INFORMATION TO USERS

This manuscript has been reproduced from the microfilm master. UMI films the text directly from the original or copy submitted. Thus, some thesis and dissertation copies are in typewriter face, while others may be from any type of computer printer.

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleedthrough, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send UMI a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps. Each original is also photographed in one exposure and is included in reduced form at the back of the book.

Photographs included in the original manuscript have been reproduced xerographically in this copy. Higher quality 6" x 9" black and white photographic prints are available for any photographs or illustrations appearing in this copy for an additional charge. Contact UMI directly to order.
Physicochemical measurements in aluminum-salt systems relevant to recycling of aluminum scrap

Roy, Raja R., Ph.D.
The Ohio State University, 1994
PHYSICOCHEMICAL MEASUREMENTS IN ALUMINUM-SALT SYSTEMS
RELEVANT TO RECYCLING OF ALUMINUM SCRAP

DISSERTATION

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

by

Raja R. Roy, B.S.

The Ohio State University
1994

Dissertation Committee

Dr. Yogeshwar Sahai
Dr. Carroll E. Mobley
Dr. Robert A. Rapp

Approved by

Yogeshwar Sahai
Adviser

Graduate Program in
Materials Science and Engineering
To My Parents and My Wife
ACKNOWLEDGMENTS

I would like to express sincere appreciation to my advisor, Professor Yogeshwar Sahai for his continuous encouragement, guidance, and support throughout the research. I would also like to thank Dr. C. E. Mobley and Dr. R. A. Rapp for their acceptance to be on my final oral examination committee and for their suggestions and comments. I gratefully acknowledge the financial support provided by Alcoa Technical Center and by Bureau of Mines through the Generic Mineral Technology Center for Pyrometallurgy.

Thanks are also due to Jian Ye, Chandrashekar Damle, Sanjeev Gupta, Mark Burval, Nouaille-Degorce Gilles and Ramesh Narayanan for useful discussions. Thanks also go to Vijay Shastry and Venkata S. Balanethiram for making my stay at Ohio State much enjoyable.

Finally, I am deeply indebted to my parents and my wife for their love and support.
VITA

July 16, 1966
Born in Darbhanga, Bihar, India

May, 1989
B. Tech. Metallurgical Engineering
Indian Institute of Technology
Kanpur, India

1990-present
Graduate Research Associate
Department of Materials Science and Engineering
The Ohio State University

PUBLICATION


FIELD OF STUDY

Major Field Materials Science and Engineering
# TABLE OF CONTENTS

DEDICATION .......................................................................................................................... ii

ACKNOWLEDGMENTS ....................................................................................................... iii

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

LIST OF TABLES ................................................................................................................... ix

LIST OF FIGURES ................................................................................................................. xi

CHAPTERS

<table>
<thead>
<tr>
<th>CHAPTERS</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>I. INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>II. RECYCLING PROCESS</td>
<td>6</td>
</tr>
<tr>
<td>2.1 Shredding</td>
<td>8</td>
</tr>
<tr>
<td>2.2 Decoating</td>
<td>8</td>
</tr>
<tr>
<td>2.3 Melting</td>
<td>9</td>
</tr>
<tr>
<td>2.4 Treatment of Dross</td>
<td>11</td>
</tr>
<tr>
<td>III. LITERATURE REVIEW</td>
<td>13</td>
</tr>
<tr>
<td>3.1 Surface Tension</td>
<td>13</td>
</tr>
<tr>
<td>3.1.1 History</td>
<td>13</td>
</tr>
</tbody>
</table>
4.8 Metal Loss Measurement.................................................................91

V. RESULTS AND DISCUSSION.................................................................92

5.1 Interfacial Tension.............................................................................92

5.2 Sodium and Potassium Content of Aluminum..............................102

5.3 Coalescence of Al Chips.................................................................103

5.4 Coalescence of UBC Alloy Chips....................................................109

5.5 Study of Oxide Removal Using Interference Microscopy..............118

5.6 Process of Oxide Removal and Coalescence.................................125
  5.6.1 Coalescence of Aluminum Drops in Fluorides..........................127
  5.6.2 Coalescence of Aluminum Drops in Chlorides..........................127
  5.6.3 Coalescence of UBC Alloy Drops in Fluorides..........................128
  5.6.4 Coalescence of UBC Alloy Drops in Chlorides..........................128

5.7 Contact Angle and Work of Adhesion............................................132

5.8 Mechanism of Oxide Removal.......................................................137

5.9 Viscosity of Salts.............................................................................148

5.10 Terminal Falling Velocity..............................................................157

VI. SUMMARY AND CONCLUSIONS......................................................161

REFERENCES..........................................................................................166

viii
# LIST OF TABLES

<table>
<thead>
<tr>
<th>TABLE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Composition of Al Alloys</td>
<td>4</td>
</tr>
<tr>
<td>2. Types of Aluminum Scrap</td>
<td>7</td>
</tr>
<tr>
<td>3. Physicochemical Requirements of a Salt Flux</td>
<td>11</td>
</tr>
<tr>
<td>4. Analysis of Non Metallic Products</td>
<td>12</td>
</tr>
<tr>
<td>5. Classification of Intermolecular Forces</td>
<td>15</td>
</tr>
<tr>
<td>6. Surface Tension and Temperature Coefficient of Surface Tension for Metals at the Melting Point</td>
<td>18</td>
</tr>
<tr>
<td>7. Surface Tension and Temperature Coefficient of Surface Tension for Salts at 800 °C</td>
<td>21</td>
</tr>
<tr>
<td>8. Materials Used in Experiments</td>
<td>73</td>
</tr>
<tr>
<td>9. Amount of Sodium and Potassium in Aluminum</td>
<td>104</td>
</tr>
<tr>
<td>10. Comparison of Amount of Sodium in Aluminum</td>
<td>104</td>
</tr>
<tr>
<td>11. Coalescence of UBC Alloy Chips in Equimolar NaCl-KCl</td>
<td>110</td>
</tr>
<tr>
<td>12. Progress of Coalescence of UBC Chips in NaCl-KCl with 5 Wt. % Fluorides as a Function of Time</td>
<td>110</td>
</tr>
<tr>
<td>Chapter</td>
<td>Title</td>
</tr>
<tr>
<td>---------</td>
<td>-------</td>
</tr>
<tr>
<td>13.</td>
<td>Contact Angle Between Aluminum and Alumina in Salt Flux</td>
</tr>
<tr>
<td>14.</td>
<td>Interfacial Tension in Aluminum, Alumina and Salt System</td>
</tr>
<tr>
<td>15.</td>
<td>Free Energy Change for Oxide Removal</td>
</tr>
<tr>
<td>16.</td>
<td>Data for Ternary Interfacial Energy Diagram</td>
</tr>
<tr>
<td>17.</td>
<td>Free Energy of Formation of Salts</td>
</tr>
<tr>
<td>18.</td>
<td>Metal Loss and Coalescence of Aluminum Drops</td>
</tr>
<tr>
<td>19.</td>
<td>Metal Loss and Coalescence of UBC Alloy Drops</td>
</tr>
<tr>
<td>20.</td>
<td>Kinematic Viscosity of Salts</td>
</tr>
</tbody>
</table>
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>FIGURE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1</td>
<td>19</td>
</tr>
<tr>
<td>3.2</td>
<td>22</td>
</tr>
<tr>
<td>3.3</td>
<td>23</td>
</tr>
<tr>
<td>3.4</td>
<td>25</td>
</tr>
<tr>
<td>3.5</td>
<td>25</td>
</tr>
<tr>
<td>3.6</td>
<td>30</td>
</tr>
<tr>
<td>3.7</td>
<td>31</td>
</tr>
<tr>
<td>3.8</td>
<td>32</td>
</tr>
<tr>
<td>3.9</td>
<td>33</td>
</tr>
<tr>
<td>3.10</td>
<td>35</td>
</tr>
<tr>
<td>3.11</td>
<td>35</td>
</tr>
<tr>
<td>3.12</td>
<td>42</td>
</tr>
<tr>
<td>3.13</td>
<td>45</td>
</tr>
</tbody>
</table>
3.14 Ternary Interfacial Energy Diagram for a Solid-Liquid-Gas System
3.15 Ternary Interfacial Energy Diagram for a Liquid-Liquid-Gas System
3.16 Variation of Viscosity with Rotational Velocity and Alumina Type
3.17 Density of Equimolar NaCl-KCl with the Addition of NaF, KF, LiF, and Cryolite at 740 °C
3.18 Thickness of Oxide Films Formed on Various Metals at Room Temperature
3.19 Effect of Alloy Thickness on Metal Loss
3.20 Effect of Alloying Element on Metal Loss
3.21 Effect of Fluoride Concentration and Temperature on Recovery
4.1 Forces Acting on a Drop Detaching from the Orifice
4.2 Typical Drop Weight Vs. Time Curve During Formation and Detachment of a Drop
4.3 Schematic of Apparatus Used for Measurement of Interfacial Tension
4.4 Set-Up for Contact Angle Measurement
4.5 Measurement of Contact Angle
4.6 Variation of "vt" with "t^2" for KOH Solution
4.7 Schematic of Apparatus Used for Viscosity Measurement
4.8 Schematic of Apparatus Used for Measurement of Density
4.9 Test for Coalescence of Metal Drops in Salts
4.10 Schematic Profile of The Surface
4.11 Interference Fringe Pattern Corresponding to the Profile in Figure 4.9
5.1 Variation of Interfacial Tension Between UBC Alloy and Salt as a Function of Additives in Equimolar NaCl-KCl Salt Solution........93

5.2 Variation of Interfacial Tension Between UBC Alloy and Salt as a Function of Additives in Equimolar NaCl-KCl Salt Solution........94

5.3 Variation of Interfacial Tension Between UBC Alloy and Salt as a Function of LiCl in Equimolar NaCl-KCl Salt Solution........95

