frac{P_{th}}{\gamma_v \lambda}
\]  

(3.6)

for SiC powder specimen, and
\[ \cos \theta = -0.34 \frac{P_{th}}{\gamma_{lv} \lambda} \] (3.7)

for B₄C powder specimen. The threshold pressure, \( P_{th} \), and the surface energy of liquid, \( \gamma_{lv} \), are used in kPa and in mJ/m², respectively. Considering eqs. (3.6) and (3.7), ± 0.3° of error is caused by ± 1 psi (6.895 kPa) when the wetting angle is about 130°. For one particulates/Al-alloy system, 8 to 15 runs were necessary to obtain the threshold pressure and infiltration behavior.

The plots of applied pressure vs. infiltration distance also used to investigate the infiltration behavior. Infiltration behaviors, linear or parabolic, can be a good clue to determine the existence and degree of interfacial reactions. The relationship between infiltration distance and applied pressure was also used to analyze the fluid flow through the packed ceramic particulates.

3.5. Microstructural Analysis

The microstructure of the infiltrated specimens was characterized with conventional optical microscopy and scanning electron microscopy (SEM).

The samples for optical microscopy were prepared by polishing the sectioned specimen. First, specimen was mechanically polished with 600 and 1000 grit emery papers, then polished with 6 and 1 μm diamond pastes for 2 min. for each step. Finally, the specimen was polished with 0.05 μm alumina for 30 seconds. Before moving to the next polishing step, specimen was rinsed with ethyl alcohol and ultrasonically cleaned for 10 min. Cu-bearing aluminum alloys, Al-2% Cu and Al-4.5% Cu, were etched with a solution of 4 g of KMnO₄ and 2 g of NaOH in 1 liter of distilled water for about 10 seconds as suggested by Mortensen et al. [109]. Other alloys were double-etched; with 5% HF for 2-3 sec. and with the same solution as for Al-Cu alloys for 5 sec. Keller's reagent, solution of 10 ml HF,
15 ml HCl, 25 ml HNO₃, and 50 ml distilled water was also used for deep etching.

Fracture surfaces of infiltrated powder specimens were analyzed with SEM (AMR or Cambridge). Since an extensive study on the mechanical properties is beyond the scope of the present work, the specimens were fractured by a simple manner: clamped in a vise and broken by striking with a hammer. Fractured specimens were coated with approximately 200 Å of gold to give a better image in SEM. The other halves of fracture specimens were used for Auger Electron Spectroscopy analysis.

3.6. Auger Electron Spectroscopy Analysis

Auger electron spectroscopy (AES), Physical Electronics Industries Inc., model 590, was used to investigate the surface chemistry of particulates. Particulates were embedded in 1 mm thick indium foil and inserted into the analyzing chamber which was maintained at a pressure of about 10⁻⁷ Pa. Auger electron spectroscopy was operated at 5 kV and 100 nA. For Ar sputtering, 2 kV and 30 μA/cm² were used as electron voltage and beam current.

AES analysis was also performed on fractured specimens in order to determine the chemistry of the metal:ceramic interfacial region. After being fractured by a hammer, the specimens were cut into 1.5 mm thickness. The electron beam conditions included a primary beam voltage of 5 kV and beam current of 100 nA. For depth profile, Ar sputtering was conducted normal to the fracture surface at 4 kV and 70 μA/cm².

Depth profiles were obtained by sputtering both to the particulate and to the matrix directions from the fracture surface. The sputtering rate was estimated as 0.1 nm/sec.
4. CHARACTERIZATION OF INFILTRATED SPECIMEN

4.1. Surface Characterization of Ceramic Particulates

The Auger Electron Spectroscopy (AES) profiles which were taken from the as-received SiC and B₄C particulates are shown in Figs. 4.1 and 4.2, respectively. As seen from the concentration profiles, there were no indications of impurities on the surfaces except small amounts of oxygen. The peaks of Auger intensities, dN/dE, are found electron kinetic energies of 92 and 1,619 eV for Si, 179 eV for B, 272 eV for C, 68 and 1,396 eV for Al, 45 and 1,186 eV for Mg, 604 and 920 eV for Cu, and 503 eV for O.

Figs. 4.3 and 4.4 show the element profiles as a function of sputtering time for SiC and B₄C particulates. The AES profile for SiC showed that atomic concentration of C is lower than that in stoichiometric SiC. This disagreement was caused by the mismatch between the sensitivity factors stored in the computer program and those of elements in the specimen. Since the sensitivity factors stored in the computer program are based on the pure elements, the sensitivity factors of elements in the specimen change with the bond type of compounds. However, it is obvious that the surfaces of both particulates are contaminated with oxygen. The oxygen concentration was higher in B₄C than that in SiC. Compared with chemical analysis data of both particulates, as listed in Table 3.1, AES results show higher concentration of oxygen even after 10 min. of sputtering.

Fig. 4.5 shows the Auger spectrum of an SiC surface which had been oxidized in an air atmosphere at 800 °C for 1 hr. The main features of the spectrum are the large peak of oxygen and severe noise due to charging. Because of the insulating nature of SiO₂, it was impossible to obtain an AES profile.

AES results on the surfaces of SiC and B₄C particulates after infiltration experiments are shown in Figs. 4.6 and 4.7. Before infiltration, each particulate was preheated for 5 min. at 800 °C in Ar atmosphere. Including 5 min. of infiltration time, the particulates were heated
for the total of 10 min. As can be seen in the AES results, SiC particulates were self-cleaned during the experiment, while, B_4C particulates seem to pick up more oxygen from the ambient atmosphere. The reactions between the particulates and gases are discussed in section 6.1.

4.2. Microstructure of Infiltrated Powder Specimen

The infiltration-tested specimen is divided into 4 different parts: (i) uninfiltrated matrix alloy, (ii) infiltrated Saffil paper, (iii) infiltrated powder compact, and (iv) uninfiltrated powder compact. As noted in section 3.3, the specimens were air cooled after infiltration.

Typical microstructures of matrix alloys are shown in Figs 4.8 to 4.10 for Al-2% Cu, Al-2% Si, and Al-2% Mg alloys. All the structure shows primary $\alpha$ dendrites and interdendritic eutectic. From the binary phase diagrams [110] of each alloy system, Figs. 4.11 to 4.13, the eutectics are expected to be $\alpha_{Al} + \theta (CuAl_2)$, $\alpha_{Al} + Si$, and $\alpha_{Al} + Al_3Mg_2$. The similar sizes of the secondary dendrite arm spacings, about 50 $\mu$m in average, indicate identical cooling rates, about 2 °C/sec [111].

The boundaries between metal matrix and Saffil paper, and between Saffil paper filter and powder compact in SiC/Al-2% Cu system are shown in Fig. 4.14 (a) and (b), respectively. As can be seen in the figures, dendritic growth is observed only in the uninfiltrated matrix region. Neither compression nor breakage of Saffil paper was not found in the present experiment, although both were reported elsewhere [112]. Also, there was no indication of disruption of the powder compact, especially at the boundary between Saffil paper filter and powder compact.

The microstructure of solidified metal in the infiltrated powder compact differs from that of uninfiltrated metal in several points: (i) no dendritic growth, (ii) modification of eutectic, and (iii) appearance of a second phase.

The histories of pressure infiltration are listed in Table 4.1. To prepare metallographic specimens of the infiltrated region, the 0.3 cm thick round pellets were cut from the middle of
the specimens which have infiltrated length larger than 2 cm. The typical microstructures of infiltrated SiC powder compact, which were infiltrated with pure Al, Al-2% Cu, Al-2% Si, and Al-2% Mg alloys are shown in Figs. 4.15 to 4.18.

Optical micrographs revealed that the distribution of particulates is quite uniform with no redistribution during pressure infiltration. The small voids between particulates are the evidence of non-infiltration due to much smaller path than the average size of the capillary channels. In agreement with the previous observations [97,113,114], preferential nucleation of the silicon phase on the particulate surfaces was found in all SiC particulates system. Due to the high volume fraction of particulates and high surface-to-volume ratio, a significant amount of SiC was dissolved in the matrix.

Since the cooling rate is relatively slow, less than 2 °C/sec for infiltrated matrix, eutectic phases are expected to exist as divorced structure, i.e., α phase on the primary α and rather coarse β or intermetallics on the surface of particulates or between primary α phases. However, the specific euctectics were hardly found because of predominant Si phases.

The micrographs of a deep-etched SiC/pure Al specimen are shown in Fig. 4.19. The matrix was dissolved in the concentrate Keller's reagent: for 30 sec. The "bridges" in the microstructure are Si phases. The serrulated surfaces of particulate are the evidence of interfacial reaction, mainly dissolution of SiC. The concentration of Si in the matrix was measured as about 5% with electron microprobe analyzer.

The different morphologies in the microstructure of top and bottom portion of the SiC/Al-2% Si samples are indicated in Fig. 4.20 (a) and (b). Longer infiltration time for the bottom of the powder specimen allowed a higher degree of interfacial reaction. In spite of the large variation in the shape of particulates, the matrix microstructures show only a little difference. The transport of the dissolved elements by flowing liquid may cause relatively even distribution of those components in the matrix.

Since interfacial reaction rate is a strong function of temperature, it is not surprising to see a variation of microstructures with temperatures. Fig. 4.21 (a) and (b) show the
microstructures of infiltrated SiC specimen with pure aluminum at 700 °C and 900 °C, respectively. From the figures, it is obvious that there was much more interfacial reaction at 900 °C.

The typical microstructures of infiltrated B₄C powder specimen with Al-alloys are shown in Figs. 4.22 to 4.25. Because of the extremely high hardness of B₄C particulates, specimen preparation for metallography was not so successful as SiC.

The Al-B phase diagram [110], Fig. 4.26, indicates very low solubility of boron in aluminum over the entire temperature range of the present experiment. Therefore, virtually no dissolution of B₄C particulates is expected in the Al-based alloys.

The second phases exist as irregular chunks between particulates in B₄C/Al-alloy systems. As can be seen in Fig. 4.25, well-developed second phases are abundant in B₄C/Al-2% Mg system. SEM micrographs of deep-etched B₄C/Al-2% Mg specimen are shown in Fig. 4.27. The white-colored second phases were produced between the B₄C particulates. EDX results, Fig. 4.28, show a high concentration of Mg in the second phase. Electron microprobe analysis indicated that the concentration of Mg in the second phase is about 13%. The Mg concentration in the matrix was measured as about 1.5%. Considering the original composition of matrix, Al-2.2% Mg, depletion of Mg due to the formation of Mg-rich second phase in the matrix is obvious.

4.3. Fracture Morphology

Fracture behavior is the least investigated aspect of particulate reinforced aluminum matrix composite behavior [115]. Even though measurement of the mechanical properties of infiltrated powder specimen is beyond scope of the present study, some fracture surfaces of samples broken in bending were examined in order to investigate the metal/ceramic interface.

Typical fracture surface morphologies are shown in Figs. 4.29 to 4.32 for SiC/Al-alloy systems, and in Figs. 4.33 to 4.36 for B₄C/Al-alloy systems. The overall fracture
morphology of the infiltrated powder specimens was generally unaffected by matrices. However, there was marked difference in the fractographs of different particulates systems, i.e., more ductile mode in B₄C/Al-alloy systems. Even though some non-infiltrated regions can be found, debonded interfaces reveal good physical contact between matrix and particulates.

Metal:particulate bonding seems to be weaker for SiC/Al-alloy systems than that of B₄C/Al-alloy systems as debonding interfaces between matrix and particulates were often found on the fracture surfaces with only a little matrix alloy adhering to them. Fine dimples, indication of ductile fracture, are barely visible on the fracture surface. The Auger electron spectroscopy analysis on the fracture surface of SiC/Al-2% Mg system are shown in Fig. 4.37. This survey shows only a large carbon peak at 272 eV, which is an indication of: (i) dissolution of SiC particulates, (ii) formation of carbon-rich region due to selective diffusion of Si into matrix, and (iii) fracture through carbon-rich layer. More details of interfacial reaction are discussed in section 6.3.

For B₄C/Al-alloy specimens, Figs. 4.33 to 4.35, most of the fracture surface consists of fine, equiaxed dimples which is indication of failure by coalescence of microvoids. The process of microvoid formation and coalescence involves considerable localized plastic deformation and requires the expenditure of a large amount of energy, which is an indication of good fracture toughness [116].

In an alloy which has second phase particles, generally, fracture occurs by coalescence of microvoids which are formed as a result of particle:matrix decohesion or cracking of second phase particles [116]. This mechanism of fracture dominates in SiC/Al-alloy systems. However, fractographs of B₄C/Al-alloy systems show fine matrix dimples with only a few debonding interfaces. Since the failure seems to occur through the matrix for B₄C/Al-alloy systems, it is concluded that the matrix:particulate interfaces were strong enough to permit transfer of loads.