5.4 Variation of Interfacial Tension Between Aluminum and Salt as a Function of NaF in Equimolar NaCl-KCl Salt Solution........97

5.5 Aluminum Chips Before the Experiment.......................................................106

5.6 Coalescence of Aluminum Drops in NaCl-KCl-5 wt. % NaF...............106

5.7 Coalescence of Aluminum Drops in Equimolar NaCl-KCl.................107

5.8 Progress of Coalescence with Time in Equimolar NaCl-KCl Plus Addition of Chlorides.................................................................108

5.9 Coalescence of UBC Alloy Drops in NaCl-KCl-5 wt. % NaF..............111

5.10 Coalescence of UBC Alloy Drops in NaCl-KCl-5 wt. % CaF₂............111

5.11 Coalescence of UBC Alloy Drops in NaCl-KCl-5 wt. % AlF₃.............111

5.12 Coalescence of UBC Alloy Drops in Equimolar NaCl-KCl...............112

5.13 Progress of Coalescence of UBC Alloy Drops as a Function of Time in Equimolar NaCl-KCl.................................................................113

5.14 Progress of Coalescence of UBC Alloy Drops as a Function of Time in Equimolar NaCl-KCl Plus Addition of Fluorides.........................114

5.15 Progress of Coalescence of UBC Alloy Drops as a Function of Time in Equimolar NaCl-KCl Plus Addition of Fluorides.........................115

5.16 Progress of Coalescence of UBC Alloy Drops as a Function of Time in Equimolar NaCl-KCl Plus Addition of NaF/AlF₃......................116

5.17 Interference Pattern from Electropolished Al Surface Oxidized for 15 Hours at 500 °C.................................................................119

5.18 Interference Pattern from Electropolished Al Surface Immersed in Equimolar NaCl-KCl for 1.5 Minutes at 740 °C.................................120
Chapter I

Introduction

Recycling of aluminum scrap, such as Used Beverage Cans (UBC) is steadily growing, because it is economically sound and saves energy. Only 5% of the energy needed for the production of primary aluminum from ore is required to produce the same amount of aluminum from recycled scrap. Recycling is good for the environment, preserves the natural resources and reduces the demands on landfills. The aluminum alloy scrap is shredded, decoated and screened for contaminants to increase the efficiency of the process. Aluminum scrap is then charged into a bath of molten salt flux, so that melting of the aluminum alloy takes place under a cover of the salt flux. Flux prevents oxidation of aluminum alloy and promotes coalescence of the molten metal. During the charging of the aluminum scrap, the aluminum alloy is further oxidized, and metal loss results from the formation of oxides as well as skim, which is molten aluminum alloy droplets completely covered with oxide layer. Due to their high tearing strength, oxide films are capable of retaining more than 20 times their weight of molten aluminum alloy(1). Skim formation is a very important contribution to metal loss. The choice of salt flux depends on its ability to free the molten aluminum alloy.
from its adhering oxide film. A large number of salt fluxes have been proposed in the literature. A significant portion of these fluxes chosen were chosen on past experience rather than on a thorough understanding of the process, and only recently has this trend changed\(^2\). The salt flux is usually based on equimolar NaCl-KCl composition corresponding to eutectic composition, because it is cheap and its melting point is low. A small amount of fluoride salt is added to the salt flux, since the use of fluoride containing salts results in an improvement of coalescencability. However, the salt becomes progressively viscous as the oxide film stripped from the metal is suspended in the flux. As the salt becomes more viscous, more metal is entrapped in the salt. Finally the thickened salt has to be replaced.

Gillet and James\(^3\) reported the problem of melting finely divided aluminum in 1916. Chlorides were reported to have no dissolving action on the oxide, whereas fluorides were effective. A flux consisting of 85\% sodium chloride and 15\% calcium fluoride was recommended. Since then a number of salt fluxes have been proposed.

For many years it was thought that these salts actually dissolved oxide to produce the desired result, until West\(^4\) showed that alumina is almost insoluble in the molten flux. Jordan and Milner\(^5\) also showed that salts detached the oxide film from the metal instead of dissolving the oxide film. In a work conducted at Alcoa Research Laboratories, alumina windows were produced by stripping away the metal substrate from anodized aluminum samples, were immersed in molten flux\(^6\). No thinning of the oxide windows was reported. Thus there remains little doubt that salt fluxes do not dissolve oxide to any appreciable extent.
Sully et al. (7) investigated the thickening of salt fluxes through metal entrapment. Metal entrapment resulted in increased viscosity due to the presence of alumina films. The viscosity of the salt flux was found to depend on the shape of the alumina particles and the viscosity was greater for thin and flat particles of alumina. Stripping of oxide films was dependent on the interfacial tension between alumina and the salt, aluminum and the salt, and alumina and aluminum.

It is generally believed that the wetting characteristics and interfacial properties play an important role during the entire remelting process (7,8). The contact angle between molten aluminum and alumina immersed in the molten salt as well as the interfacial tension between aluminum and alumina, between aluminum and the salt flux, and between alumina and the salt flux are important factors. Interfacial tension between pure aluminum and salts based on equimolar NaCl-KCl and containing metal chlorides and fluorides in varying amounts has been measured by several researchers (9-11). The interfacial tension was found to decrease for all salt additions. The addition of metal fluorides was found to be more effective than metal chlorides containing the same metal in lowering interfacial tension. The lowering of interfacial tension between aluminum and the salt by fluoride addition has been credited to improved metal recovery (12), though the mechanism of this process is still not clear.

The aim of the present investigation is to gain fundamental understanding about the role of the salt flux in the recycling process. It is expected that such an understanding will lead to the development of a salt flux with better coalescencability.
Two types of aluminum alloys are used to make beverage cans. The top of the can is made of alloy AA5182 and the body, which comprises 75% of the can weight, is made of alloy AA3004. The composition of the melted UBC can be calculated from the composition of these two alloys. Due to loss of magnesium to the melt, the actual composition of melted UBC differs from the calculated value. Table 1 gives the compositions of these two alloys. A can typically weighs about 15 grams.

<table>
<thead>
<tr>
<th></th>
<th>% Mg</th>
<th>% Mn</th>
<th>% Si (Max)</th>
<th>% Fe (Max)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AA 5182</td>
<td>4.0 - 5.0</td>
<td>0.20 - 0.50</td>
<td>0.20</td>
<td>0.35</td>
</tr>
<tr>
<td>AA 3004</td>
<td>0.8 - 1.3</td>
<td>1.0 - 1.5</td>
<td>0.30</td>
<td>0.70</td>
</tr>
<tr>
<td>UBC (calculated)</td>
<td>1.91</td>
<td>1.03</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>UBC (practice)</td>
<td>1.30</td>
<td>1.03</td>
<td>0.16</td>
<td>0.35</td>
</tr>
</tbody>
</table>
In this study, the coalescencability of molten salts based on equimolar NaCl-KCl was determined for aluminum drops as well as UBC alloy drops. The progress of coalescence in different salts was observed as a function of time. Based on these observations, a model to explain the process of coalescence was developed. Coalescence is related to the removal of oxide layer from the metal by the salts. Removal of the oxide layer was observed using interference microscopy for the equimolar NaCl-KCl and equimolar NaCl-KCl containing 5 wt. % NaF. The interfacial tension between UBC alloy and molten salts was measured using the drop detachment method. The variation of interfacial tension with salt composition was related to the adsorption of surface active elements at the metal-salt interface. Experimental verification of adsorption was done by analyzing metal samples using electron microprob analysis (EMPA). The contact angle between aluminum and alumina immersed in the molten salts was measured using the sessile drop method. The interfacial tension between alumina and the salt and the work of adhesion between aluminum and alumina immersed in molten salts were calculated from the values of the contact angles. A ternary interfacial energy diagram was constructed for aluminum-alumina-salt systems and its relation to the removal of oxide from the metal was discussed. The viscosity and density of molten salts were measured and their importance for the recycling process was explained.
The first attempt to recycle aluminum scrap was started by the automobile industry at the beginning of this century. Since then a secondary aluminum industry has grown steadily, except for a significant deviation after World War II. Aluminum scrap can be either new or old. New scrap is generated during the manufacturing of a product and old scrap is generated when a consumer discards a product such as a used beverage can or an automobile. Various types of aluminum scrap are listed in Table 2 (13). U.S. consumers recycled 59.5 billion aluminum cans, approximately 63% of the 94.2 billion aluminum cans produced in 1993 and the aluminum industry spent $800 million to obtain these cans, which were recycled through 10,000 U.S.-wide buy-back centers, state-mandated recycling programs, and municipal curbside recycling programs (14).