However, B₄C/Al-2% Mg samples show cleavage-like fracture surfaces with few
dimples as shown in Fig. 4.36. For this system, therefore, it can be said that brittle fracture occurs through the metal:particulate interface with little plastic deformation. It was reported [117] that Mg in the matrix degraded the mechanical properties such as tensile strength and bending strength of SiC fiber reinforced aluminum alloys.
5. WETTING OF CERAMIC PARTICULATES

5.1. Energetic Considerations

The infiltration of liquid into particulate compacts shows very different behavior depending on whether the system is wetting or non-wetting. These two situations are illustrated in Fig. 5.1. For a wetting system as shown in Fig. 5.1 (a), wetting angle, $\theta$, is less than $90^\circ$, and infiltration occurs through the narrow gaps leaving pores between the neighboring particles. When the capillary pressure is increased, the pores vanish by filling with liquid. Since the pressure inside the liquid is less than the outside pressure, an adhesive pressure is exerted by a wetting liquid, giving an attractive force between particles.

For a non-wetting system as shown in Fig. 5.1 (b), $\theta$ is larger than $90^\circ$, and the liquid phase infiltrates through the large gaps. The uninfiltrated regions are filled when the external pressure is high enough to overcome the capillary pressure resisting liquid infiltration. In this case, the infiltrated liquid causes a repulsive force between particles and will not fill pores where particulates touch. The structure of porous media was reviewed extensively by Dullien and Batra [118].

For modelling simplicity, the powder compacts for the present study is considered as an assemblage of cylindrical capillary tubes. Since the present ceramic particulates/liquid metal systems are non-wetting, the liquid front makes an advancing angle, $\theta>90^\circ$, as shown in Fig. 5.2. The capillary pressure is defined by the surface energy of liquid, wetting angle, and the radius of capillary tube, as given in eq. (2.2). If the concept of hydraulic radius, $r_h$, is used, the capillary pressure, $P_c$, exerted is expressed by:

$$
P_c = \frac{\gamma_{lv} \cos \theta}{r_h}
$$

(5.1)
where, \( \gamma_{lv} \) is the surface energy of liquid and \( \theta \) is the wetting angle. Inserting eq. (2.17) for \( r_h \), eq. (5.1) becomes

\[
P_c = \frac{6 \lambda \gamma_{lv} \cos \theta (1-w)}{D \cdot w}
\]  

(5.2)

where, \( \lambda \) is the shape factor, \( w \) is the void fraction of powder compact, and \( D \) is the particle size.

The liquid metal starts infiltration when the applied pressure exceeds the capillary pressure. However, the wetting angle changes with time, mainly due to the reduction of the solid-liquid interfacial energy. Since the threshold pressure after time \( t \), \( P_{th}(t) \), is smaller than the initial value, \( P_i \), infiltration of liquid can occur at a lower pressure. In other words, the liquid infiltration occurs after some period of time, the incubation time, when the applied pressure, \( P_a \), is lower than the initial capillary pressure. The change of the capillary pressure with time is shown schematically in Fig. 5.3. Obviously, the incubation time for infiltration is shorter for higher applied pressure. This tendency is believed to be the reason of high infiltration rate at 700 °C, where the applied pressure is much higher than at 800 or 900 °C. Details on the infiltration behavior will be discussed in later section.

If the wetting angle reverts back to the original value immediately after a certain amount of infiltration, the liquid infiltration will stop and resume after the wetting angle reaches the threshold value, \( \theta_t \). This tendency may be true for reaction-assisted wetting. However, if the breaking of an oxide film is involved, once initiated, infiltration may proceed more or less continuously.

If there is an oxide film on the liquid front, an additional pressure is required to commence the infiltration. In this case, the threshold pressure for infiltration is a sum of
two pressures from the different sources:

\[ P_{th} = P_c + P_f. \] (5.3)

where, \( P_c \) is the capillary pressure and \( P_f \) is the pressure needed to break the oxide film on the liquid front. The pressure for the breaking of oxide film is a function of the liquid moving velocity as well as the concentration of oxygen in the powder compact. If the incubation time for infiltration is long, the effect of oxide film on the threshold pressure will be significant.

A different approach to calculate the threshold pressure for infiltration was made by Mortensen and Cornie [119]. They considered the energy change during the infiltration and deduced an equation for the threshold pressure, \( P_{th} \), as:

\[ P_{th} = (\gamma_{sl} - \gamma_{sv}) S \] (5.4)

where, \( \gamma_{sl} \) is the solid-liquid interfacial energy, \( \gamma_{sv} \) is the surface energy of solid, and \( S \) is the surface area of solid per unit volume of liquid. Assuming the powder compact as a packed spheres of diameter \( D \) with a void fraction of \( W \), eq. (5.4) was converted as:

\[ P_{th} = \frac{6 (\gamma_{sl} - \gamma_{sv}) (1 - w)}{D \cdot w}. \] (5.5)

In the partial wetting regions, \( 0^\circ < \theta < 180^\circ \), one may use Young's equation and shape factor to show that eq.(5.5) is identical to eq.(5.2) which was derived from the concept of capillary pressure. Since the information on the solid-liquid interfacial energy, \( \gamma_{sl} \), and the surface energy of solid, \( \gamma_{sv} \), is scarce, eq.(5.2) may be more practical.
5.2. Estimation of Wetting Angle

The threshold pressure, measured in the present study, gives a practical measure of wettability by characterizing the minimum pressure, neglecting fluidity effects, required for the fabrication of composites by pressure casting.

Although wettability is generally indicated by wetting angle, \( \theta \), the wetting angle is not a sufficient measure of wettability, especially in the sense of infiltration. Since a low value of wetting angle may be associated with a low value of the surface energy of liquid, \( \gamma_{lv} \), the combined value of surface energy of liquid and cosine of wetting angle, \( \gamma_{lv} \cdot \cos \theta \), should be considered. Since the threshold pressure is a linear function of \( \gamma_{lv} \cdot \cos \theta \), as shown in eq.(5.2) a small value of wetting angle does not necessarily indicate good infiltration.

However, the threshold pressure must be converted to the wetting angle in order to compare it with data obtained by other wetting tests, such as the sessile drop technique. The calculation of the wetting angle from the threshold pressure can be done easily by using eq. (3.5). Unlike the case of wetting system, there is no information on the shape factor because only a few studies have been conducted on the infiltration of non-wetting liquid through the porous media.

The shape factor dependence of the wetting angle is shown in Figs. 5.4 and 5.5 for SiC/pure Al and B\(_4\)C/pure Al systems, respectively. Since there are no reliable data on the wetting angle of either SiC or B\(_4\)C with liquid aluminum alloys, the shape factor can not be determined precisely. Indeed, the significant differences on the experimental values of wetting angle of ceramic/liquid aluminum systems, as shown in Fig. 2.7, make the determination of shape factor more difficult. Considering the results of sessile drop test [120], 1.4 [46] seems to a reasonable number for the shape factor for the powder compact used in this experiment. The calculated values of wetting angles for SiC and B\(_4\)C

- 62 -
particulates with liquid aluminum alloys are shown in Figs. 5.6 to 5.11, as functions of time, temperature, and alloying element.

5.3. Effect of Time

Because several kinetic processes are involved in wetting, the change of wettability with time is common in solid ceramic/liquid metal systems. The change of the threshold pressure with time was discussed in the previous sections, 5.1, in a qualitative manner. The time dependences of the threshold pressure for wetting in SiC and B₄C particulates with liquid aluminum alloys are shown in Figs. 5.12 and 5.13.

For SiC, near-equilibrium wettings were achieved in 5 min. at 800 °C for pure aluminum Al-2% Si, and Al-2% Mg alloys. However, the threshold pressure decreased with time almost linearly for Al-2% Cu alloy. These tendencies of time dependence of wetting may be explained in terms of reaction kinetics in ceramic/metal systems.

For a system of high reactivity, metal: ceramic interfacial reactions proceed quickly shortly after the physical contact between solid and liquid phases. If the reaction products at the interface are stable both chemically and physically, further reaction will be stopped or retarded significantly. Subsequently, the equilibrium wetting occurs in a short time. However, quick wetting equilibrium can also occur in an inert system which does not involve interfacial reactions, such as a water drop on a platinum plate.

In general, wettability is poor and the wetting process is slow for less reactive systems. Therefore, it takes a longer time to reach an equilibrium wetting. Even though SiC/Al-alloy systems are often regarded as a chemically inert system [73], a significant amount of dissolution was observed in the present study as observed in the microstructure of the SiC powder specimens infiltrated with aluminum alloys, as shown in Figs. 4.15 to 4.21. The high rate of dissolution of SiC in the liquid Al-alloys can be connected to the high
surface-to-volume ratio of particulates as well as high Si solubility in Al.

For \(B_4C\) particulates, Al-2\% Cu and Al-2\% Si alloys achieved near-equilibrium wetting in 5 min. For pure aluminum and Al-2\% Mg alloys, however, the threshold pressures decreased with time even after 5 min.

Chemical reaction-assisted wetting is expected for \(B_4C\) particulates in more reactive alloys, such as Al-2\% Mg. Liquid boron oxide, \(B_2O_3\), exists on the surface of \(B_4C\) above 450 °C [62] and enhances wettability through liquid-liquid reaction when contacted with liquid metal. Cu or Si in aluminum seems to make chemical reaction less active, probably due to adsorption of the less reactive element, Cu or Si, at the metal:ceramic interface. However, wettability of \(B_4C\) with Al-alloys is better than that of SiC due to the more active interfacial reaction. In spite of its lower stability than SiC [62], \(B_4C\) particulates were not dissolved much in liquid aluminum alloys mainly due to the extremely low solubility of B in Al [110].

Near-linear decreases of wetting angle for SiC/Al system were also observed at 980 °C and 900 °C by Köhler [68] and by Halverson et al. [75], respectively. The linear behavior of time dependence of wetting angle were observed also for \(Al_2O_3/Al\) system by Brennan and Pask [66]. Achievements of equilibrium wetting in 5 min. were reported by Samsonov et al. [7] for TiC/Al system at 950 °C, and by Ueki et al. [121] for \(ZrO_2/Al\) system at 900 °C.

If the attainment of equilibrium wetting is also related to the formation, reaction, and breakdown of the oxide film on the liquid metal surface, the time dependence of wetting will be much more complicated. The breakdown of the oxide layer on the solid ceramic phase either physically or chemically has also been considered as one of factors affecting the kinetics of wetting [32,73]. Due to the self-cleaning of SiC particulates and liquid oxide layer formation in \(B_4C\) particulates, the breakdown of solid oxide film on the ceramic phase is not expected in the present systems.
Newman [122] expressed the time dependence of the wetting angle, $\theta(t)$, as:

$$\cos \theta(t) = \cos \theta(eq) [1 - a \cdot \exp(-b \cdot t)] \quad (5.6)$$

where, $\cos \theta(eq)$ is the wetting angle at equilibrium, $a$ and $b$ are the constant, and $t$ is time. Since the threshold pressure is a linear function of $\cos \theta$, eq.(5.6) can be applied to the time dependence of threshold pressure with minor modification:

$$P_{th}(t) = P_{th}(eq) [1 + c \cdot \exp(-d \cdot t)] \quad (5.7)$$

where, $P_{th}(eq)$ is the threshold pressure at equilibrium, and $c$ and $d$ are constants. The calculated values of constants, $c$ and $d$ are listed in Table 5.1. Fig. 5.14 shows good agreement between the experimental and calculated values of threshold pressure as a function of time for the wetting of SiC and $B_4C$ particulates with Al-2% Si alloy at 800 °C.

5.4. Effect of Temperature

The threshold pressures measured after 5 min. of holding time for SiC/Al-alloy and B$_4$C/Al-alloy systems are shown as a function of temperature in Figs. 5.15 and 5.16, respectively. As expected, the threshold pressure decreased with temperature for all the ceramic particulate/Al-alloy systems. This effect may be caused partly by thermodynamics due to the changes in surface energies, and by partly kinetics due to more active interfacial reactions at higher temperature.

For SiC/Al-alloy systems, the threshold pressure decreased almost linearly with temperature except for SiC/pure aluminum system. For B$_4$C/Al-alloy systems, as shown in Fig. 5.16, however, different slopes of threshold pressure vs. temperature were observed
in different temperature ranges at a modestly between 700 and 800 °C, and sharply between 800 °C and 900 °C, except for B₄C/Al-2% Mg system which showed the opposite behavior.

Different slopes at different temperatures may be due to the different dominant interfacial reactions or kinetics. In many cases, rapid decreases in wetting angle were observed at 900 °C for ceramic/Al-alloy systems [14,32,68,71]. This behavior was explained by either the breakdown of oxide film on the surface of ceramic [32,73] or the change of characteristics of oxide layer on the surface of liquid metal [14]. Due to the lack of information on the thermodynamics and kinetics on the metal-ceramic interfacial reactions, it is quite difficult to explain the time and temperature dependences of wetting behavior even qualitatively.

As shown in eq. (2.2), both the threshold pressure and wetting angle are functions of the surface energy of liquid. The temperature dependence of the surface energy of liquid aluminum, dy/dT, was determined as - 0.104 mJ/°C by Lang [23]. In the absence of a the change of wetting angle with temperature, decrease of surface energy of liquid aluminum per 100 °C, 10.4 mJ, will cause the decrease of threshold pressure as much as 19.9 kPa for SiC and 21.6 kPa for B₄C particulates systems. The actual decreases in threshold pressure per 100 °C, as shown in Tables 5.2 and 5.3, are much larger than those due to the changes only in surface energy of the liquid metal. This result indicates that other processes are involved in wetting than the change of surface energy of liquid metal with temperature.

The linear dependence of \( \cos \theta \) on temperature, the so-called Zisman type relationship [15,123], was not found in the present work, as shown in Figs. 5.17 and 5.18 for SiC/Al-alloy and B₄C/Al-alloy systems, respectively.

Passerone and co-workers [124] also introduced a simple relationship between the wetting angle and temperature for Ti-glass system:

\[
\cos \theta = a + b \cdot T + c \cdot T^2
\]  \hspace{1cm} (5.8)
where, T is the temperature in °K and a, b, and c are constants. Even though eq. (5.8) modified the Zisman relationship by adding $T^2$ term, this equation also do not match with the present experimental results.

As can be seen in Figs. 5.15 and 5.16, the rates of threshold pressure change with time vary depending on the system. For SiC particulates, the threshold pressure decreases more rapidly at higher temperature for Al-2% Cu and Al-2% Si alloys. However, pure Al and Al-2% Mg alloys show a saturation of threshold pressure with time. For $B_4C$ particulates, all the alloy system shows more rapid decrease of threshold pressure at higher temperature except in Al-2% Mg alloy.

The relationship between $\log P_{th}$ (kPa) and $1/T$ (K) are shown in Figs. 5.19 and 5.20 for SiC/Al-alloys and $B_4C$/Al-alloy systems, respectively. As can be seen in these figures, experimental results do not show the linear relationships in the $\log P$ vs. $1/T$ plots i.e., do not obey the so-called Arrhenius-type law.

Since complex interfacial reactions are involved in the wetting of these ceramic particulates/liquid aluminum alloy systems, it may be natural that each system shows different relationship between the wettability and the temperature. Therefore, a thorough knowledge of the physics and chemistry of interfacial reactions is required to derive a universal relationship to explain the temperature dependence of wetting in ceramic/Al-alloy system.

5.5. Effect of Alloying Elements

There has been no systematic study on the effect of alloying elements on wetting between ceramic and liquid metal. Thus, the effective alloying elements for promoting wetting have been found more or less by trial and error.

The present experimental results show that alloying with Mg is the most effective in
promoting wetting of both SiC and B\textsubscript{4}C particulates by aluminum alloys. Conversely, Cu and Si were not effective for improving wettability.

The relationship between the threshold pressure and the solute concentration at 800 °C is shown in Figs. 5.21 and 5.22 for SiC/Al-alloy and B\textsubscript{4}C/Al-alloy systems, respectively. Based on the Gibbs adsorption equation, eq. (2.41), there have been arguments that small addition of solutes will be sufficient to change the surface energy as long as they can form a monatomic layer at the free surface of liquid or solid-liquid interface. The experimental results, however, show that the threshold pressure changes with the solute concentration. This tendency implies that the surface modification through adsorption is not a dominant process in wetting.

As can be seen in eq. (2.40), liquid aluminum has an extremely high oxygen affinity. Therefore, chemical reactions involving oxygen are inevitable at the liquid aluminum/ceramic interface. These interfacial reactions may reduce the interfacial energy of solid ceramic and liquid metal. Subsequently, the wetting angle will be decreased to make a force equilibrium, as shown in Fig. 2.1 and 2.2.

Figs. 5.23 and 5.24 indicate the relationship between the free energy of oxide formation of alloying elements and the threshold pressure for wetting in SiC and B\textsubscript{4}C with aluminum alloys. As can be seen in these figures, there are good correlations between the free energy of oxide formation and the threshold pressure. The larger the negative values of free energy of formation, the lower the threshold pressures are. However, the effectiveness of alloying varied with temperature and ceramic/metal system. The different degree of contribution of alloying element at different temperature and system is believed to be connected with kinetics of each interfacial reaction as well as different interfacial reactions other than oxide formation.

Again, the threshold pressure for wetting is a function of wetting angle as well as of surface energy of liquid. Therefore, if there is no other reaction than simple adjustment of
wetting angle due to the change in the surface energy of liquid, there will be no change in the threshold pressure with solute concentration. Thus, the changes in threshold pressure with the amount of alloying elements for the present experiment is evidence for changing wettability through complex interfacial phenomena.

Wetting angles calculated from the threshold pressure are shown as a function of the solute concentration in Figs. 5.10 and 5.11 for SiC/Al-alloy and B₄C/Al-alloy systems, respectively. One thing noticeable is that the increase of wetting angle with content of Mg in SiC/Al-Mg system. This observation can be explained by the lower rate of decrease in the threshold pressure than that in surface energy of liquid. The dependence of surface energy of liquid aluminum alloys on the solute concentration at 700 °C is given as: - 2.12 mJ/m²/%Mg, - 2.17 mJ/m²/% Si, and - 41.90 mJ/m²/% Mg [24]. As mentioned earlier, a lower surface energy of liquid makes a larger wetting angle for non-wetting systems. For B₄C/Al-Mg systems, the degree of improvement in wettability with solute concentration seems to be high enough to surpass the increase of wetting angle by decreasing surface energy of liquid with Mg alloying.

Oki et al. [125] investigated the effect of alloying elements in the wetting of SiC plate by new method, i.e., dipping SiC into molten metal and measuring the wetted area after a set period of time. The order of effectiveness of alloying elements on the wetting was; Si, Mn, Fe, and Cu, in decreasing order. Even though the experimental results can not be correlated directly with wetting angle or threshold pressure, effectiveness in promoting wetting shows a good correlation with the free energy of formation of oxide for each alloying element.

5.6. Effect of Gas Atmosphere

The threshold pressures for SiC/Al-alloy and B₄C/Al-alloy systems in Ar and air
atmospheres are listed in Table 5.4. In general, the threshold pressure in air atmosphere is greater than that in Ar atmosphere.

Compared with the infiltration in Ar atmosphere, several different phenomena are expected in air atmosphere including oxidation of particulates, formation of oxide layer on the surface of liquid metal. Obviously, the oxide film on the particulates and the oxide layer on the liquid metal surface change the wetting process as well as wettability.

Confirmed in AES analysis, as shown in Fig. 4.5, oxide film is formed on the SiC particulates in air atmosphere. Since SiO$_2$ has a much lower surface energy, 307 mJ/m$^2$ at 1,000 °C [49], than that of SiC, 840 mJ/m$^2$ at 1,200 °C [32], the wetting angle may increase after oxidation of SiC. However, as seen in step-like behavior of infiltration in air atmosphere, the oxide layer on the liquid metal surface can be regarded as the main cause of increased threshold pressure.

For some B$_4$C/Al-alloy systems tested in air atmosphere, decreased threshold pressures were observed. The decrease in threshold pressure, or increased wettability, is believed to be caused by the formation of a thicker layer of liquid B$_2$O$_3$ on the B$_4$C particulates in an air atmosphere. However, if the oxide layer on the surface of liquid metal is thick and mechanically strong, the threshold pressure will increase.

The three typical behaviors of infiltration in air atmosphere are shown in Figs. 5.25, to 5.27 for B$_4$C/Al-4.5% Cu, SiC/Al-4.5% Cu, and B$_4$C/Al-2% Mg systems, respectively. The difference in infiltration behavior, step, linear, or exponential behavior as shown in Figs. 5.25 to 5.27, as well as different amount of change in the threshold pressure is related to the different wetting processes.

5.7. Effect of Surface Chemistry of Particulates

Surface treatments of dispersed phases for metal matrix composites have been
conducted to modify the surface characteristics. By changing surface chemistry properly, two major advantages can be obtained; enhancement of wettability and prevention of deterioration of solid second phase during the fabrication or service at elevated temperature. The techniques for surface treatments of fibers and particulates are reviewed by several authors [126, 127].

Katzman [128] coated carbon fiber with silica to improve wetting with Mg-alloys through the formation of aluminum silicates. Possible reactions proposed by Katzman are:

\[
\begin{align*}
\text{SiO}_2 + 2 \text{Mg} & = 2 \text{MgO} + \text{Si} \quad (5.9 \text{ a}) \\
\Delta G_{943 \text{ K}} & = -318.1 \text{ kJ} \\
\text{SiO}_2 + \text{MgO} & = \text{MgSiO}_3 \quad (5.9 \text{ b}) \\
\Delta G_{943 \text{ K}} & = -96.3 \text{ kJ} \\
\text{SiO}_2 + 2/3 \text{Mg} & = 2/3 \text{MgSiO}_3 + 1/3 \text{Si} \quad (5.9 \text{ c}) \\
\Delta G_{943 \text{ K}} & = -340.5 \text{ kJ} \\
\text{SiO}_2 + 2 \text{MgO} & = \text{Mg}_2\text{SiO}_4 \quad (5.9 \text{ d}) \\
\Delta G_{943 \text{ K}} & = -117.2 \text{ kJ} \\
\text{SiO}_2 + \text{Mg} & = 1/2 \text{Mg}_2\text{SiO}_4 + 1/2 \text{Si} \quad (5.9 \text{ e}) \\
\Delta G_{943 \text{ K}} & = -217.7 \text{ kJ}
\end{align*}
\]

Even though all the above reaction is thermodynamically possible, the reaction kinetics should be considered in wetting process.

The wettability of surface-oxidized SiC particulates with Al-2% Mg alloy was measured to investigate the effect of oxide on the surface of particulates. The results of the tests, shown in Fig. 5.28, show that silica does not improve wettability. The rate of
chemical reaction to form aluminum silicates may be slow in Al-alloys with low Mg contents.

The microstructure of the oxidized-SiC powder specimen infiltrated with Al-2% Mg alloy at 800 °C is shown in Fig. 5.29. This figure indicates that the dissolution of SiC was suppressed by the silica layer on the surface of particulates. Therefore, the higher threshold pressure for oxidized-SiC particulates system may be explained by less decrease of solid-liquid interfacial energy with less interfacial reaction, i.e., dissolution.

5.8. Infiltration Behavior

Since the wetting phenomena was the primary concern of the present work, the infiltration experiments were conducted in order to obtain the threshold pressures for infiltration. Therefore, the data for infiltration behavior are not sufficient to allow the precise studies on the infiltration behavior of liquid metals into the packed ceramic powder. Compared others reported so far, the infiltration behaviors observed in the present work, however, show quite different behaviors. Even though it is more or less naive, some efforts are made to explain the infiltration behavior of liquid aluminum alloy into packed ceramic particulates observed in the present experiments.

The infiltration distance is shown in Fig. 5.30 as a function of applied pressure in the SiC/Al-2% Cu system which was infiltrated at 900 °C for 5 min. Each data point represents results of a separate experimental run. The linear relationship between the applied pressure and the infiltration distance seems to be typical for non-reactive systems such as SiC/Al-Cu alloy systems.

The infiltration behavior of the B₄C/Al-2% Mg system at 800 °C, however, is quite different from that of SiC/Al-alloy systems, as shown in Fig. 5.31. The exponential type of relationship between the applied pressure and the infiltration distance is observed when the ceramic/Al-alloy systems is reactive.
As shown in Fig. 5.30, the threshold pressure for infiltration in SiC/Al-2% Cu system at 900 °C is 558.5 kPa and the slope of the infiltration distance vs. applied pressure of plot is about 0.03 cm/kPa. If hydrostatic equilibrium were obtained, the infiltration distance should have the form:

\[ h = \frac{P - P_{th}}{\rho \cdot g} \quad (5.10) \]

where, \( h \) is the infiltration distance, \( P \) is the applied pressure, \( P_{th} \) is the threshold pressure, \( \rho \) is the density of liquid, and \( g \) is the gravity force. The slope calculated by using eq. (5.10), 3.78 cm/kPa, is larger than the experimental result by some two orders of magnitude which means that the equilibrium has not been achieved.

The resistance to flow of liquid metal through the powder compact in a non-wetting system has at least two sources: (i) negative capillary force, i.e., threshold pressure for infiltration, acting before infiltration, and (ii) pressure drop during the infiltration. The threshold pressure for infiltration is an evidence of a capillary force which is governed by the surface energy of liquid, wetting angle, and capillary radius, as given by eq. (2.2). Due to the negative value of \( \cos \theta \), external pressure should be applied for infiltration.