The steps involved in recycling are: shredding, decoating, remelting and treatment of dross. Shredding is described in section 2.1, decoating in section 2.2, remelting in section 2.3, and treatment of dross in section 2.4.
<table>
<thead>
<tr>
<th></th>
<th>Types of aluminum scrap(13)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>New pure aluminum clippings</td>
</tr>
<tr>
<td>2</td>
<td>New pure aluminum wire/cable</td>
</tr>
<tr>
<td>3</td>
<td>Old pure aluminum wire/cable</td>
</tr>
<tr>
<td>4</td>
<td>Segregated new aluminum clippings</td>
</tr>
<tr>
<td>5</td>
<td>Mixed new aluminum clippings</td>
</tr>
<tr>
<td>6</td>
<td>Mixed low copper aluminum clippings</td>
</tr>
<tr>
<td>7</td>
<td>Mixed old alloy sheet aluminum</td>
</tr>
<tr>
<td>8</td>
<td>Scrap sheet and sheet utensil aluminum</td>
</tr>
<tr>
<td>9</td>
<td>Segregated new aluminum castings, forgings and extrusions</td>
</tr>
<tr>
<td>10</td>
<td>Mixed new aluminum forgings</td>
</tr>
<tr>
<td>11</td>
<td>Mixed new aluminum castings</td>
</tr>
<tr>
<td>12</td>
<td>Aluminum auto castings</td>
</tr>
<tr>
<td>13</td>
<td>Aluminum airplane castings</td>
</tr>
<tr>
<td>14</td>
<td>Mixed aluminum castings</td>
</tr>
<tr>
<td>15</td>
<td>Aluminum pistons</td>
</tr>
<tr>
<td>16</td>
<td>Wrecked airplane sheet</td>
</tr>
<tr>
<td>17</td>
<td>New aluminum foil</td>
</tr>
<tr>
<td>18</td>
<td>Old aluminum foil</td>
</tr>
<tr>
<td>19</td>
<td>All other aluminum base foils</td>
</tr>
<tr>
<td>20</td>
<td>Aluminum borings and turnings</td>
</tr>
<tr>
<td>21</td>
<td>Mixed aluminum borings and turnings</td>
</tr>
<tr>
<td>22</td>
<td>Sweated aluminum</td>
</tr>
<tr>
<td>23</td>
<td>Aluminum grinding's</td>
</tr>
<tr>
<td>24</td>
<td>Aluminum drosses, spatters, spillings, skimnings and sweepings</td>
</tr>
<tr>
<td>25</td>
<td>Aluminum hair wire</td>
</tr>
<tr>
<td>26</td>
<td>Aluminum wire screen</td>
</tr>
<tr>
<td>27</td>
<td>Coated scrap</td>
</tr>
<tr>
<td>28</td>
<td>New aluminum can stock</td>
</tr>
<tr>
<td>29</td>
<td>Old can stock</td>
</tr>
<tr>
<td>30</td>
<td>Painted siding</td>
</tr>
<tr>
<td>31</td>
<td>Aluminum copper radiators</td>
</tr>
<tr>
<td>32</td>
<td>Containers of all types</td>
</tr>
<tr>
<td>33</td>
<td>Automobile shredder scrap</td>
</tr>
<tr>
<td>34</td>
<td>Items not covered above</td>
</tr>
</tbody>
</table>
2.1 SHREDDING

UBCs from the collection centers are received in the form of bales of 1.5 m$^3$ weighing 400 kg or as briquettes of density up to 500 kg/m$^3$ (15). During shredding, bales and briquettes are broken apart and cans are shredded to ensure that no trapped liquid or extraneous material reaches the melters and to expose the maximum possible surface to the decoating process. Shredded scrap then passes through a magnetic separator to remove ferrous contaminants.

2.2 DECOATING

Decoating of paint, lacquer, plastic paper or oil is intended to cause a minimal interference to the aluminum surface. Such coatings contain mostly organic and very volatile chemical compounds. Thermal processing is the most cost-effective method for decoating. Decoating reduces the energy requirement, the environmental emissions and loss during melting(16). Thermal processing involves either keeping the shredded scrap at lower temperature (around 520 °C) for a relatively longer time or at temperatures just below the liquidus temperature of the scrap (around 615 °C) for a very short exposure time(15). The temperature and exposure time has to be controlled properly. Lower temperature or shorter exposure time leave a tar-like coating, which increases metal loss during melting due to premelt burning. Higher temperature or longer exposure time results in increased metal loss due to increased oxidation of scrap. Moisture content of the scrap is
normally less than 5%. An increase in moisture content leads to increased energy consumption.

The optimum decoating process should satisfy the following capabilities (16):

- shredding of the scrap to expose the maximum possible surface to the decoating process
- screening and separation of tramp materials and fines from incoming scrap
- magnetic separation of free iron and iron-aluminum content in the scrap
- substantial removal of organic coating
- kiln temperature and residence time held to lowest practicable levels to minimize oxidation of the scrap
- optimize oxygen level in the system to retard oxidation and prevent fires in the kiln
- maximize thermal efficiency of the process by recycling the hot waste gas
- ensure compliance with statutory environmental regulations covering waste gas emissions

2.3 MELTING

When the first UBCs were melted in reverberatory furnaces, the metal loss was 65% of the melt. If the volume to surface area ratio of the Al scrap is high, scrap melts fairly uniformly. The entire charge melts at nearly same time, because aluminum is a good conductor of heat. The melting of shredded UBC's is completely different, because UBC's have typically a wall thickness of 0.13 mm. Shredded and decoated UBC's have a large surface to volume ratio and a thick oxide layer due to thermal processing. Heat transfer
is poor and the surface of metal heats up while metal below the surface remains cold. When the melting particle deforms, the oxide layer breaks and fresh metal is exposed to the environment, so a new oxide skin forms. By the time the entire charge melts, a thick layer of oxide skins, trapped metal and air covers the melt(15).

To reduce the huge metal loss caused by melting Al scrap in air, a new process was developed. The aluminum alloy scrap is charged into a bath of molten salt flux, so that melting of the aluminum alloy takes place under the cover of salt flux. The main requirements for the flux are to prevent oxidation of aluminum alloy, to promote coalescence of the molten metal and to dissolve or suspend oxides(2). Physicochemical requirements of a salt flux are listed in Table 3. The salt becomes progressively viscous as the oxide films stripped from metal are suspended in the flux. As the salt becomes more and more viscous, metal is entrapped in the salt. Finally, the thickened salt, called dross, has to be discarded. Dross contains salts, oxides and a considerable amount of entrapped metal. Dross is further treated to recover metal and salts.

Decoating of the UBC’s reduces the metal loss to about 30 %. Introduction of a salt flux for melting UBC’s reduces the metal loss to 15 % and dross treatment has brought the metal loss to below 10 %.

2.4 TREATMENT OF DROSS

Dross is treated to recover metal, non-metal and salt, and to minimize landfill wastes. The following products can be reclaimed from dross: salt
fluxes, aluminum recycled secondary ingot (RSI) and non-metallic products (NMP). Metal is separated from the oxides and the flux by a series of crushing and screening steps. Flux used in recycling of aluminum is mainly sodium and potassium chloride, which are soluble in water, and can therefore be separated from oxides by leaching. Non-metallic products can be further refined by homogenizing and calcining to remove chlorides, AlN and any carbon or organic compound present. Refined non-metallic products can be used for various refractory or ceramic products. Table 4 shows approximate analysis of non metallic products and refined non metallic products \cite{17}.

Table 3  

<table>
<thead>
<tr>
<th>Physicochemical requirements of a salt flux\cite{2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting point equal to or below 660 °C</td>
</tr>
<tr>
<td>Density less than 2.3 gm/cm³</td>
</tr>
<tr>
<td>Inert to the refractory walls</td>
</tr>
<tr>
<td>Non-poisonous</td>
</tr>
<tr>
<td>Low vapor pressure</td>
</tr>
<tr>
<td>Not hygroscopic</td>
</tr>
<tr>
<td>Low viscosity</td>
</tr>
</tbody>
</table>
Table 4  Analysis of non metallic products (17)

<table>
<thead>
<tr>
<th></th>
<th>Non-metallic Products</th>
<th>Refined Non-metallic Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₂O₃</td>
<td>1-1.85 %</td>
<td>1.2 %</td>
</tr>
<tr>
<td>CaO</td>
<td>1-1.49 %</td>
<td>1.35 %</td>
</tr>
<tr>
<td>MgO</td>
<td>13-17.5 %</td>
<td>16.7 %</td>
</tr>
<tr>
<td>TiO₂</td>
<td>1.2 %</td>
<td>0.89 %</td>
</tr>
<tr>
<td>K₂O</td>
<td>1.5 %</td>
<td>1.32 %</td>
</tr>
<tr>
<td>SiO₂</td>
<td>4-9.0 %</td>
<td>10.72 %</td>
</tr>
<tr>
<td>Na₂O</td>
<td>2.0 %</td>
<td>1.82 %</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>60.0-70.0 %</td>
<td>65.94 %</td>
</tr>
<tr>
<td>C</td>
<td>5.0 %</td>
<td></td>
</tr>
<tr>
<td>AlN</td>
<td>1-10.0 %</td>
<td></td>
</tr>
<tr>
<td>Chlorides</td>
<td>&lt; 1.0 %</td>
<td></td>
</tr>
</tbody>
</table>
CHAPTER III

LITERATURE REVIEW

3.1 SURFACE TENSION

3.1.1 History

It is believed that Leonardo da Vinci (1452-1519) first observed and recorded the rise of a liquid in a tube of small bore as "fine as a hair" (18). Thus this phenomena became known as "Capillarity" (Latin: Capillus = hair). Newton (1642-1727) attributed the rise of liquid in a capillary to forces of cohesion and adhesion (19). Hawksbee observed the rise of liquids in capillary tubes of the same internal diameter, but having different thicknesses at the end of 17th century (20). He found that the behavior did not depend on the thickness of the tube and concluded that attractive forces arose from the matter near the inside surface of the tubes. In 1751, Segner (21) proposed the first theory of capillarity. He proposed that cohesive forces created a pressure, which was resisted by surface tension (21). Young (22) and Laplace (23) subsequently published theoretical treatments of surface tension, deriving the equations named after them. Gauss (24) derived the Young's equation and the Laplace equation more rigorously. Later Gibbs (25) derived equations relating surface tension to intensive properties of the liquid.
3.1.2 Definition

Surface tension is defined as the work required to produce a unit surface area. If \( W \) is the work required to produce an incremental surface area \( d\Sigma \), then

\[
W = -\gamma d\Sigma
\]

(3.1)

where \( \gamma \) is the surface tension.

Work needs to be done against the attraction forces to form a surface. Table 5 shows the types of attraction forces according to Houwink(26). The total energy of formation of a unit surface area is not necessarily the work done against the attraction forces. Once the surfaces have been formed, a further change occurs as the molecules at the surface relax into their equilibrium positions, because the molecules at the surface are no longer in a symmetric field. The physical dimensions of surface tension are \([\text{MT}^{-2}]\). The unit of surface tension in cgs is \(\text{dyne cm}^{-1}\) or \(\text{erg cm}^{-2}\).