The experimental values of threshold pressure and slope are listed in Table 5.5. Generally, the slopes of infiltration increase with temperature. Even though the total length of powder compact was not changed after infiltration, optical microscopy examination shows some redistribution of particulates during the infiltration with a pressure higher than about 850 kPa. This behavior can be a reason for extremely high rate of infiltration at 700 °C, which occurred in SiC powder specimen infiltrated with pure Al, Al-2% Cu, or Al-2% Si alloys. The relationship between the applied pressure and infiltration distance at different temperatures for the SiC/Al-2% Cu system is shown in Fig. 5.32. The linear
dependence of the infiltration distance on the applied pressure also observed by Fukunaga and Goda [129] when they infiltrated liquid aluminum into the glass fiber preform kept at 600 °C.

The infiltration distance at different holding times is shown as a function of the applied pressure for SiC/Al-2% Cu system in Fig. 5.33. Since the threshold pressure for infiltration varies with time, it is difficult to predict the infiltration distance as a function of time. The infiltration distance as a function of the applied pressure for B₄C/Al-2% Si system at different holding time is shown in Fig. 5.34. Fig. 5.5 shows the time dependence of infiltration distance which is estimated from the data in Fig. 5.34. Two main features can be observed in this figure: (i) an incubation time for infiltration and (ii) non-square root time dependency. As can be seen in Fig. 5.35, the incubation time for infiltration decreases with applied pressure.

The decrease in incubation time at higher pressure can be explained by two phenomena: (i) higher degree of interfacial reaction through better physical contact and higher driving force for reaction, and (ii) quick breakage of oxide film on the liquid front, if it exists. This tendency is believed to be connected with the higher infiltration rate at lower melt temperature where a higher external pressure is required for infiltration.

Taking into the effects of surface energy of liquid, viscous resistance, and gravity on the rate of infiltration, Semlak and Rhines [47] proposed an equation for the upward flow of liquid metals through a porous body in wetting situation (θ < 90°) which, for the beginning of flow, is written:

\[
L = \frac{2}{\pi} \left( \frac{r \gamma_v \cos \theta t}{2 \eta} \right)^{1/2}
\]  \(5.11\)

where, \(L\) is the infiltration distance, \(r\) is the capillary radius, \(\gamma_v\) is the surface energy of the
liquid, $\theta$ is the wetting angle, $t$ is the infiltration time, and $\eta$ is the viscosity of liquid.

For non-wetting system, eq. (5.11), can be modified as:

$$L = \frac{r}{\pi} \left( P + \frac{2 \gamma_v \cos \theta}{r} \right)^{1/2} \left( \frac{t}{\eta} \right)^{1/2}$$

(5.12)

or

$$L = \frac{r}{\pi} \left( P - P_{th} \right)^{1/2} \left( \frac{t}{\eta} \right)^{1/2}$$

(5.13)

where, $P$ is the applied pressure and $P_{th}$ is the threshold pressure for infiltration.

The calculated values of infiltration distance using eqs.(5.13) and (5.14), and the experimental results are compared in Fig. 5.36 and Fig. 5.37 for B$_4$C/Al-2% Si system at 800 °C. As the two figures indicate, the infiltration distances calculated by eq.(5.13) do not agree well with experimental results in infiltration behavior as well as infiltration distance. This discrepancy indicates that the fluid flow phenomena observed in the present experiment can not be explained by eqs. (5.11) to (5.13) properly.

Even though it was neglected in eqs. (5.11) to (5.13) because of slow infiltration, the pressure drop by inertia losses due to repeated changes of direction in passing through the tortuous channels of the powder compact should be considered. The pressure drop due to repeated compression and expansion of the fluid in passing through the throats of the powder compact should also be counted.

The mismatch between the existing model and the present experimental results may also be caused by the following reasons: (i) time dependence of wetting angle or threshold pressure, i.e., change of wettability by interfacial reaction, (ii) change of wettability by different liquid velocity, and (iii) redistribution of particulates at high pressure.

There have been many studies on flow through porous media. The velocity of liquid
flow through the porous media, $v$, has the general form of:

$$v = K \frac{\Delta P}{\eta \cdot L}$$  \hspace{1cm} (5.14)

where, $K$ is a constant which differs from study to study, $\Delta P$ is the pressure drop from end to end, $\eta$ is the viscosity of liquid, and $L$ is the infiltration distance. The Hagen-Poiseuille equation, Blake-Kozeny equation, and Darcy's law are the typical flow equations of this type [41,130,131].

Surprisingly, almost all the flow equations was derived with a assumption that the pressure drop, $\Delta P/L$, is a linear function of viscosity as well as velocity of moving liquid. Then, they estimated constant, $K$, to match experimental data with an equation similar as eq. (5.14). However, some studies [155,156] showed that the pressure drop depends on the velocity of fluid flow, density and viscosity of the fluid, and the size and shape of particulates. Since these variables have unique relationship with pressure drop, there may not be a universal equation describing every fluid behavior.

Since wetting is a kinetic process, the wetting angle changes with interfacial velocity in the system which has moving liquid over the solid surface. Fig 5.38 shows advancing wetting angle as the liquid velocity increases in the capillary system. Elliott and Riddiford [134] investigated the effect of liquid moving velocity in the water/siliconed glass system in air atmosphere. They observed that the wetting angle increased from 105° at equilibrium to 180° when the liquid moving velocity was over 6 mm/min. Taking into account that the typical infiltration velocity for the present ceramic/liquid metal system is a order of a few mm/min, there seems to be an increase of wetting angle during the infiltration. Rose and Heins [135] also observed the change in wetting angle with moving velocity of liquid front.

The exponential behavior of infiltration, as in $B_4C/Al\text{-}Mg$ alloy systems, may be
caused by interfacial reaction-assisted infiltration. Interfacial reactions decrease the solid:liquid interfacial energy. As shown in Fig. 2.2 for non-wetting system, the wetting angle, $\theta$, will be decreased with decreasing interfacial energy, $\gamma_{sl}$. Thus, the resistance due to the negative capillary pressure will be decreased, i.e., higher infiltration at given applied pressure. To be effective, the solid:liquid interfacial reaction should be fast enough to operate at the vicinity of moving liquid front. The exponential curve of infiltration distance can be obtained by adding the infiltration distance due to interfacial reaction to the normal infiltration distance without any reaction:

$$L_{total} = L_p + L_r$$

(5.15)

where, $L_{total}$ is the total infiltration distance, $L_p$ is the infiltration distance due to normal pressure infiltration, and $L_r$ is the infiltration distance due to interfacial reaction. Fig. 5.39 shows the infiltration behavior in the system which has interfacial reactions proceed quickly during the pressure infiltration.

The pressure dependences of infiltration distance in $\text{B}_4\text{C}/\text{Al}$-alloy systems are shown in Fig. 5.40. As can be seen in this figure, $\text{B}_4\text{C}/\text{Al}$-2% system indicates the tendency of "reaction-assisted infiltration." However, all other alloy systems shows simple pressure infiltration. Again, the slopes of infiltration distance vs. applied pressure are high at higher applied pressure due to the tendency of shorter incubation time at higher applied pressure. If a non-reactive $\text{B}_4\text{C}$/alloy system has a threshold pressure around 600 kPa, the rate of infiltration will be similar as that of $\text{B}_4\text{C}/\text{Al}$-2% Mg system at the pressure higher than 600 kPa. In other words, these two systems will show the typical behaviors of "reaction-assisted infiltration" and simple pressure infiltration.
6. INTERFACE PHENOMENA

6.1. Gas-solid Reaction of Particulates

Several studies have been conducted on reactions of SiC with gaseous environments. However, information on the reaction of B\textsubscript{4}C with gases is scarce. Since the surface characteristics of solid phase play an important role in wetting, gas-solid reaction of ceramic phases with gases should be considered carefully.

The free energies of formation of SiC, B\textsubscript{4}C, and Al\textsubscript{4}C\textsubscript{3} are shown as a function of temperature in Fig. 6.1. They have relatively low values of free energy of formation when they are compared with the free energies of formation of other carbides at 298 °K, such as TiC, 180.6 kJ/mole, or ZrC, 181.8 kJ/mole [62]. In spite of disagreement between different researchers, as shown in Fig. 6.1, it can be estimated that the negative value of free energy of formation of SiC is the largest among the three and that of B\textsubscript{4}C is the smallest, making it the least stable.

Unlike their carbides, free energies of formation of oxides for Si, B, and Al have very large negative values. Thermodynamically, therefore, SiC and B\textsubscript{4}C are very prone to oxidation. The free energy of formation of oxides for Si, B, Al, Cu, Mg, and C are given in Fig. 6.2. All the data for this plot was obtained from the JANAF Thermochemical Tables [62].

The oxidation behavior of SiC have been studied extensively by Humphrey et al. [138] and Ervin [139]. Humphrey and his co-workers [134] listed 8 possible oxidation reactions of SiC along with the free energy of formation as:

\[
\text{SiC} + 2 \text{O}_2 = \text{SiO}_2 + \text{CO}_2(g) \tag{6.1 a}
\]

\[
\Delta G_{298 \text{ K}} = -1168.7 \text{ kJ}
\]

- 78 -
\[ \text{SiC} + \frac{3}{2} \text{O}_2 = \text{SiO}_2 + \text{CO(g)} \]  \hspace{2cm} (6.1 \text{~b}) \]
\[ \Delta G_{298 \text{~K}} = -911.3 \text{~kJ} \]

\[ \text{SiC} + \text{O}_2 = \text{SiO}_2 + \text{C} \]  \hspace{2cm} (6.1 \text{~c})
\[ \Delta G_{298 \text{~K}} = -774.0 \text{~kJ} \]

\[ \text{SiC} + \frac{3}{2} \text{O}_2 = \text{SiO(g)} + \text{CO}_2(g) \]  \hspace{2cm} (6.1 \text{~d})
\[ \Delta G_{298 \text{~K}} = -460.9 \text{~kJ} \]

\[ \text{SiC} + \text{O}_2 = \text{SiO(g)} + \text{CO(g)} \]  \hspace{2cm} (6.1 \text{~e})
\[ \Delta G_{298 \text{~K}} = -203.4 \text{~kJ} \]

\[ \text{SiC} + \frac{1}{2} \text{O}_2 = \text{SiO(g)} + \text{C} \]  \hspace{2cm} (6.1 \text{~f})
\[ \Delta G_{298 \text{~K}} = -66.1 \text{~kJ} \]

\[ \text{SiC} + \text{O}_2 = \text{Si} + \text{CO}_2(g) \]  \hspace{2cm} (6.1 \text{~g})
\[ \Delta G_{298 \text{~K}} = -342.8 \text{~kJ} \]

\[ \text{SiC} + \frac{1}{2} \text{O}_2 = \text{Si} + \text{CO(g)} \]  \hspace{2cm} (6.1 \text{~h})
\[ \Delta G_{298 \text{~K}} = -85.4 \text{~kJ} \]

All the above reaction has negative free energy of reaction, which means that they are thermodynamically possible. These reaction products can react further, and there are at least twenty more possible reactions. Therefore, it is expected that the reaction kinetics will be too complex to be determined accurately.

It is known that the oxidation behavior of SiC is quite similar as oxide film formation in metals [73,136]. When heated in air or oxygen atmosphere, a layer of silica is formed on the surface of SiC particulates. The silica film, then, retards further oxidation.

A strong oxygen peak, as shown in Fig. 4.5, confirms the formation of silicon oxides on the surface of SiC heated in an air atmosphere at 800 °C for 1 hr. The amounts of reaction products were too small to be analyzed by X-ray diffraction. The insulating nature of silica made the AES analysis impossible.
As in metals, the passive state of oxidation can be broken down below a critical oxygen partial pressure. In a vacuum or low oxygen partial pressure, the active oxidation can take place due to the formation of volatile SiO [73,138] as in eqs.(6.1 d, e, and f). Even after silica formation on the surface of SiC, it was reported that the breakdown of oxide film is possible by the reaction of [73]:

\[
\text{SiC}(s) + 2 \text{SiO}_2(s) = 3 \text{SiO(g)} + \text{CO(g)}
\]  

(6.2)

Compared with Fig. 4.3 for as-received SiC particulates, the AES result for SiC after infiltration experiment, as shown in Fig. 4.6, shows that the surface of SiC was cleaned by the reaction of gaseous SiO formation. The remaining oxygen in SiC, about 1 at.%, is believed to be related to the unreacted SiO\(_2\) remaining after production of SiC particulates. The experimental results as well as thermodynamic data show that the heating the SiC particulates in an inert or vacuum atmosphere can be used to clean the surface of SiC.