3.1.3 Surface tension of solutions

Surface tension of a solution is not expected to obey a linear relationship with the variation of concentration. Guggenheim(27) obtained an expression for surface tension of a binary liquid mixture assuming an ideal solution.

\[
\exp(-\gamma \alpha/RT) = X_1 \exp(-\gamma_1 \alpha/RT) + X_2 \exp(-\gamma_2 \alpha/RT)
\]

(3.2)
Table 5  Classification of Intermolecular Forces(26)

I. Attraction forces

A. Primary bonds

1. Homopolar (atomic or covalent bonds)
2. Heteropolar (ionic bonds)
3. Hydrogen bonding (very strongly polar)

B. Metallic bonds

C. Secondary bonds

1. Dispersion forces (nonpolar-nonpolar)
2. Debye forces (induced polar-polar)
3. Keesom forces (polar-polar)

II. Repulsion force

A. Born repulsion

1. Overlapping filled electron shells
where $\gamma$ is the surface tension of the solution, $\gamma_1$ is the surface tension of pure component 1, $\gamma_2$ is the surface tension of pure component 2, $X_1$ is the mole fraction of component 1, $X_2$ is the mole fraction of component 2 and $\alpha$ is the surface area per mole, which is assumed to be same for both components. $\alpha$ is given by the following equation:

$$\alpha = \frac{1}{\rho N_0^{2/3}} \left( M_1 X_1 + M_2 X_2 \right)$$  \hspace{1cm} (3.3)$$

where $M_1$ is the molecular weight of component 1, $M_2$ is the molecular weight of component 2, $\rho$ is the density of the mixture and $N_0$ is the Avogadro's number.

Two modifications have been made to equation (3.2) by introducing molar volume and surface area of each component in the equation instead of assuming them to be same for each component\(^{(28)}\). Equation (3.4) shows the modification in which mole fraction $X_i$ has been replaced by volume fraction $\phi_i$.

$$\exp(-\gamma A/RT) = \phi_1 \exp(-\gamma_1 A/RT) + \phi_2 \exp(-\gamma_2 A/RT)$$  \hspace{1cm} (3.4)$$

with,

$$\phi_1 = \frac{V_1 X_1}{(V_1 X_1 + V_2 X_2)}$$  \hspace{1cm} (3.5)$$

$$\phi_2 = \frac{V_2 X_2}{(V_1 X_1 + V_2 X_2)}$$  \hspace{1cm} (3.6)$$

$$A = \frac{1}{\rho N_0^{2/3}} \left( \phi_1 V_1 + \phi_2 V_2 \right)$$  \hspace{1cm} (3.7)$$

where $V_i$ is the molar volume of component i.
Equation (3.8) shows the modification in which the surface area per molecule of each component is taken into account.

$$\exp(-\gamma A/RT) = \phi_1 \exp(-\gamma_1 A_1/RT) + \phi_2 \exp(-\gamma_2 A_2/RT)$$

(3.8)

with,

$$A_1 = (V_1 / N_0)^{2/3}$$

(3.9)

$$A_2 = (V_2 / N_0)^{2/3}$$

(3.10)

where $A_i$ is the surface area per molecule of component $i$.

Eberhart(29) assumed the surface tension to be a linear function of the surface mole fractions.

$$\gamma = \gamma_1 Y_1 + \gamma_2 Y_2$$

(3.11)

where $Y_i$ is the surface mole fraction of component $i$. By assuming the activities to be equal to concentrations, he derived the following equation

$$\gamma = (S X_1 \gamma_1 + X_2 \gamma_2) / (S X_1 + X_2)$$

(3.12)

where $S$ is a surface enrichment factor.

3.1.4 Surface tension of liquid metals

The surface tension of liquid metals is found to be higher than other liquids, e.g. water and liquid argon. Surface tension decreases with increase in temperature. Table 6 shows the surface tension and temperature coefficient of surface tension for some metals(30). The effect of various solutes on the
surface tension of liquid aluminum is shown in Figure 3.1 (31). Adsorption of solutes on the surface results in the decrease of surface tension.

Table 6  Surface tension in vacuum and temperature coefficient of surface tension for liquid metals at the melting point(30)

<table>
<thead>
<tr>
<th>Metal</th>
<th>( \gamma \text{(dyne cm}^{-1}) )</th>
<th>( \text{d}\gamma/\text{dT} \text{(dyne cm}^{-1} \text{oK}^{-1}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>191</td>
<td>-0.10</td>
</tr>
<tr>
<td>K</td>
<td>115</td>
<td>-0.08</td>
</tr>
<tr>
<td>Li</td>
<td>398</td>
<td>-0.14</td>
</tr>
<tr>
<td>Ca</td>
<td>361</td>
<td>-0.10</td>
</tr>
<tr>
<td>Al</td>
<td>914</td>
<td>-0.35</td>
</tr>
<tr>
<td>Mg</td>
<td>559</td>
<td>-0.35</td>
</tr>
<tr>
<td>Fe</td>
<td>1872</td>
<td>-0.49</td>
</tr>
</tbody>
</table>
Figure 3.1  Surface tension of aluminum in vacuum with the addition of metals at 50 - 80 °C above its liquidus temperature (31)
3.1.5 Surface tension of molten salts

Surface tensions in air of pure metal halides and their binary and ternary solutions have been studied extensively. Table 7 shows the surface tension of some metal chlorides (28) and metal fluorides (32) at 800 °C and the temperature coefficient of surface tension. Grjotheim et al. (28) measured the surface tension of binary liquid chloride mixtures of alkali chloride-CaCl$_2$ and alkali chloride-MgCl$_2$ and ternary mixture of NaCl-CaCl$_2$-MgCl$_2$ and KCl-CaCl$_2$-MgCl$_2$ by pin detachment method. Surface tension of binary mixture deviated from Guggenheim equation. Deviations resulted from polarization effects, enrichment of the surface by the element with lowest surface tension and formation of complexes. Bertozzi and Soldani (33) measured the surface tension isotherms at 850 °C for 12 binary systems of alkali metal halides with alkali earth metal halides. Isotherms deviated from linearity and deviation was related to the difference between ionic radii. Bertozzi (34) measured the surface tension of pure alkali chlorides and bromides and their binary mixtures from the melting point to 900 °C. Surface tension of all pure salts and their mixtures showed a linear dependence on temperature. Surface tension of binary mixture with common cation showed a linear variation. Patrov et al. (35) measured the surface tension of the binary mixture of NaCl-KF and NaF-KCl using maximum bubble pressure method at 900 °C. Surface tension varied between 106 to 144 dyne/cm for NaCl-KF system and between 86 and 143 for NaF-KCl system. Grjotheim et al. (36) measured the surface tension of binary mixture of NaF-NaCl, NaF-NaBr and NaCl-NaBr by pin detachment method at 900 °C. Isotherms were compared to equation derived by Guggenheim and its two modified forms and a model proposed by
Eberhart. Ye(37) measured surface tension of NaCl-KCl and ternary mixture of salts based on equimolar NaCl-KCl. Figure 3.2 shows the surface tension of binary mixture of equimolar NaCl-KCl at 740 °C.

Table 7  Surface tension in air and temperature coefficient of surface tension for chlorides(28) and fluorides(32) at 800 °C

<table>
<thead>
<tr>
<th>Salt</th>
<th>Surface tension (dyne cm⁻¹)</th>
<th>Temperature coefficient (dyne cm⁻¹ degree⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KCl</td>
<td>97</td>
<td>-0.070</td>
</tr>
<tr>
<td>NaCl</td>
<td>116</td>
<td>-0.073</td>
</tr>
<tr>
<td>LiCl</td>
<td>116</td>
<td>-0.070</td>
</tr>
<tr>
<td>MgCl₂</td>
<td>62</td>
<td>-0.004</td>
</tr>
<tr>
<td>CaCl₂</td>
<td>147</td>
<td>-0.046</td>
</tr>
<tr>
<td>NaF</td>
<td>202</td>
<td>-0.082</td>
</tr>
<tr>
<td>KF</td>
<td>146</td>
<td>-0.075</td>
</tr>
<tr>
<td>LiF</td>
<td>256</td>
<td>-0.109</td>
</tr>
<tr>
<td>Na₃AlF₆</td>
<td>160</td>
<td>-0.128</td>
</tr>
</tbody>
</table>
Figure 3.2  Surface tension in air of NaCl-KCl binary mixture at 740 °C(37)
3.1.6 Surface tension of alumina

The surface tension of a solid is also referred to as the surface energy of the solid. Surface energy of alumina in air compiled from various sources by Impey et al. (38) is shown in Figure 3.3.

Figure 3.3  Surface energy of alumina in air(38)
- Data from Livey and Murray(39)
- Data from Parkins(40)
- Data from Hardie and Petch(41)
3.2 INTERFACIAL TENSION

An interface is a boundary between two phases. An apparent surface of a solid or liquid is in fact an interface between that solid or liquid and the gas. Interfacial tension of a fluid interface can be viewed in two different ways, from a thermodynamic point of view or from a mechanical point of view.

Two different models for defining the thermodynamic properties of an interface are shown in Figures 3.4 and 3.5. In the model due to Gibbs, the thermodynamic properties of the two bulk phases are homogeneous up to the interface, where a mathematical surface divides the two bulk phases. The interface in this model has zero thickness. The other model due to Guggenheim assumes an interface of small but uniform thickness.

Thermodynamical definition of surface tension is

\[ \gamma = \left( \frac{\partial E}{\partial S} \right)_s, n_\alpha, n_\beta, V_\alpha, V_\beta \]  

(3.13)

where \( \gamma \) is the surface tension, \( E \) the internal energy, \( S \) the surface area, \( s \) the entropy, \( n_i \) the number of moles of phase \( i \), \( V_i \) is the volume of phase \( i \).