For boron oxides, three chemical forms are reported, i.e., B\(_2\)O, B\(_2\)O\(_2\), and B\(_2\)O\(_3\) [62]:

\[
4 \text{B(s)} + \text{O}_2(\text{g}) = 2 \text{B}_2\text{O(g)} \quad (6.3 \text{a})
\]
\[
\Delta G_{298 \text{K}} = 124 \text{ kJ}
\]

\[
2 \text{B(s)} + \text{O}_2(\text{g}) = \text{B}_2\text{O}_2(\text{g}) \quad (6.3 \text{b})
\]
\[
\Delta G_{298 \text{K}} = -463.9 \text{ kJ}
\]

\[
4/3 \text{B(s)} + \text{O}_2(\text{g}) = 2/3 \text{B}_2\text{O}_3(\text{g}) \quad (6.3 \text{c})
\]
\[
\Delta G_{298 \text{K}} = -548.7 \text{ kJ}
\]

\[
4/3 \text{B(s)} + \text{O}_2(\text{g}) = 2/3 \text{B}_2\text{O}_3(\text{l}) \quad (6.3 \text{d})
\]
\[
\Delta G_{298 \text{K}} = -786.9 \text{ kJ}
\]

\[
4/3 \text{B(s)} + \text{O}_2(\text{g}) = 2/3 \text{B}_2\text{O}_3(\text{s}) \quad (6.3 \text{e})
\]
\[
\Delta G_{298 \text{K}} = -794.6 \text{ kJ}
\]
The AES profile for B₄C particulates in the uninfiltreted region after infiltration experiment, as shown in Fig. 4.7, shows the higher concentration of oxygen than that of the particulates before infiltration test as in Fig. 4.4. B₄C particulates might pick up oxygen from the Ar atmosphere during the infiltration test. The main reason for higher oxygen concentration indicated in the AES results, however, is thought to be connected with the condensed B₂O₃ on the surface of B₄C particulates. Since the melting point of B₂O₃ is 450 °C [61], solid B₂O₃ on the surface of particulates in uninfiltreted region will be melt during the infiltration test and condensed on the surface of B₄C during cooling to room temperature. B₂O₃ is in part from the unreacted portion during the production, and in part from the reaction between loosely bonded oxygen on the surface of B₄C and B in B₄C.

Fig. 6.3 shows the AES profile of B₄C particulate which was cleaned in vacuum oven at 220 °C for 30 min. Comparing Fig. 6.3 with Fig. 4.4 for as-received B₄C particulate, it can be seen that oxygen concentration decreased from 5 - 17 at.% to 2 at.% This results confirms that oxygen is bonded so loosely on the surface of B₄C as to be removed in the vacuum oven at the relatively low temperature of 200 °C.

6.2. Liquid Metal:Gas Interface

Due to its extremely high affinity for oxygen, liquid aluminum has a layer of Al₂O₃ on the liquid:gas interface. For binary alloys of aluminum, alloying elements may adsorbed on the liquid:gas boundary, i.e., free surface. However only Mg is thought to form an oxide or a compound such as spinel, MgAl₂O₄. Other alloying elements used in the present experiments, Cu and Si, are not likely involved in oxidation or compound formation due to the greater stability of Al₂O₃.

Spinel formation is probable in Al-Mg alloys due both to the adsorption of Mg in the interface and to the large negative value of free energy change for the reaction:
\[ \text{Mg (in Al)} + 2 \text{Al(l)} + 2 \text{O}_2(\text{g}) = \text{MgAl}_2\text{O}_4(\text{s}) \quad (6.4) \]
\[ \Delta G_{1073 \text{ K}} = -1,852.0 \text{ kJ} [62]. \]

Delannay et al. [140] speculated that elements more reactive than Al may substitute for Al in the \( \text{Al}_2\text{O}_3 \), bringing about a weakening of the oxide film.

Miedema [141] introduced an expression for the ratio of the concentration of the solute atoms in the first atomic layer, \( C_1^A \), and that in the bulk, \( C_b^A \):

\[ \frac{C_1^A}{C_b^A} = \exp \left[ \frac{(\Delta H_{\text{sol}}^A - \Delta H_{\text{vap}}^A + \Delta H_{\text{vap}}^B)}{3 \text{ R T}} \right] \quad (6.5) \]

where, \( \Delta H_{\text{sol}}^A \) is the partial molar heat of solution of metal A in metal B, \( \Delta H_{\text{vap}}^A \) and \( \Delta H_{\text{vap}}^B \) are the heats of vaporization of the solute and solvent, respectively. Taking appropriate values for the heat of solution and heat of vaporization from various sources [49, 142, 143], the ratio of concentration of alloying element on the surface to that in bulk are calculated as; 0.142, 0.021 and 330 for Al-Cu, Al-Si, and Al-Mg alloys. Therefore, the free surface of Al-Mg alloy is expected to be covered with almost pure Mg, if the velocity of moving liquid front is reasonably low. Indeed, a pronounced enrichment of Mg at Al:SiC [101] and at Al:C interfaces [144] has been reported.

For the present experimental conditions, any other elements are probably not involved in any chemical reactions. However, providing sufficient time for reaction, following chemical reactions are possible thermodynamically:

\[ 2 \text{Si(in Al)} + 6 \text{Al} + 13/2 \text{O}_2(\text{g}) = 3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2(\text{s}) \quad (6.6) \]
\[ \Delta G_{1073 \text{ K}} = -5,450.3 \text{ kJ/mole} [62] \]
\[
\text{Si (in Al) } + 2 \text{Mg (in Al) } + 2 \text{ O}_2 \quad = \quad \text{Mg}_2\text{SiO}_4(s) \quad \quad (6.7)
\]
\[
\Delta G_{1073 \, K} \quad = \quad -2,124.7 \, \text{kJ/mole} \, [62]
\]
\[
\text{Cu (in Al) } + 2 \text{Al(l) } + 2 \text{ O}_2 \quad = \quad \text{CuAl}_2\text{O}_4 \quad \quad (6.8)
\]
\[
\Delta G_{910 \, K} \quad = \quad -1,467.0 \, \text{kJ/mole} \, [94].
\]

Considering the adsorption as well as thermodynamics and kinetics of chemical reactions, only \text{Al}_2\text{O}_3 and \text{MgO} formation may occur in the liquid metal:gas interface. These oxide layer, if they exist, should affect the threshold pressure for infiltration.

Cappleman et al. [97] calculated that monolayer oxide formation can keep pace with rapid infiltration, up to about 100 m/sec, even when the fibers are fine and densely packed.

Oxide formation on the particulates is shown schematically in Fig. 6.4. Their estimated velocity seems high because they did not count the effect of reaction kinetics. With such a high liquid front velocity, trapping of oxygen may occur first at the solid:liquid interface, later trapped oxygen will react with liquid aluminum alloys to form oxide.

However, the minimum amount of oxygen can be calculated with the assumption of oxide monolayer formation. Using the oxygen-oxygen distance of 2.50 Å at elevated temperatures [65], the area of hexagon, unit cell area of (0001) plane, of \text{Al}_2\text{O}_3 is 16.24 Å². Since there are 3 oxygen atoms on this hexagon, the density of oxygen is 1.85×10^{19}/m^2. Assuming the particle size is 10 μm and volume fraction of particulates is 0.52, the total area of particulates in the powder specimen is 0.18 m². Therefore the minimum concentration of oxygen to form a monolayer of \text{Al}_2\text{O}_3 is 3.33×10^{18} \text{ atoms/specimen}, i.e., 5.65×10^6 \text{ atoms/m}^3. Since the number of \text{Ar} atoms inside the specimen is 9.29×10^{24}/m^3 at 800 °C, 6×10^{-13} \text{ ppm of oxygen can make monolayer of oxide film on all the particulates. Considering the commercial purified-Ar has several ppm ox oxygen in it, oxide formation on the liquid front is unavoidable.}
Counting the oxide formation on the liquid front, especially during the incubation time, the contribution of the stress of breaking oxide film on the threshold pressure is quite probable. The magnitude of the stress required to break oxide film depends on the composition of the film as well as the thickness of the film. However, there may be a saturation point in the growth of oxide layer because the diffusion through the oxide layer is required for further oxide formation. If the solid:liquid unferfacial reaction reduces solid:liquid interfacial energy significantly, long holding times may be beneficial for wetting in spite of some amount of oxide formation on the liquid:gas interface.

6.3. Metal:Ceramic Interface

The ceramic/metal systems are much more stable chemically than metal/metal systems. Therefore, the reactivity at the metal:cereamic interface is quite low, generating only a small amount of reaction products. A number of studies [65,67,74,94-101,103,144-152] have been conducted to investigate the ceramic:Al-alloy interface phenomena. In most cases, the specimens were kept in liquid metal or heat-treated for times ranging from tens of min. to hundreds of hours to produce detectable amounts of reaction products.

Since relatively short periods of thermal exposure are provided, at most 10 min. in the melt, the present ceramic/metal systems did not show any strong evidence of interfacial reaction except dissolution in the case of SiC/Al-alloy systems. However, Auger analyses on the fracture surface show some indications of chemical reaction including carbide and oxide formation.

6.3.1. Dissolution of particulates

Due to high solubility of Si in Al, the dissolution of SiC particulates in the liquid
Al-alloys is to be expected. The microstructures of SiC specimens infiltrated with Al-alloys show clear evidence of particulate dissolution, in the appearance of Si phases in the matrix and rugged surfaces of particulates.

The results of Auger analyses performed on the fractured SiC/pure Al specimen are shown in Figs. 6.5 and 6.6, obtained by sputtering into the matrix and into the particulate respectively. Inside the matrix, the concentration of Al increased rapidly, finally becoming constant. The concentration of C changed in an exactly opposite behavior of Al, as expected. However, the concentration of Si did not change much with sputtering time. This tendency can be explained by fast diffusion of Si after dissolution of SiC particulates, and pile-up of C on the undissolved part of SiC particulates due to its extremely low solubility in Al. Considering the sputtering rate, Approximately 0.1 nm/sec, the interfacial region is about 300 Å thick.

The AES profile obtained by sputtering the fracture surface into particulate direction in SiC/Al-2% Mg system is shown in Fig. 6.7. Compared with the element profile for SiC/pure Al specimen, Fig. 6.6, slow decrease of Si can be observed for SiC/Al-2% Mg specimen. Examining the peak-to-peak AES data from each specimen, Figs. 6.8 and 6.9, the changes in absolute concentrations of Si and C are almost identical for both specimens except the irregular change in Si concentration in Al-2% Mg alloy. Careful examining the correlation between the change in concentrations of Si, Al, Mg provides an information that the discontinuities in Si profile occur at the point of Al- or Mg-rich region. Therefore, it can be postulated that the islands of Al₂O₃ or MgO blocked the diffusion of Si into the matrix. If each peak of Al and Mg is from their oxides, the size of oxide phase are about 100 - 200 Å. Probably the oxygen was provided from the unconverted SiO₂ inside the SiC particulates.

For B₄C/Al-alloy systems, less dissolution of particulates was observed due to almost zero solubility of B and C in Al. The AES element profile and peak-to-peak data obtained
by sputtering the fracture surface into matrix and particulate direction in B₄C/pure Al specimen are shown in Figs. 6.10 to 6.13.

6.3.2. Chemical reaction

The ternary phase diagrams are shown in Fig. 6.14 (a) and (b) for Al-Si-C and Al-B-C, respectively.

Since the section SiC-Al lies in the three phase field, L+Al₄C₃+SiC, the formation of Al₄C₃ after dissolution of SiC was assumed [73]:

$$3 \text{SiC}(s) + 4 \text{Al}(l) = \text{Al}_4\text{C}_3(s) + 3 \text{Si}(\text{in Al})$$ (6.9)

The thermodynamics and structure of Al₄C₃ have been studied extensively [100,106,146,151,153]. Isaikin and his co-workers [151] investigated the relationship between the Al₄C₃ formation and the activity of Si in Al by considering 4 separate reactions:

$$3 \text{SiC}(s) = 3 \text{Si}(s) + 3 \text{C}(s)$$ (6.10 a)

$$\Delta G_a = 53,304 - 4.02 T \ln T + 2.97 \times 10^{-3} T^2$$
$$+ 2.51 \times 10^4 T^{-1} + 17.07 T \ (J/mole)$$

$$3 \text{Si}(s) = 3 \text{Si}(l)$$ (6.10 b)

$$\Delta G_b = 46,024 - 27.2 T \ (J/mole)$$

$$3 \text{Si}(l) = 3 \text{Si}(\text{in Al})$$ (6.10 c)

$$\Delta G_c = RT \ln [a_{\text{si}}] \ (J/mole)$$

$$4 \text{Al}(l) + 3 \text{C}(s) = \text{Al}_4\text{C}_3$$ (6.10 d)

$$\Delta G_d = -184,096 + 53.12 T \ (J/mole)$$
Summing up the free energy changes for all 4 reactions gives:

\[ \Delta G_{Al_4C_3} = 113,888 - 12.05 T \ln T + 8.91 \times 10^{-3} T^2 + 21.51 T \]
\[ 7.53 \times 10^4 T^{-1} + 3 RT \ln [a_{si}] \] (J/mole) (6.11)

Eq. (6.11) indicates that the activity of Si, $a_{si}$, should be lower than 0.135 to form $Al_4C_3$ phase at 800 °C. In order to have free energy change as low as - 50 kJ/mole, the activity of Si should be 0.02. The relationship between the activity of Si and the free energy of formation of $Al_4C_3$ shows that $Al_4C_3$ formation is difficult at high Si concentrations.

Even though the dissolution of SiC was confirmed in various ways, no solid evidence of $Al_4C_3$ formation was found in the present experiments. This observation may be resulted from the extremely small size of $Al_4C_3$ particles due to short reaction time. However, the big Al peak in Fig. 6.8 may be from the $Al_4C_3$ Phase. If there is an $Al_4C_3$ cluster at that position, the size is estimated as 250 Å. No evidence of $Al_4C_3$ in conventional analytic tools, such as TEM or XRD, were reported by others [98,101] when they used similar experimental conditions to this investigation. Of course, large flakes of $Al_4C_3$ were found in the case of long thermal exposure [99,144].

In spite of various phases in the Al-B-C phase diagram and the results of investigations [75,154,155], none of these phases are expected in the $B_4C$/Al-alloy systems, partly due to the near-zero solubility of B and C in Al, and partly due to the short reaction time. As can be seen in AES profiles, Figs. 4.4 and 4.7, the surface of the $B_4C$ particulate is severely contaminated by oxygen. The oxygen on the surface of particulates is believed to exist as boron oxide, $B_2O_3$. Due to its low melting point, 450 °C, $B_2O_3$ will form a thin liquid layer on the particulate during preheating. The liquid layer of $B_2O_3$ is expected to react quickly with liquid aluminum alloys to form oxide compound, such as $B_2O_3\cdot Al_2O_3$ and $B_2O_3\cdot MgO$ during infiltration.

The AES peak-to-peak data, as shown in Figs. 6.12 and 6.13, indicate relatively high concentration of oxygen at the $B_4C$ particle:matrix interfacial region which is an evidence of
$\text{B}_2\text{O}_3\cdot\text{Al}_2\text{O}_3$ compound formation during the wetting process.

The different wetting processes for SiC and $\text{B}_4\text{C}$ particulates with liquid aluminum alloys are shown schematically in Fig. 6.15. For SiC/Al-alloy systems, no significant interfacial reactions are expected except small amounts of oxidation reactions at particle:metal interface. Dissolution of SiC particulate into matrix occurs after infiltration due to its slow reaction rate. Therefore, dissolution of particulates can only affect wetting when the time for solid:liquid contact is sufficiently long.

For $\text{B}_4\text{C}$/Al-alloy systems, however, liquid:liquid reaction between $\text{B}_2\text{O}_3$ and matrix are expected to proceed fast enough to affect wetting. This liquid:liquid reaction is the key reason for better wettability of $\text{B}_4\text{C}$ particulates than SiC particulates with liquid aluminum alloys.

The reactions mentioned in the liquid metal:gas reaction, section 6.2, can also occur at the ceramic:metal interface if sufficient reaction time is provided.
7. SUMMARY

7.1. Summary and Conclusion

A major effort was made to investigate wetting of ceramic particulates by liquid aluminum alloys. A technique was developed to measure the wettability of particulates with a non-wetting liquid, i.e., which has a wetting angle higher than 90°.

Two different particulates, SiC and B₄C, and 4 different alloys, pure Al, Al-Cu, Al-Si, and Al-Mg alloys were used for the study of particulate wetting with liquid metal. The particle sizes were 9.6 and 8.9 μm for SiC and B₄C, respectively. Binary aluminum alloys had two different nominal compositions, 2% and 4.5%.

Five major variables were tested to study wetting phenomena in ceramic/metal systems. Tested variables include holding time, melt temperature, solute concentration, gas atmosphere, and particulate. The metal-ceramic interfaces were analyzed with optical microscopy, SEM, EPMA, and Auger electron spectroscopy.

The results of this work are summarized in the following statements.

1. A tamping device was developed to make uniformly packed ceramic powder specimens.

2. A pressure chamber was made to conduct pressure infiltration tests.

3. Pressure infiltration tests were conducted to measure the threshold pressure for infiltration mostly in Ar atmospheres under isothermal conditions.

4. The threshold pressure for infiltration was used as a measure of wettability. Wetting angles obtained from the threshold pressure showed good correlation with those
measured by conventional techniques.

5. The threshold pressure decreased with time for all the ceramic/metal system, generally, reaching near-equilibrium value in 5 min. The time dependence of threshold pressure was in good agreement with an exponential function of time:

$$P_{th}(t) = P_{th}(eq) [1 + c \cdot \exp (-d \cdot t)].$$

The time dependence of threshold pressure was explained by the decrease in solid-liquid interfacial energy due to metal:ceramic interfacial reactions.

6. The threshold pressure decreased with temperature, probably due to different kinetics and degrees of reactions on the solid surface, liquid surface, and solid-liquid interface at different temperature.

7. Generally, more reactive alloying elements were more effective in improving wettability. The good correlation was found between the alloying effect in the threshold pressure and the free energy of formation of oxide phase of alloying elements. Mg alloying decreased threshold pressure in both particulate systems significantly, and, as expected, Cu and Si had little effect much on the wettability of ceramic/Al-alloy systems.

8. $B_4C$ particulates showed lower threshold pressure than $SiC$ particulates. The better wettability of $B_4C$ also can be explained by liquid ($B_2O_3$):liquid (Al) reaction.

9. Microstructure of infiltrated $SiC$ specimens showed $Si$ phase as a result of dissolution of $SiC$ into matrix, the degree of dissolution varied with time and temperature.

10. Infiltrated $B_4C$ specimens did not show any evidence of dissolution of particulates.
11. Fracture morphologies indicated that failure occurred in a more or less brittle manner in infiltrated SiC specimens. However, fracture surfaces of infiltrated B₄C specimens showed small dimples which are indication of plastic deformation. Generally, fracture occurred through the metal:cubic interfacial region, especially though the carbon-rich layer.

12. AES element profiles showed fast diffusion of Si, and pile-up of C at the ceramic:metal boundary.

13. The major interfacial reactions affecting wettability expected to be dissolution of particulates and liquid:liquid reaction for SiC and B₄C particulates systems, respectively.

14. In air atmospheres, the threshold pressure usually increased markedly as a result of thick oxide layer formation on the liquid front. The decrease of threshold pressure in B₄C/Al-Mg systems in air atmosphere is connected with the formation of thicker liquid layer of B₂O₃ on the particulates.

7.2. Suggestions for Further Work

Since the present work just initiated the experimental study on the particulate wetting, many questions remain unanswered. Therefore, each section of this thesis could be extended to better understanding on wetting in ceramic:liquid aluminum-alloy systems. The following subjects should have high priority:
1. Test with other ceramic particulates which have different bond structures, such as transition metal carbides (TiC, ZrC, etc.), oxides (Al$_2$O$_3$, ZrO$_2$, etc.), or borides (TiB$_2$, etc.).

2. Test with particulates with different pure metals, such as Mg, Zn, and Cu.

3. Development of model for metal-ceramic interaction.

4. Test with different surface chemistry of particulates.

5. Test with different size of particulates.
Fig. 2.1. Schematic diagram of a liquid drop on the solid surface showing the interfacial forces and wetting angle for (a) wetting and (b) non-wetting systems, respectively.
Fig. 2.2. Equilibrium at (a) wetting and (b) non-wetting capillary systems.
Fig. 2.3. Three fundamental types of wetting: (a) adhesional wetting, (b) spreading wetting, and (c) immersional wetting.
Fig. 2.4. Parameters used in the calculation of the surface energy of liquid.
Fig. 2.5. Surface energy and dihedral angles in solid:liquid:vapor equilibrium.
Fig. 2.6.  Free energy vs. composition diagram for the solid and liquid pseudo-binary system.
Fig. 2.7. Wetting angle vs. temperature for Al₂O₃/Al system [71].
Fig. 3.1. SEM photographs of (a) SiC and (b) B₄C particulates used for the present study.
Fig. 3.2. Size distribution of SiC particulates.

Average size = 9.63 μm
Average size = 8.89 μm

Size distribution of B₄C particulates.

Fig. 3.3.
Fig. 3.4. Sketch of tamping device.
Fig. 3.5. SEM photographs of (a) packed SiC particulates and (b) Saffil paper used as filter.
Fig. 3.6. Sketch of the pressure chamber used for pressure infiltration.
Fig. 3.7. Array of equipments in (a) heating system and (b) pressure system.
Fig. 3.8.  Sequence of infiltration of liquid metal through powder specimen under pressure.
Fig. 4.1. AES spectrum taken from the as-received SiC particulates.
Fig. 4.2. AES spectrum taken from the as-received $B_4C$ particulates.
Fig. 4.3. AES element profile as a function of sputtering time for as-received SiC particle.
Fig. 4.4. AES element profile as a function of sputtering time for as-received $B_4C$ particle.
Fig. 4.5. AES spectrum obtained from the oxidized SiC particulate.
Fig. 4.6. AES element profile for uninfilttrated SiC particulate after wetting experiment.
Fig. 4.8. Microstructure of Al-2% Cu alloy solidified inside the quartz tube after pressure infiltration.

Fig. 4.9. Microstructure of Al-2% Si alloy solidified inside the quartz tube after infiltration test.
Fig. 4.10. Microstructure of Al-2% Mg alloy solidified inside the quartz tube after infiltration test.
Fig. 4.12. Al-Si binary phase diagram [110].
Fig. 4.13. Al-Mg binary phase diagram [110].
Fig. 4.14. Microstructure of SiC powder specimen infiltrated with Al-2% Cu at (a) matrix:Saffil paper boundary and (b) Saffil paper:powder compact boundary.
Fig. 4.15. Typical microstructure of SiC/pure Al system infiltrated at 800 °C.

Fig. 4.16. Typical microstructure of SiC/Al-2% Cu system infiltrated at 800 °C.
Fig. 4.17. Typical microstructure of SiC/Al-2% Si system infiltrated at 800 °C.

Fig. 4.18. Typical microstructure of SiC/Al-2% Mg system infiltrated at 800 °C.
Fig. 4.19. SEM micrographs of deep-etched SiC/pure Al system infiltrated at 800°C.
Fig. 4.20. Microstructure of SiC/Al-2% Si system.
(a) At the top, and (b) at the bottom portion of the specimen infiltrated at 800 °C.
Fig. 4.21. Microstructure of SiC/pure Al system infiltrated (a) at 700 °C, and (b) at 900 °C.
Fig. 4.22. Typical microstructure of $\text{B}_4\text{C}/\text{pure Al}$ system infiltrated at 800 °C.

Fig. 4.23. Typical microstructure of $\text{B}_4\text{C}/\text{Al-2\% Cu}$ system infiltrated at 800 °C.
Fig. 4.24. Typical microstructure of $\text{B}_4\text{C}/\text{Al-2\% Si}$ system infiltrated at 800 °C.

Fig. 4.25. Typical microstructure of $\text{B}_4\text{C}/\text{Al-2\% Mg}$ system infiltrated at 800 °C.
Fig. 4.26.  Al-B binary phase diagram.
Fig. 4.27. SEM photograph of deep-etched $\text{B}_4\text{C}/\text{Al-2\% Mg}$ specimen infiltrated at 800 °C.
Fig. 4.28. EDX peaks obtained (a) from the matrix and (b) from the second phase shown in Fig. 4.34 (b).
Fig. 4.29. Fracture surface of SiC powder specimen infiltrated with pure Al with 724 kPa at 800 °C.

Fig. 4.30. Fracture surface of SiC powder specimen infiltrated with Al-2% Cu alloy with 827 kPa at 800 °C.
Fig. 4.31. Fracture surface of SiC powder specimen infiltrated with Al-2% Si alloy with 765 kPa at 800 °C.

Fig. 4.32. Fracture surface of SiC powder specimen infiltrated with Al-2% Mg alloy with 621 kPa at 800 °C.
Fig. 4.33. Fracture surface of $\text{B}_4\text{C}$ powder specimen infiltrated with pure Al alloy with 288 kPa at 800 °C.

Fig. 4.34. Fracture surface of $\text{B}_4\text{C}$ powder specimen infiltrated with Al-2% Cu alloy with 758 kPa at 800 °C.
Fig. 4.35. Fracture surface of $B_4C$ powder specimen infiltrated with Al-2% Si alloy with 731 kPa at 800 °C.

Fig. 4.36. Fracture surface of $B_4C$ powder specimen infiltrated with Al-2% Mg alloy with 724 kPa at 800 °C.
Fig. 4.37. AES spectrum obtained from the surface of fractured B₄C/Al-2% Mg specimen.
Fig. 5.1. Infiltration of liquid between particulates. Top and side views for (a) wetting system, and (b) non-wetting system.
Fig. 5.2. Sketch of liquid front valancing with surface energy and wetting angle at (a) initial, (b) after time (t).
Fig. 5.3. Schematic dependence of the threshold pressure on time. Infiltration begins at time $t_0$. 