From a mechanical point of view, the interfacial tension is a force per unit length parallel to the interface and is same in all directions along the interface. Thus interfacial tension is a two-dimensional counterpart of pressure in the bulk of a fluid. Both the approaches lead to same quantitative value for interfacial tension.
Figure 3.4 Gibb's surface separating two bulk phases

Figure 3.5 Surface phase between two bulk phases
3.2.1 Interfacial tension measurement

Interfacial tension can be measured using the same methods as those for measuring surface tension.

1. Sessile drop method\(^{(42-45)}\) : A picture of an axi-symmetric drop resting on the desired substrate is taken using light or X-ray. The surface or interfacial tension is calculated from the curvature of the drop, which results from the balance of surface or interfacial tension and the pressure difference across the interface.

2. Drop detachment method\(^{(46-48)}\) : A drop of metal is formed at the tip of a capillary submerged in the liquid. The change in the recorded weight, \(W\), at the point of detachment of the drop is related to the interfacial tension by the formula

\[
\gamma_{s/m} = \frac{W}{2\pi r \psi}
\]  

(3.14)

where \(\gamma_{s/m}\) is the interfacial tension between the metal and salt, \(r\) is the radius of orifice in the capillary and \(\psi\) is a correction factor, which can be obtained from tabulated or plotted values in literature\(^{(49-52)}\).

3. Drop pressure method\(^{(53-54)}\) : Metal drops are formed inside the liquid through a hollow needle. The pressure required to form the drops is related to the interfacial tension.

4. Capillary depression method\(^{(55)}\) : When a capillary tube is immersed into a wetting liquid, the liquid rises or depresses to a certain height. Interfacial
tension is calculated by examining the liquid-liquid interface formed in the capillary tube.

5. Pin detachment method\(^{56,57}\): The interfacial tension is determined from the measurement of the force required to detach a rod from the interface.

3.2.2 Interfacial tension between aluminum and salts

The interfacial tension between aluminum and salts has been measured by several researchers. Zhemchuzina et al.\(^{58}\) measured the dependence of the interfacial tension between aluminum and cryolite on the variation of NaF/AlF\(_3\) ratio. They measured the influence of dissolved alumina in molten cryolite on the interfacial tension as well. The dependence of the interfacial tension on NaF/AlF\(_3\) ratio has been studied by Gerasimov and Belyaev\(^{59}\), Dewing and Desclaux\(^{60}\), Utigard and Toguri\(^{61}\), Jing et al.\(^{62}\) and Fan\(^{63}\).

Dewing and Desclaux\(^{60}\) proposed that the lowering of the interfacial tension between aluminum and the salt due to an increase in the NaF/AlF\(_3\) ratio is related to adsorption of sodium at the interface. Utigard and Toguri\(^{61}\) proposed that the activity of the metal in equilibrium with aluminum and the surface tension of the pure metal are two important factors which determine whether the addition of metal halide increases or decreases the interfacial tension. Utigard et al.\(^{64}\) calculated surface concentrations using surface chemical potentials and incorporated Girifalco and Good's equation\(^{65}\) in their model to calculate interfacial tension values.
between the molten aluminum and cryolite melt. Changes in interfacial
tension in the aluminum-cryolite system with the variation in the ratio of
NaF/AlF₃ are explained by the sodium enrichment in the aluminum-
cryolite interface. Figure 3.6 shows the variation of interfacial tension
between aluminum and the salt as a function of sodium activity together
with experimental results(66). The dotted vertical line represents the cryolite
composition. Jing et al.(62) have measured the interfacial tension between
liquid aluminum and molten salt using the sessile drop method combined
with X-ray radiography. They discussed the influence of the ratio of
NaF/AlF₃, the content of Li₂CO₃ and rare earth oxides in molten salt on the
interfacial tension between aluminum and the salt. Fan(63) has measured
interfacial tension between molten aluminum and cryolite using the pin
detachment method in the temperature range 1000-1100 °C. The mole ratio of
NaF/AlF₃ was varied between two and five and the alumina content was
varied between zero % and alumina content at saturation.

Interfacial tensions between aluminum and salts based on NaCl-KCl
with additions of halides have been measured by Martin-Garin et al.(67),
Kurdyumov et al.(68) and Ho(69). Martin-Garin et al.(67) measured the
interfacial tension with the addition of NaF, KF, LiF and cryolite in equimolar
NaCl-KCl at 740 °C. The interfacial tension decreased for all the additions in
the following order : cryolite < LiF < NaF < KF as shown in Figure 3.7.
Interfacial tension between aluminum and equimolar NaCl-KCl is less than
the surface tension of aluminum at 740 °C. Ho(69) measured the interfacial
tension with the addition of NaF, KF, LiF, CaF₂, MgF₂, AlF₃, cryolite, LiCl,
and CaCl₂ in equimolar NaCl-KCl at 740 °C. Figure 3.8 shows the interfacial
tension between aluminum and equimolar NaCl-KCl with the addition of
NaF, KF, LiF, CaF$_2$ and MgF$_2$ and Figure 3.9 shows the interfacial tension between aluminum and equimolar NaCl-KCl with the addition of LiCl and CaCl$_2$ at 740 °C (69). Additions of sodium fluoride and potassium fluoride were found to be the most effective in lowering interfacial tension. Addition of aluminum fluoride was found to be the least effective in lowering of interfacial tension among all fluoride additions. Additions of metal chlorides were not effective in lowering the interfacial tension.

3.3 CONTACT ANGLE

The contact angle, a measure of wettability, is defined as the angle between the tangent at the three-phase contact line and the solid surface. When the contact angle is 0° then the liquid is said to be completely wetting, and when the contact angle is 180°, then it is called completely non-wetting. When the contact angle of less than 90°, the liquid is called partially wetting, and for a contact angle of greater than 90°, it is called partially non-wetting. Young (22) linked the contact angle to surface energetics in 1805 and in 1878 Gibbs (70) developed the basic thermodynamics of wetting. Figure 3.10 shows a liquid drop resting on a solid. A free liquid drop tries to minimize the free energy by changing its shape. In the absence of gravity, minimization of the free energy of the system requires a minimization of the sum

$$G = \gamma_{lv} S_{lv} + \gamma_{sv} S_{sv} + \gamma_{sl} S_{sl}$$

(3.15)

where \(\gamma\) is the surface or interfacial tension, \(S\) is area and the subscripts \(lv, sv\) and \(sl\) refer to liquid-vapor, solid-vapor and solid-liquid, respectively. Gibbs (70) showed that minimizing the free energy for a plane, homogeneous and nondeformable surface leads to the following equation
Figure 3.6  Interfacial tension between aluminum and cryolitic melts as a function of sodium activity at 1000 °C(66)

1- theoretical curve by Utigard and Toguri(66)
2- data from Dewing and Desclaux(60)
3- data from Gerasimov and Belyaev(59)
4- data from Utigard and Toguri(61)
Figure 3.7 Interfacial tension between aluminum and equimolar NaCl-KCl with the addition of NaF, KF, LiF and cryolite at 740 °C (67)
Figure 3.8  Interfacial tension between aluminum and equimolar NaCl-KCl with the addition of NaF, KF, LiF, CaF$_2$ and MgF$_2$ at 740 °C$^{(69)}$
Figure 3.9 Interfacial tension between aluminum and equimolar NaCl-KCl with the addition of LiCl and CaCl$_2$ at 740 °C\(^{(69)}\)
\[ \gamma_{lv} \cos \theta = \gamma_{sv} - \gamma_{sl} \quad (3.16) \]

where \( \theta \) is the contact angle between the solid and liquid. The assumption of nondeformable surface is unrealistic, and therefore the vertical components of interfacial tension forces shown in Figure 3.10 do not balance. Equation (3.16) is known as the Young-Dupre equation. The contact angle is the result of a balance between cohesive forces in the liquid and adhesive forces between the solid and the liquid. Thus the contact angle is a measure of the interaction between the solid and the liquid.

When a liquid drop is resting on another denser liquid, a liquid lens forms as shown in Figure 3.11. Minimization of the free energy in this case leads to Neumann's relation given by equation (3.19).

\[ \gamma_{12}^2 = \gamma_{1v}^2 + \gamma_{2v}^2 - 2 \gamma_{2v} \gamma_{1v} \cos \alpha \quad (3.19) \]

where \( \gamma \) is the surface or interfacial tension, subscripts 12, 1v, 2v refer to liquid 1-liquid 2, liquid 1-vapor, liquid 2-vapor, respectively, and \( \alpha \) is the visible contact angle.

### 3.3.1 Effect of gravity

A liquid drop resting on a solid flattens under the action of gravity. The liquid drop displays a curvature, which is described by Laplace equation given by equation (3.20)

\[ \Delta P = \gamma_{lv} \left( \frac{1}{R_1} + \frac{1}{R_2} \right) \quad (3.20) \]
Figure 3.10  A liquid drop resting on a solid substrate

Figure 3.11  A liquid drop resting on another denser liquid
where $\Delta P$ is the pressure difference across a point on the surface, $\gamma_{lv}$ is the surface tension and $R_1, R_2$ are radii of curvature. Gibbs showed that minimization of the free energy still leads to Young-Dupre equation.

### 3.3.2 Work of adhesion

Work of adhesion is the reversible work required to separate a unit area of liquid from a solid. When a unit area of solid is separated from the liquid, then a unit area of solid-vapor interface and a unit area of liquid-vapor interface is created and a unit area of solid-liquid interface disappears. Thus the work of adhesion, $W_a$, is given by the expression

$$W_a = \gamma_{lv} + \gamma_{sv} - \gamma_{sl} \tag{3.21}$$

or, using the Young-Dupre equation (3.15),

$$W_a = \gamma_{lv} (1 + \cos\theta) \tag{3.22}$$

### 3.3.3 Work of cohesion

The work of cohesion is the reversible work required to separate a unit area of liquid from itself. Work of cohesion, $W_c$, is a good measure of molecular interactions in the liquid and is given by the following expression:

$$W_c = 2 \gamma_{lv} \tag{3.23}$$

The work of adhesion and the work of cohesion can be related to contact angle by the following equation:

$$\cos\theta = 2 \left( \frac{W_a}{W_c} \right) - 1 \tag{3.24}$$
which shows that the contact angle is the result of a balance between cohesive forces in the liquid and adhesive forces between the solid and the liquid.

3.3.4 Contact angle measurement

The following methods can be used to measure contact angle.

1. Sessile drop (74-76): Sessile drop method is currently the most widely used method to measure the contact angle and is the most convenient method to measure contact angle if a high degree of accuracy is not required. Accuracy of this method is claimed to be 2° (77). The contact angle may be measured by using a telescope equipped with a goniometer eyepiece or from a photograph. If the drop size is very small (< 10⁻⁴ ml) so that the gravitational effect is negligible, then it can be shown that

\[ \frac{2h}{\Delta} = \tan(\theta/2) \]  

(3.25)

where h is the height of the spherical cap, \( \Delta \) is the base length and \( \theta \) is the contact angle.

2. Vertical rod method (78): A vertical rod or plate is partially immersed in the liquid and the contact angle is measured directly from the liquid profile. The contact angle may be measured by using a telescope equipped with a goniometer eyepiece. This method is very useful for measurement of contact angle of viscous liquids. This method can lead to large errors, if the rod is thinner than 50\( \mu \) (79).

3. Tensiometric method (80-82): The force exerted on a thin, wettable plate is measured when the plate is brought in contact with the liquid. The force, F, is given by following equation
\[ F = p \gamma \cos \theta - V \rho g \quad (3.26) \]

where \( p \) is the perimeter of the plate, \( \gamma \) the surface tension of the liquid, \( \theta \) the contact angle, \( V \) the volume of the liquid displaced by the plate and \( \rho \) the density of the liquid. The contact angle can be determined from this force, if the density and surface tension of the liquid are known.

4. Horizontal liquid surface method (83-88): A solid is immersed in the liquid with an inclination so that liquid surface is horizontal up to the three-phase boundary. The solid can be a plate, a cylinder or a sphere. The contact angle is determined from the slope of the solid surface.

5. Capillary method (89,90): When a capillary is immersed in a liquid, there is a rise or depression in the liquid level in the capillary. The contact angle can be calculated from the height of the rise or depression in the liquid level by the following equation

\[ \cos \theta = \frac{hr \rho g}{2\gamma} \quad (3.27) \]

where \( \theta \) is the contact angle, \( h \) the liquid height, \( r \) the capillary radius, \( \rho \) the density of the liquid, and \( \gamma \) the surface tension of the liquid.

6. Interference microscopy (91,92): In certain cases the contact angle can be measured using interference microscopy. There can be several arrangements possible depending on the relative values of the reflectivities of the solid and the liquid. If the reflectivities are comparable, interference fringes can be produced. The contact angle is related to the wavelength, refractive index of the liquid and the separation between dark fringes. This method is suitable for very small drops of liquid with a low contact angle.
3.4 THEORETICAL DETERMINATION OF INTERFACIAL TENSION

Girifalco and Good\(^{(65)}\) derived an equation for the interfacial tension between two liquid phases:

\[
\gamma_{12} = \gamma_1 + \gamma_2 - 2(\gamma_1 \gamma_2)^{1/2}
\]  

(3.28)

where \(\gamma_{12}\) is the interfacial tension between two phases, and \(\gamma_1\) and \(\gamma_2\) are the surface tensions of phases 1 and 2. Equation (3.28) was found to be a good approximation for fluorocarbon-hydrocarbon systems, but failed for other systems. Therefore an interaction parameter, \(\phi\), was introduced in the equation.

\[
\gamma_{12} = \gamma_1 + \gamma_2 - 2 \phi (\gamma_1 \gamma_2)^{1/2}
\]  

(3.29)

If the interaction parameter is close to unity, then the predominant intermolecular forces acting within each phase and between these phases are same. When the intermolecular forces acting in each phase are unlike, e.g. nonpolar vs. polar, or metallic vs. ionic, then low values of the interaction parameter are expected\(^{(93)}\). This interaction parameter can not be evaluated theoretically.

Fowkes\(^{(94)}\) followed a similar approach to Girifalco and Good. He proposed that surface energy of a liquid can be broken up into dispersion, induction and bipolar components, and further assumed that only the dispersion component of surface energy contributes to the interaction between the two phases. Based on these assumptions, Fowkes derived an expression for interfacial tension given by

\[
\gamma_{12} = \gamma_1 + \gamma_2 - 2 (\gamma_1^{d} \gamma_2^{d})^{1/2}
\]  

(3.30)
where \( \gamma_{12} \) is the interfacial tension between the two phases, \( \gamma_1 \) and \( \gamma_2 \) are the surface tensions of phases 1 and 2 and \( \gamma_{1d} \) and \( \gamma_{2d} \) are dispersion components of the surface tensions of phases 1 and 2.

Combining equation (3.21) and equation (3.30), the work of adhesion is given by:

\[
W_a = 2 (\gamma_{1d} \cdot \gamma_{2d})^{1/2}
\]  
(3.31)

Owens and Wendt(95) extended Fowkes' argument to include other intermolecular forces.

\[
W_a = W_{ad} + W_{ah} + W_{ap}
\]  
(3.32)

where \( W_{ad} \) is the work of adhesion due to dispersion forces, \( W_{ah} \) is the work of adhesion due to hydrogen bonding and \( W_{ap} \) is the work of adhesion due to polar interactions

Neumann et al.(96) proposed the surface equation of state theory, which attempts to prove thermodynamically that all liquids having same surface tension will have same contact angle on a given solid. This has been shown to be wrong experimentally(97), because the contact angle depends not only on the surface tension of the liquid, but also on the interaction between the solid and the liquid.

3.5 IMPORTANCE OF SURFACE AND INTERFACIAL TENSION

The role of surface and interfacial tension is very important in many industrial applications. The work of adhesion between two phases defined by equation (3.20) is the energy required to separate these two phases. A decrease
in the work of adhesion promotes the separation of these phases\(^{(98)}\). The importance of surface and interfacial tension is illustrated by the example of floatation, inclusion removal and pigment wetting in following sections.

3.5.1 Floatation

McKenzie, Minto and Devenport\(^{(99)}\) studied the floatation of metal in a slag and defined a film coefficient \(\phi\) and a floatation coefficient \(\Delta\),

\[
\phi = \gamma_{\text{slag/gas}} - \gamma_{\text{metal/slag}} - \gamma_{\text{metal/gas}} \tag{3.33}
\]

\[
\Delta = \gamma_{\text{slag/gas}} + \gamma_{\text{metal/slag}} - \gamma_{\text{metal/gas}} \tag{3.34}
\]

The gas bubble carries an intact metallic film in the slag phase if the film coefficient is positive. The metallic film breaks, but the resulting metallic drops attach to the gas bubble and are floated in the slag, if the floatation coefficient is positive. The metallic film breaks and floatation does not take place, if the floatation coefficient is negative. These three conditions are illustrated in Figure 3.12\(^{(99)}\). Emulsion forms when a large number of metal drops are dispersed in the slag phase, and therefore the emulsion formation is favored by a low value of \(\gamma_{\text{metal/slag}}\) and foam is formed by injection of gas bubbles in the slag and thus foam formation is favored by low value of \(\gamma_{\text{slag/gas}}\).

3.5.2 Inclusion removal

Kozakevitch and Olette\(^{(100, 101)}\) developed the thermodynamics of separation of inclusions from the liquid metal and its assimilation in the slag. For the inclusion to move from the metal phase to the metal-slag interface, the change in free energy is given by,
Figure 3.12 Illustration of mechanisms by which metal is transported in the slag by a rising bubble\textsuperscript{(99)}
\[ \Delta G/S = \gamma_{\text{inclusion/slag}} - \gamma_{\text{metal/slag}} - \gamma_{\text{inclusion/metal}} \] (3.35)

If the inclusion moves from the metal phase to the metal-gas interface, then the change in free energy is given by,

\[ \Delta G/S = \gamma_{\text{inclusion/gas}} - \gamma_{\text{metal/gas}} - \gamma_{\text{inclusion/metal}} \] (3.36)

For removal of the inclusion from the metal-slag interface to the slag phase, the change in free energy is given by,

\[ \Delta G/S = \gamma_{\text{inclusion/slag}} + \gamma_{\text{metal/slag}} - \gamma_{\text{inclusion/metal}} \] (3.37)

and for removal of the inclusion from the metal-gas interface to the slag phase, the change in free energy is given by,

\[ \Delta G/S = \gamma_{\text{inclusion/gas}} + \gamma_{\text{metal/gas}} - \gamma_{\text{inclusion/metal}} \] (3.38)

Thus the free energy change for the removal of the inclusion from the metal phase to the slag phase is given by,

\[ \Delta G/S = 2 \left( \gamma_{\text{inclusion/slag}} - \gamma_{\text{inclusion/metal}} \right) \] (3.39)

The free energy change should be negative for the process to be spontaneous. If the inclusion dissolves in the slag, then the free energy change for removal of the inclusion from metal phase to the slag phase is always spontaneous and simply given by,

\[ \Delta G/S = -2 \gamma_{\text{inclusion/metal}} \] (3.40)
3.5.3 Pigment wetting

Patton(102) has considered the wetting of a solid pigment particle by a liquid. Treating the pigment particle as a cube, Patton considers the wetting of pigment particle in three stages as shown in Figure 3.13. The first stage is initial adhesion, when the bottom face of the cube touches the surface of the liquid. The second stage is immersion, in which stage the four sides of the pigment submerge in the liquid and the final phase is spreading over the top of the particle. The change in free energy during these three stages is given by following equations:

\[
\Delta G_1 = \gamma_{\text{solid/liquid}} - \gamma_{\text{liquid/vapor}} - \gamma_{\text{solid/vapor}} \tag{3.41}
\]

\[
\Delta G_2 = 4 (\gamma_{\text{solid/liquid}} - \gamma_{\text{solid/vapor}}) \tag{3.42}
\]

\[
\Delta G_3 = \gamma_{\text{solid/liquid}} + \gamma_{\text{liquid/vapor}} - \gamma_{\text{solid/vapor}} \tag{3.43}
\]

The total change in free energy for submersionge of pigment particle in liquid is given by

\[
\Delta G = 6 (\gamma_{\text{solid/liquid}} - \gamma_{\text{solid/vapor}}) \tag{3.44}
\]

Stage one is normally spontaneous, while stage three is not. Thus penetration of the liquid by the pigment particle is easy; however, complete submersion is not.