Capillary pressure $p$, Time $t$, Infiltration $p_{th}(t)$.
Fig. 5.4. Effect of shape factor on the wetting angle for SiC/Al system.
Fig. 5.5. Effect of shape factor on the wetting angle for $\text{B}_4\text{C}/\text{Al}$ system.
Fig. 5.6. Change in wetting angle with time for SiC/Al-alloy system at 800 °C.
Fig. 5.7. Change in wetting angle with time for $\text{B}_4\text{C}/\text{Al}$-alloy system at 800 °C.
Fig. 5.8. Change in wetting angle with temperature for SiC/Al-alloy system.
Fig. 5.9. Change in wetting angle with temperature for B₄C/Al-alloy system.
Fig. 5.10. Change in wetting angle with alloying element in SiC/Al-alloy system at 800 °C.
Fig. 5.11. Change in wetting angle with alloying element in $\text{B}_4\text{C}/\text{Al}$-alloy system at $800\, ^\circ\text{C}$. 
Fig. 5.12. Change in threshold pressure with time for SiC/Al-alloy systems.
Fig. 5.13. Change in threshold pressure with time for B$_4$C/Al-alloy systems.
Fig. 5.14. Comparison of time dependence of calculated and experimental values of threshold pressure for SiC and $B_4C$ specimen infiltrated with Al-2% Si alloy at 800 °C.
Fig. 5.15. Change in threshold pressure with temperature for SiC/Al-alloy systems.
Fig. 5.16. Change in threshold pressure with temperature for $B_4C/\text{Al}$-alloy systems.
Fig. 5.17. The relationship between $\cos \theta$ and temperature for SiC/Al-alloy systems.
Fig. 5.18. The relationship between $\cos \theta$ and temperature for $\text{B}_4\text{C}/\text{Al}$-alloy systems.
Fig. 5.19. Plot of \( \log P_{th} \text{ (kPa)} \) vs. \( 1/T \text{ (K)} \) for SiC/Al-alloy systems.
Fig. 5.20. Plot of $\log P_{th}$ (kPa) vs. $1/T$ (K) for $\text{B}_4\text{C}/\text{Al}$-alloy systems.
SiC/Al-alloy, 800°C, 5 min.

Alloying element, %

Threshold pressure, kPa

Al - Cu
Al - Si
Al - Mg

Fig. 5.21. Change in threshold pressure with alloying element for SiC/Al-alloy system at 800°C.
Fig. 5.22. Change in threshold pressure with alloying element for B₄C/Al-alloy system at 800 °C.
Fig. 5.23. Relationship between the threshold pressure and the free energy of formation of oxide of each alloying element in SiC/Al-alloy system.
Fig. 5.24. Relationship between the threshold pressure and the free energy of formation of oxide of each alloying element in $\text{B}_4\text{C}/\text{Al}$-alloy system.
Fig. 5.25. Infiltration behavior in Ar and in air atmosphere for $\text{B}_4\text{C}/\text{Al}-4.5\% \text{ Cu}$ system at 800 °C.
Infiltration behavior in Ar and in air atmosphere for SiC/Al-4.5% Cu system at 800 °C.

Fig. 5.26.
Fig. 5.27. Infiltration behavior in Ar and in air atmosphere for $B_4C/Al-2\%$ Mg system at 800 °C.
Fig. 5.28. Variation of infiltration distance as a function of applied pressure for untreated SiC and oxidized SiC powder specimen tested with Al-2% Mg alloy at 800 °C.
Fig. 5.29. Microstructure of oxidized-SiC powder specimen infiltrated with Al-2% Mg alloy at 800 °C.
SiC/Al-2% Cu, 900 °C, 5 min.

Fig. 5.30. Variation of the infiltration distance as a function of the applied pressure for SiC/Al-2% Cu system at 900 °C.
Fig. 5.31. Variation of the infiltration distance with the applied pressure for SiC and B₄C powder specimen infiltrated with Al-2% Mg alloy at 800 °C.
Fig. 5.32. Variation of the infiltration distance as a function of the applied pressure for SiC/Al-2% Cu system at different melt temperatures.
Fig. 5.33. Variation of the infiltration distance as a function of the applied pressure for SiC/Al-2% Cu system at different holding times at 800 °C.
Fig. 5.34. Variation of the infiltration distance as a function of the applied pressure for B₄C/Al-2% Si system at different holding times at 800 °C.
Fig. 5.35. Infiltration distance as a function of time for B\textsubscript{4}C/Al-2\% Si system at 800 °C.
B4C/Al-2% Si, 800 C, 724 kPa

Fig. 5.36. Comparison of the time dependence of calculated and experimental values of infiltration distance for B4C/Al-2% Si system infiltrated with 724 kPa at 800 °C.
Fig. 5.37. Comparison of pressure dependence of calculated and experimental values of infiltration distance for B₄C/Al-2% Si system infiltrated at 800 °C for 5 min.
Fig. 5.38. Sketch of changes in wetting angle with velocity of moving liquid.
Fig. 5.39. Contribution of reaction-assisted infiltration to the total infiltration distance.
Fig. 5.40. Infiltration distance vs. applied pressure for B₄C/Al-alloy systems at 800 °C for 5 min.
Fig. 6.1. Free energy change of carbides as a function of temperature.
Fig. 6.2. Free energy change of oxides as a function of temperature.
Fig. 6.3. AES element profile of $B_4C$ particulate after vacuum cleaning at 220°C for 30 min.
Fig. 6.4. Sketch of oxide layer formation on the particulates during the infiltration.
Fig. 6.5. AES element profile for matrix-side from the fracture surface of SiC/pure Al specimen.
Fig. 6.6. AES element profile for particle-side from the fracture surface of SiC/pure Al specimen.
Fig. 6.7. AES element profile for particle-side from the fracture surface of SiC/Al-2% Mg specimen.
Fig. 6.8. AES peak-to-peak profile for particle-side from the fracture surface of SiC/pure Al specimen.
Fig. 6.9. AES peak-to-peak profile for particle-side from the fracture surface of SiC/Al-2% Mg specimen.
Fig. 6.10. AES element profile for matrix-side from the fracture surface of $B_4C$/pure Al specimen.
Fig. 6.11. AES element profile for particle-side from the fracture surface of $B_4C$/pure Al specimen.
Fig. 6.12. AES peak-to-peak profile for matrix-side from the fracture surface of $\text{B}_4\text{C}$/pure Al specimen.
Fig. 6.13. AES peak-to-peak profile for particle-side from the fracture surface of $B_4C$/pure Al specimen.
Fig. 6.14.  (a) Al-Si-C phase diagram at 800 °C [73].  
(b) Al-B-C phase diagram at 900 °C [75].
Fig. 6.15. Schematic description of wetting processes for (a) SiC and (b) B$_4$C particulates with liquid aluminum alloys.
Table 2.1. Surface energy of liquid aluminum.

<table>
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<tr>
<th>Temp.(°C)</th>
<th>$\gamma_V$(mJ/m²)</th>
<th>d$\gamma$/dT</th>
<th>Range (°C)</th>
<th>Atmosphere(Pa)</th>
<th>Method</th>
<th>Ref.</th>
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</thead>
<tbody>
<tr>
<td>660</td>
<td>825</td>
<td>-0.05</td>
<td>660 - 850</td>
<td>Ar</td>
<td>MBP*</td>
<td>23</td>
</tr>
<tr>
<td>660</td>
<td>760</td>
<td>-0.202</td>
<td>707 - 817</td>
<td>6.7x10^{-5}</td>
<td>SD**</td>
<td>15</td>
</tr>
<tr>
<td>660</td>
<td>855</td>
<td>-0.104</td>
<td>700 - 910</td>
<td>Ar</td>
<td>MBP</td>
<td>24</td>
</tr>
<tr>
<td>660</td>
<td>870</td>
<td>-0.195</td>
<td>660 - 1020</td>
<td>1.3x10^{-4}</td>
<td>SD</td>
<td>25</td>
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<td>690 - 915</td>
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<tr>
<td>660</td>
<td>865</td>
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<td>694 - 904</td>
<td>2.7x10^{-4}</td>
<td>SD</td>
<td>26</td>
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<td>1100</td>
<td>-</td>
<td>-</td>
<td>Ar</td>
<td>MBP</td>
<td>27</td>
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</table>

* Maximum bubble pressure method

** Sessile drop method
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<th>Liquid</th>
<th>Vacuum (Pa)</th>
<th>Temp.(°C)</th>
<th>Angle (θ)</th>
<th>Ref.</th>
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<td>139</td>
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<td>870</td>
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<td></td>
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<td>Al₂O₃</td>
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<td>950</td>
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<td>N.A.</td>
<td>900</td>
<td>80</td>
<td>69</td>
</tr>
<tr>
<td>SiO₂</td>
<td>pure Al</td>
<td>N.A.</td>
<td>700</td>
<td>80</td>
<td>69</td>
</tr>
<tr>
<td></td>
<td>pure Al</td>
<td>N.A.</td>
<td>800</td>
<td>75</td>
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<tr>
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<td>N.A.</td>
<td>900</td>
<td>72</td>
<td>69</td>
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<tr>
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<td>4x10^{-3}</td>
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<tr>
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<td>4x10^{-3}</td>
<td>800</td>
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<td>4x10^{-3}</td>
<td>900</td>
<td>92</td>
<td>72</td>
</tr>
<tr>
<td>SiC</td>
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<td>2.7x10^{-4}</td>
<td>710</td>
<td>155</td>
<td>68</td>
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<td>pure Al</td>
<td>2.7x10^{-4}</td>
<td>870</td>
<td>150</td>
<td>68</td>
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<tr>
<td></td>
<td>pure Al</td>
<td>2.7x10^{-4}</td>
<td>950</td>
<td>102</td>
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<td></td>
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<td>2.7x10^{-4}</td>
<td>900</td>
<td>150</td>
<td>73</td>
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<tr>
<td>B₄C</td>
<td>Al-1.39 Mg</td>
<td>1.3x10^{-3}</td>
<td>840</td>
<td>155</td>
<td>74</td>
</tr>
<tr>
<td></td>
<td>Al-1.62 Cu</td>
<td>1.3x10^{-3}</td>
<td>840</td>
<td>148</td>
<td>74</td>
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<td>Al-2.58 Si</td>
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<td>840</td>
<td>138</td>
<td>74</td>
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<td>pure Al</td>
<td>6.5x10^{-4}</td>
<td>900</td>
<td>135</td>
<td>75</td>
</tr>
<tr>
<td>TiC</td>
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<td>2.7x10^{-5}</td>
<td>1000</td>
<td>95</td>
<td>15</td>
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<tr>
<td></td>
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<td>6.5x10^{-2}</td>
<td>1000</td>
<td>117</td>
<td>76</td>
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<tr>
<td>TiB₂</td>
<td>pure Al</td>
<td>2.7x10^{-5}</td>
<td>1000</td>
<td>115</td>
<td>15</td>
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<tr>
<td></td>
<td>pure Al</td>
<td>6.5x10^{-2}</td>
<td>1000</td>
<td>114</td>
<td>76</td>
</tr>
</tbody>
</table>
Table 3.1. Chemical analysis of particulates *

(a) SiC

<table>
<thead>
<tr>
<th>Element</th>
<th>%</th>
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</thead>
<tbody>
<tr>
<td>SiC</td>
<td>97.87</td>
</tr>
<tr>
<td>Free SiO₂</td>
<td>0.38</td>
</tr>
<tr>
<td>Free Si</td>
<td>0.37</td>
</tr>
<tr>
<td>Free C</td>
<td>0.31</td>
</tr>
<tr>
<td>Total C</td>
<td>29.63</td>
</tr>
<tr>
<td>Al</td>
<td>0.13</td>
</tr>
<tr>
<td>Fe</td>
<td>0.08</td>
</tr>
<tr>
<td>Mg</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Cu</td>
<td>0.01</td>
</tr>
<tr>
<td>B</td>
<td>&lt;10 ppm</td>
</tr>
</tbody>
</table>

(b) B₄C

<table>
<thead>
<tr>
<th>Element</th>
<th>%</th>
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</thead>
<tbody>
<tr>
<td>Total B</td>
<td>77.0</td>
</tr>
<tr>
<td>Total C</td>
<td>19.85</td>
</tr>
<tr>
<td>B₂O₃</td>
<td>0.13</td>
</tr>
<tr>
<td>Fe</td>
<td>0.36</td>
</tr>
</tbody>
</table>

* Analyzed by Norton Company
Table 3.2. Chemical analysis of alloys

(a) Al-4.5% Cu *

<table>
<thead>
<tr>
<th>Element</th>
<th>Cu</th>
<th>Si</th>
<th>Fe</th>
<th>Zn</th>
<th>Mn</th>
<th>Ni</th>
<th>Mg</th>
<th>Cr</th>
<th>Ti</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>%</td>
<td>4.61</td>
<td>0.01</td>
<td>0.014</td>
<td>0.006</td>
<td>0.002</td>
<td>0.003</td>
<td>&lt;0.002</td>
<td>&lt;0.002</td>
<td>&lt;0.002</td>
<td>bal</td>
</tr>
</tbody>
</table>