3.6 TERNARY INTERFACIAL ENERGY DIAGRAM

A ternary interfacial energy diagram developed by Conochie and Robertson(103) is a graphical presentation of interfacial energy values. The
Figure 3.13 The three stages of pigment wetting (a) initial adhesion (b) immersion (c) spreading (102)
diagram explains the effect of relative values of interfacial energies on the behavior of the system. This ternary interfacial energy diagram for a solid-liquid-gas system and a liquid-gas-liquid system is discussed in the following sections.

3.6.1 Solid-liquid-gas system

Phase 1 is the liquid phase, phase 2 is the gas phase and phase 3 is the solid phase.

Let,

\[ \Sigma = \gamma_{1/3} + \gamma_{2/3} + \gamma_{1/2} \]  \hspace{1cm} (3.45)

\[ x = \gamma_{1/3}/\Sigma, \quad y = \gamma_{2/3}/\Sigma, \quad \text{and} \quad z = \gamma_{1/2}/\Sigma \]  \hspace{1cm} (3.46)

where \( x, y, \) and \( z \) can have a maximum value of one and they are interrelated by equation (3.43):

\[ x + y + z = 1 \]  \hspace{1cm} (3.47)

\( x, y, \) and \( z \) can be plotted on a ternary diagram as shown in Figure 3.14. The Young-Dupre equation can be satisfied in the center of the diagram and lines of constant \( \theta \) can be constructed. In the bottom right hand corner,

\[ \gamma_{2/3} > \gamma_{1/3} + \gamma_{1/2} \]  \hspace{1cm} (3.48)

and therefore the solid phase will disperse in liquid phase. In the bottom left hand corner,

\[ \gamma_{1/3} > \gamma_{2/3} + \gamma_{1/2} \]  \hspace{1cm} (3.49)
Figure 3.14 Ternary interfacial energy diagram for a solid-liquid-gas system (103)
and, solid phase will attempt to move in the gaseous phase. In the center and left-hand corner,

\[ \gamma_{2/3} < \gamma_{1/3} + \gamma_{1/2} \]  

(3.50)

and floatation occurs in this region.

3.6.2 Liquid-gas-liquid system

Phase 1 is the denser liquid phase, phase 2 is the gas phase and phase 3 is another liquid phase. Consider a drop of phase 3 resting at phase 1 as in top of Figure 3.15. The quantities x, y, and z are defined from equation (3.45) to equation (3.47). The following relations exist between the three interfacial tensions.

\[ \gamma_{2/3} = \frac{\gamma_{1/3} \cos \theta + \gamma_{1/2}}{2} \]  

(3.51)

and,

\[ \gamma_{2/3} \sin \theta = \gamma_{1/3} \sin \phi \]  

(3.52)

which can be rewritten as

\[ 1 - x - y = y \cos \theta + x \cos \phi \]  

(3.53)

and,

\[ y \sin \theta = x \sin \phi \]  

(3.54)

Equation (3.53) and (3.54) can be rearranged to give,

\[ \cos \theta = \frac{(x + y - x y - y^2 - 0.5)}{[y(x + y - 1)]} \]  

(3.55)
\[
\cos \phi = \frac{1 - x - (1 + \cos \theta) y}{x}
\]  
(3.56)

There are four limiting combinations for \( \theta \) and \( \phi \).

1. \( \theta = 0^\circ \) and \( \phi = 0^\circ \). In this case phase 3 spreads between phase 1 and phase 2.
   \[ x + y = 0.5 = z \]  
(3.57)

2. \( \theta = 0^\circ \) and \( \phi = 180^\circ \). In this case phase 3 is dispersed in phase 1.
   \[ y = 0.5 \]  
(3.58)

3. \( \theta = 180^\circ \) and \( \phi = 0^\circ \). In this case phase 3 is dispersed in phase 2.
   \[ x = 0.5 \]  
(3.59)

4. \( \theta = \phi \). In this case phase 3 is in equal contact with phase 1 and phase 2.
   \[ x = y \]  
(3.60)

Figure 3.15 shows the ternary interfacial energy diagram with the four boundaries given by equations (3.57) to (3.60). Within the boundaries, \( x, y \) and \( z \leq 0.5 \), \( \theta \) and \( \phi \) have values between \( 0^\circ \) and \( 180^\circ \). When \( \theta < \phi \), floatation occurs as phase 3 is predominantly outside the bubble. When \( \theta > \phi \), phase 3 is predominantly inside the bubble, and this condition has been termed "ball contact". Outside the boundaries, \( x, y \) and \( z \leq 0.5 \), three phase contact is energetically unfavorable, as one of the interfacial energies is greater than sum of other two interfacial energies. When \( x > 0.5 \), the phase 1-phase 3 interface disappears and phase 1 balls up inside the phase 3 bubble. When \( y > 0.5 \), phase 2-phase 3 interface disappears and phase 3 is dispersed in phase 1.
Figure 3.15 Ternary interfacial energy diagram for a liquid-liquid-gas system (103)
When \( z > 0.5 \), the phase 1-phase 2 interface disappears and phase 3 forms a film between phase 1 and phase 2.

3.7 ADSORPTION

The surface tension and interfacial tension of liquid metals can be changed drastically by a small amount of addition of solute, if the solute is surface active, i.e. adsorbs at the surface preferentially. The relation of surface tension to adsorption is described in the following sections.

3.7.1 Gibbs Adsorption Equation

Gibbs derived the following expression for the adsorption of a solute on the interface, which is known as the Gibbs adsorption equation.

\[
\Gamma^S = -\frac{1}{RT} \left( \frac{\partial \gamma}{\partial \ln a} \right)_T
\]  

(3.61)

where \( \Gamma^S \) is the surface excess of solute per unit area, \( \gamma \) is the surface tension of the solution and \( a \) is the thermodynamic activity of the solute. From equation (3.61), the surface tension of a solution decreases with addition of the solute, if the solute is adsorbed at the surface. On the other hand, the surface tension of a solution increases if the solute is depleted from the surface. The Gibbs adsorption equation is the basis of most of the adsorption measurements in liquid solutions.

3.7.2 Langmuir's Isotherm

Langmuir assumed that a surface has a number of well-defined sites, which can be occupied by only one atom of the surface active species and there is no mutual interaction between the adsorbed species. Based on these
assumptions, Langmuir derived the following expression relating the thermodynamic activity of surface active species to the adsorption of the species at the surface.

\[ \theta = \frac{K_a}{1 + K_a} \]  

(3.62)

where \( \theta \) is the fraction of surface area occupied by solute, \( K \) is a constant and \( a \) is the activity of the solute. At infinite dilution, the activity is very small and equation (3.62) can be written as

\[ \theta = K_a \]  

(3.63)

At high concentrations \( K_a \gg 1 \) and \( \theta = 1 \), i.e. surface active species occupies all the available sites.

3.7.3 The Szyszkowski equation

Gibbs adsorption equation (3.61) can be combined with Langmuir's isotherm (3.62) to obtain the following equation

\[ \gamma^P - \gamma = RT \Gamma^O \ln(1 + K_a) \]  

(3.64)

where \( \gamma^P \) is the surface tension of pure solvent and \( \Gamma^O \) is the surface coverage at saturation with solute. Equation (3.64) is known as Szyszkowski equation, empirically found in 1908(104).

3.7.4 Fowler and Guggenheim model

Fowler and Guggenheim(105) made the same assumptions as Langmuir, except that the adsorbed atoms were allowed to interact with each other and derived the following relation between activity and adsorption
where $Z$ is the number of nearest neighbors within the surface layer and $\omega$ is equal to the regular solution parameter $u_{12} - 1/2 (u_{11} + u_{22})$, with $u_{ij}$ being the bonding energy between atoms $i$ and $j$. The Gibbs adsorption equation (3.62) can be combined with equation (3.65) to yield

$$
\frac{(\gamma_P - \gamma)}{RT} \Gamma^0 = -\ln(1-\theta) - \frac{(Z\omega/kT) \theta^2}{2}
$$

(3.66)

3.7.5 Utigard's Model

Utigard\(^{(106)}\) derived the following expression for surface tension of a multicomponent system

$$
\gamma = \frac{\Sigma (\theta_i \gamma_i / \Gamma_i)}{\Sigma (\theta_i / \Gamma_i)}
$$

(3.67)

where $i$ refers to component $i$. Equation (3.67) relates the surface tension of the mixture to the surface tension of individual species and the fraction of surface area occupied by that species. From equation (3.67) the surface tension can be lowered considerably if a species having low surface tension occupies the surface area preferentially.