(b) Al-2.3% Mg *

<table>
<thead>
<tr>
<th>Element</th>
<th>Mg</th>
<th>Si</th>
<th>Fe</th>
<th>Zn</th>
<th>Mn</th>
<th>Ni</th>
<th>Cu</th>
<th>Cr</th>
<th>Ti</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>%</td>
<td>2.31</td>
<td>0.012</td>
<td>0.008</td>
<td>0.005</td>
<td>0.002</td>
<td>&lt;0.002</td>
<td>&lt;0.002</td>
<td>&lt;0.002</td>
<td>&lt;0.002</td>
<td>bal</td>
</tr>
</tbody>
</table>

(c) Al-2% Cu **

<table>
<thead>
<tr>
<th>Element</th>
<th>Cu</th>
<th>Al</th>
<th>Trace</th>
</tr>
</thead>
<tbody>
<tr>
<td>%</td>
<td>2.21</td>
<td>97.60</td>
<td>0.19</td>
</tr>
</tbody>
</table>

(d) Al-4.5% Mg **

<table>
<thead>
<tr>
<th>Element</th>
<th>Mg</th>
<th>Al</th>
<th>Trace</th>
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</thead>
<tbody>
<tr>
<td>%</td>
<td>4.71</td>
<td>95.27</td>
<td>0.02</td>
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</tbody>
</table>

(e) Al-2% Si **

<table>
<thead>
<tr>
<th>Element</th>
<th>Si</th>
<th>Al</th>
<th>Trace</th>
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</thead>
<tbody>
<tr>
<td>%</td>
<td>2.37</td>
<td>97.57</td>
<td>0.06</td>
</tr>
</tbody>
</table>

(f) Al-4.5% Si **

<table>
<thead>
<tr>
<th>Element</th>
<th>Si</th>
<th>Al</th>
<th>Trace</th>
</tr>
</thead>
<tbody>
<tr>
<td>%</td>
<td>4.93</td>
<td>94.99</td>
<td>0.08</td>
</tr>
</tbody>
</table>

* Analyzed by Reinolds Metals Company

** Analyzed by Luvak Inc., in Boylston, Massachusetts
Table 4.1. Infiltrated specimens* used for metallography, fractography, and AES analysis.

<table>
<thead>
<tr>
<th>Particulate</th>
<th>Matrix</th>
<th>Temperature (°C)</th>
<th>Pressure (kPa)</th>
<th>Infiltration (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiC</td>
<td>Pure Al</td>
<td>700</td>
<td>930</td>
<td>3.0</td>
</tr>
<tr>
<td></td>
<td>Pure Al</td>
<td>800</td>
<td>724</td>
<td>1.9</td>
</tr>
<tr>
<td></td>
<td>Pure Al</td>
<td>900</td>
<td>634</td>
<td>1.8</td>
</tr>
<tr>
<td></td>
<td>Al-2% Cu</td>
<td>800</td>
<td>827</td>
<td>3.0</td>
</tr>
<tr>
<td></td>
<td>Al-2% Si</td>
<td>800</td>
<td>765</td>
<td>3.0</td>
</tr>
<tr>
<td></td>
<td>Al-2% Mg</td>
<td>800</td>
<td>621</td>
<td>1.1</td>
</tr>
<tr>
<td>B₄C</td>
<td>Pure Al</td>
<td>800</td>
<td>758</td>
<td>2.6</td>
</tr>
<tr>
<td></td>
<td>Al-2% Cu</td>
<td>800</td>
<td>758</td>
<td>2.8</td>
</tr>
<tr>
<td></td>
<td>Al-2% Si</td>
<td>800</td>
<td>731</td>
<td>2.8</td>
</tr>
<tr>
<td></td>
<td>Al-2% Mg</td>
<td>800</td>
<td>724</td>
<td>2.3</td>
</tr>
</tbody>
</table>

* Infiltrated for 5 min.
Table 5.1. Values of the coefficients $c$ and $d$ in eq. (5.7) for SiC and $B_4C$ particulates systems at 800 °C.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>SiC</th>
<th></th>
<th>B$_4$C</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$c$</td>
<td>$d$</td>
<td>$c$</td>
<td>$d$</td>
</tr>
<tr>
<td>Pure Al</td>
<td>79.886x10^{-2}</td>
<td>16.829x10^{-3}</td>
<td>-</td>
<td>-</td>
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<tr>
<td>Al-2% Cu</td>
<td>-</td>
<td>-</td>
<td>61.582x10^{-2}</td>
<td>13.798x10^{-3}</td>
</tr>
<tr>
<td>Al-2% Si</td>
<td>2.997x10^{-2}</td>
<td>3.851x10^{-3}</td>
<td>18.550x10^{-2}</td>
<td>7.338x10^{-3}</td>
</tr>
<tr>
<td>Al-2% Mg</td>
<td>6.218x10^{-2}</td>
<td>13.569x10^{-3}</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Table 5.2. Threshold pressure, surface energy, and wetting angle for SiC/Al-alloy systems.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Temp.(°C)</th>
<th>$P_{th}(kPa)^{a}$</th>
<th>$\gamma_{lv}(mJ/m^2)^{b}$</th>
<th>$\theta^{c}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure Al</td>
<td>700</td>
<td>917.0</td>
<td>851</td>
<td>106.3</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>686.1</td>
<td>840</td>
<td>102.3</td>
</tr>
<tr>
<td></td>
<td>900</td>
<td>620.6</td>
<td>830</td>
<td>101.2</td>
</tr>
<tr>
<td>Al-2% Cu</td>
<td>700</td>
<td>934.3</td>
<td>843</td>
<td>106.7</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>758.5</td>
<td>832</td>
<td>103.7</td>
</tr>
<tr>
<td></td>
<td>900</td>
<td>558.5</td>
<td>822</td>
<td>100.2</td>
</tr>
<tr>
<td>Al-4.5% Cu</td>
<td>800</td>
<td>717.1</td>
<td>831</td>
<td>103.0</td>
</tr>
<tr>
<td></td>
<td>700</td>
<td>882.6</td>
<td>847</td>
<td>105.7</td>
</tr>
<tr>
<td>Al-2% Si</td>
<td>800</td>
<td>737.8</td>
<td>836</td>
<td>103.6</td>
</tr>
<tr>
<td></td>
<td>900</td>
<td>503.3</td>
<td>826</td>
<td>99.1</td>
</tr>
<tr>
<td>Al-4.5% Si</td>
<td>800</td>
<td>730.9</td>
<td>831</td>
<td>103.2</td>
</tr>
<tr>
<td></td>
<td>700</td>
<td>744.7</td>
<td>767</td>
<td>104.6</td>
</tr>
<tr>
<td>Al-2% Mg</td>
<td>800</td>
<td>565.4</td>
<td>757</td>
<td>101.2</td>
</tr>
<tr>
<td></td>
<td>900</td>
<td>462.0</td>
<td>747</td>
<td>99.3</td>
</tr>
<tr>
<td>Al-4.5% Mg</td>
<td>800</td>
<td>524.0</td>
<td>652</td>
<td>102.1</td>
</tr>
</tbody>
</table>

a) present experimental result
b) from ref. [24]
c) calculated from $P_{th}(\lambda = 8.5/6)$
Table 5.3. Threshold pressure, surface energy, and wetting angle for B₄C/Al-alloy systems.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Temp.(°C)</th>
<th>$P_{th}$(kPa)(^a)</th>
<th>$\gamma_{lv}$(mJ/m²)(^b)</th>
<th>$\theta$(^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure Al</td>
<td>700</td>
<td>799.8</td>
<td>851</td>
<td>103.0</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>751.6</td>
<td>840</td>
<td>102.4</td>
</tr>
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<td>900</td>
<td>572.3</td>
<td>830</td>
<td>99.5</td>
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<tr>
<td>Al-2% Cu</td>
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<td>786.0</td>
<td>843</td>
<td>102.9</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>710.2</td>
<td>832</td>
<td>101.8</td>
</tr>
<tr>
<td></td>
<td>900</td>
<td>586.1</td>
<td>822</td>
<td>99.9</td>
</tr>
<tr>
<td>Al-4.5% Cu</td>
<td>800</td>
<td>668.8</td>
<td>831</td>
<td>101.1</td>
</tr>
<tr>
<td>Al-2% Si</td>
<td>700</td>
<td>765.3</td>
<td>847</td>
<td>102.0</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>686.1</td>
<td>836</td>
<td>101.4</td>
</tr>
<tr>
<td></td>
<td>900</td>
<td>468.9</td>
<td>826</td>
<td>97.8</td>
</tr>
<tr>
<td>Al-4.5% Si</td>
<td>800</td>
<td>627.4</td>
<td>831</td>
<td>100.4</td>
</tr>
<tr>
<td>Al-2% Mg</td>
<td>700</td>
<td>675.7</td>
<td>767</td>
<td>102.2</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>241.3</td>
<td>757</td>
<td>94.4</td>
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<tr>
<td></td>
<td>900</td>
<td>137.9</td>
<td>747</td>
<td>92.5</td>
</tr>
<tr>
<td>Al-4.5% Mg</td>
<td>800</td>
<td>69.0</td>
<td>652</td>
<td>91.5</td>
</tr>
</tbody>
</table>

a) present experimental result  
b) from ref.[24]  
c) calculated from $P_{th}$ ($\lambda = 8.5/6$)
Table 5.4. Threshold pressure for SiC and B\textsubscript{4}C particulates in Ar and in air atmosphere at 800 °C. \( (P_{th} \text{ in kPa}) \)

<table>
<thead>
<tr>
<th>Alloy</th>
<th>SiC in Ar</th>
<th>SiC in Air</th>
<th>B\textsubscript{4}C in Ar</th>
<th>B\textsubscript{4}C in Air</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure Al</td>
<td>686.1</td>
<td>710.2 (S)*</td>
<td>751.6</td>
<td>724.0 (S)</td>
</tr>
<tr>
<td>Al-2% Cu</td>
<td>758.5</td>
<td>744.7 (S)</td>
<td>710.2</td>
<td>717.1 (L)</td>
</tr>
<tr>
<td>Al-2% Si</td>
<td>737.8</td>
<td>779.1 (L)+</td>
<td>686.1</td>
<td>737.8 (L)</td>
</tr>
<tr>
<td>Al-2% Mg</td>
<td>565.4</td>
<td>779.1 (S)</td>
<td>241.3</td>
<td>69.0 (E)</td>
</tr>
<tr>
<td>Al-4.5% Cu</td>
<td>717.1</td>
<td>806.7 (L)</td>
<td>668.8</td>
<td>724.0 (S)</td>
</tr>
<tr>
<td>Al-4.5% Si</td>
<td>730.9</td>
<td>730.9 (L)</td>
<td>627.4</td>
<td>655.0 (L)</td>
</tr>
<tr>
<td>Al-4.5% Mg</td>
<td>524.0</td>
<td>730.9 (E)#</td>
<td>69.0</td>
<td>69.0 (E)</td>
</tr>
</tbody>
</table>

* Step behavior

+ Linear behavior

# Exponential behavior
Table 5.5. Threshold pressure and slope of infiltration distance vs. pressure for SiC/Al alloy and B₄C/Al alloy systems.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Temp.(°C)</th>
<th>Time(min)</th>
<th>SiC</th>
<th>B₄C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Pₓh(kPa)</td>
<td>Slope(cm/kPa)</td>
</tr>
<tr>
<td>Pure Al</td>
<td>700</td>
<td>5</td>
<td>917.0</td>
<td>&gt;0.435</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>2</td>
<td>755.0</td>
<td>0.139</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>5</td>
<td>686.1</td>
<td>0.139</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>10</td>
<td>682.6</td>
<td>0.073</td>
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<tr>
<td></td>
<td>900</td>
<td>5</td>
<td>620.6</td>
<td>0.087</td>
</tr>
<tr>
<td>Al-2% Cu</td>
<td>700</td>
<td>5</td>
<td>934.3</td>
<td>&gt;0.435</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>2</td>
<td>813.6</td>
<td>0.140</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>5</td>
<td>758.5</td>
<td>0.044</td>
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<tr>
<td></td>
<td>800</td>
<td>10</td>
<td>703.3</td>
<td>0.064</td>
</tr>
<tr>
<td></td>
<td>900</td>
<td>5</td>
<td>558.5</td>
<td>0.030</td>
</tr>
<tr>
<td>Al-4.5% Cu</td>
<td>800</td>
<td>5</td>
<td>717.1</td>
<td>0.045</td>
</tr>
<tr>
<td>Al-2% Si</td>
<td>700</td>
<td>5</td>
<td>882.6</td>
<td>&gt;0.435</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>2</td>
<td>744.7</td>
<td>0.123</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>5</td>
<td>737.8</td>
<td>0.145</td>
</tr>
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*exponential behavior in infiltration
BIBLIOGRAPHY


120. V. Laurent, D. Chatain and N. Eustathopoulos, "Wettability of SiC by Aluminum and Al-Si alloys," J. Mat. Sci. 22 (1987) 244-250.