3.8 STRUCTURE OF MOLTEN SALTS

Molten salts are ionic liquids, but their physical properties are similar to other liquids in some aspects, e.g. ionic liquids and water have comparable surface tension and viscosity. However, the melting point and the electrical conductivity of ionic liquids are many orders of magnitude higher than that of water. Ionic liquids are composed mostly of ions. The main difference between the structure of ionic liquids and molecular liquids arises from the
fact that oppositely charged ions will remain in nearest-neighbor shells in ionic liquids and therefore a locally ordered arrangement is found in ionic liquids. There are many models to describe the structure of ionic liquids.

3.8.1 The Quasi-Lattice (or Vacancy) Model

After melting, the molar volume of ionic liquids increases by 10-30%. X-ray studies of ionic liquids have found that the internuclear distance remains constant and the coordination number decreases, but local order is maintained after melting (107). The quasi-lattice model seeks to explain these facts by assuming a structure which is similar to a crystal lattice, but the lattice contains a large number of vacancies in a way that no long-range order is maintained. The number of vacancies reflects the increase in volume after melting.

3.8.2 The Hole Model

The hole model assumes the existence of free volume between ionic pairs. The hole model differs from the quasi-lattice model in that the hole model does not assume the existence of a lattice in the liquid and holes, whose size depends on surface tension of liquid, arise due to density fluctuations.

3.8.3 The Significant Structures Model

This model is similar to the quasi-lattice model; however vacancies as well as dislocations are introduced upon melting of ionic liquids. The motion of particles is considered to be of two types: solid-like particles moving in a
3.9 VISCOSITY

Viscosity is the property of a fluid which characterizes its flow behavior. The measurement of viscosity is of considerable importance. Viscosity finds application in diverse fields: flow of liquid in pipelines, bearings, spraying, injection molding, extrusion, surface coating, mixing, heat transfer etc. To obtain a measure of viscosity, a hypothesis about the mechanism of fluid flow was needed. Newton provided such a hypothesis in Principia, a book dealing with analytical and experimental study of the resistance to motion of solids through fluids. Newton's hypothesis can be expressed in mathematical form by the following equation

\[ \tau = -\eta \frac{dv}{dx} \]  

(3.68)

where \( \tau \) is the shear stress, \( \frac{dv}{dx} \) is the velocity gradient and the constant of proportionality, \( \eta \), is the viscosity coefficient, dynamic viscosity or simply the viscosity of the fluid. The physical dimensions of viscosity are \([\text{ML}^{-1}\text{T}^{-1}]\). The unit of viscosity in C.G.S. is \(\text{gm.cm}^{-1}\text{sec}^{-1}\), which is called poise. The quotient of viscosity by density is called kinematic viscosity, which has the dimensions \([\text{L}^2\text{T}^{-1}]\). The unit of kinematic viscosity in cgs. is \(\text{cm}^2\text{sec}^{-1}\), which is called a stoke. The reciprocal of viscosity is known as fluidity.

Fluids that follow the relationship given by equation (3.68) are called Newtonian fluids, while those fluids that do not follow the relationship are called non-Newtonian. Concentrated suspensions and emulsions are examples of non-Newtonian fluids.
3.9.1 Viscosity measurement

There are four groups of methods to measure viscosity, as presented below:

1. Capillary methods (108-110): These methods are based on Poiseuille principle. Two variations are possible, the vertical capillary method and the horizontal capillary method. Time taken by a liquid to flow from one point to other under the action of gravity or applied pressure is related to the viscosity. Capillary methods have been widely used for clean salts due to simplicity of construction and ease of measurement (111).

2. Concentric Cylinders methods (112,113): Liquid, whose viscosity is to be measured, is kept between two concentric cylinders. Two variations are possible. If the inner cylinder is rotated, torque required to maintain a constant angular velocity is related to viscosity. If the crucible is rotated at constant angular velocity, the torque produced on the inner cylinder is related to viscosity. Below a viscosity of 50 poise, the error increases to about ± 20 %, and therefore this method is not suitable for measurement of viscosity of salts or liquid metals.

3. Oscillational methods (114,115): A disc, sphere or cylinder is oscillated in the liquid. A logarithmic decrement in oscillations is produced due to damping, which is related to viscosity. Calculation of the viscosity involves tedious successive approximations.

4. Falling body methods (116-118): Stoke's law is used to calculate the viscosity of a liquid using a freely falling sphere or a restrained sphere. The major experimental difficulty at high temperatures is the timing of the fall. These
methods are suitable for relatively viscous liquids and not suitable for molten salts(119).

3.9.2 Viscosity of Molten Salts

The viscosity of most molten salts is between $0.5$ to $5$ centipoise. For measurement of the viscosity of molten salts, capillary methods and oscillation methods have been widely used. Bloom et al.\(^{120}\) first applied the vertical capillary method to measure the viscosity of salts. The system investigated was a binary mixture of cadmium chloride and cadmium bromide. The results obtained matched very well with those obtained by the oscillating sphere method. Poignet and Barbier\(^{121}\) have measured the viscosity of molten salts using a capillary viscometer.

The viscosities of mixtures of metal chlorides have been measured by several researchers. Zuca and Borgan\(^{122}\) investigated LiCl-KCl, LiCl-RbCl, LiCl-CsCl, KCl-RbCl, KCl-CsCl and RbCl-CsCl systems. The viscosities of zinc chloride-based binary molten alkali chloride systems have been measured by Ezima et al.\(^{123}\) using the rotating cylinder method. The viscosity of molten alkali chlorides (NaCl, KCl, LiCl, RbCl and CsCl) has been measured by Brockner et al.\(^{124}\) using the oscillating cylinder method. The viscosity of alkali chlorides has been measured by Ejima et al.\(^{125}\) using capillary viscometer. The viscosity of alkali chlorides has been measured by Dumas et al.\(^{126,127}\) as well. Ballouki et al.\(^{128}\) measured the viscosity of NaCl-KCl, NaCl-LiCl, KCl-LiCl binary system and NaCl-KCl-LiCl ternary system using vertical capillary method. The viscosity of a mixture of LiCl, KCl, RbCl and CsCl has been measured by Thomas et al.\(^{129}\) at 266 °C and 277 °C using the
vertical capillary method. The viscosity of the four component eutectic was 48.72 cP at 266 °C, which is an order of magnitude higher than expected.

The viscosity of eutectic LiF-NaF-KF melt has been measured by Toerklep and Oeye (130) using the oscillating cylinder method as a function of temperature. The result can be expressed by \( \eta = 1.633 \exp(-2762.9 T^{-1} + 3.1095 \times 10^6 T^{-2}) \). The viscosity of molten alkali fluorides has been measured by Ejima et al. (131) using the oscillating vessel viscometer. LiF and KF show the highest and the lowest values of viscosity respectively at their melting points.

The viscosity of Na₃AlF₆-Al₂O₃ melts has been measured by Abramov et al. (132), Desclaux and Rolin (133), Votava and Matiasovsky (134) and Toerklep and Oeye (135). Viscosity of the melt increased sharply with increase in oxide concentration in these melts.

Sully et al. (7) measured the effect of plate-like \( \gamma\text{-}\text{Al}_2\text{O}_3 \) on the viscosity of the 90 % NaCl-10 % CaF₂ melt using rotating outer-cylinder viscometer. The melt containing 3 % \( \gamma\text{-}\text{Al}_2\text{O}_3 \) was thixotropic, whose viscosity was 68 cP at 20 rpm and decreased to 2.5 cP at 84 rpm. Similar results were obtained for the melt containing 7.7 % \( \gamma\text{-}\text{Al}_2\text{O}_3 \). The viscosity decreased from 470 cP at 13 rpm to 40 cP at 100 rpm. Experiments were also conducted with other types of alumina, bauxilite, ball-milled \( \alpha\text{-}\text{Al}_2\text{O}_3 \) and aloxite. Figure 3.16 shows the effect of the alumina type and the rotational velocity on the viscosity of melt. Only plate-like \( \gamma\text{-}\text{Al}_2\text{O}_3 \) caused the melt to become thixotropic and caused the increased viscosity. Thus the increase in viscosity is related to shape of the alumina particles in the melt.
3.10 DENSITY OF MOLTEN SALTS

The density of single salts has been well documented\(^\text{32}\). Ye\(^\text{136}\) has measured the densities of salts which can be used as flux for recycling aluminum. Figure 3.17 shows the density of equimolar NaCl-KCl with the addition of NaF, KF, LiF and cryolite at 740 °C.

3.11 SOLUBILITY OF ALUMINUM IN SALTS

Arthur\(^\text{137}\) determined the solubility of aluminum in cryolite-alumina melts by analyzing rapidly quenched samples of the melt. The aluminum content was measured by treating the quenched samples with hydrochloric acid and measuring the volume of hydrogen evolved. Addition of alumina decreased the solubility at 1020 °C to 0.081 wt. % with 5 % Al\(_2\)O\(_3\) and to 0.073 wt. % Al in melts saturated with alumina. The solubility in pure cryolite was found to be 0.085 wt. % at 1020 °C.

Sum and Skyllas-Kazacos\(^\text{138}\) used current reversal chronopotentiometry to measure the rate of aluminum dissolution in NaF-AlF\(_3\)-Al\(_2\)O\(_3\) melts. The rate increased as the flow rate of the gas increased but did not depend on chemical activity of the gas (Ar or CO\(_2\)).

Odegard et al.\(^\text{139}\) measured the solubility of aluminum in NaF-AlF\(_3\)-Al\(_2\)O\(_3\) melts with various additives. The solubility of aluminum increased with the increase in the NaF/AlF\(_3\) ratio and decreased with additions of Al\(_2\)O\(_3\), CaF\(_2\), MgF\(_2\) and LiF.
Figure 3.16 Variation of viscosity with rotational velocity and alumina type (7)
Figure 3.17  Density of equimolar NaCl-KCl with the addition of NaF, KF, LiF and cryolite at 740 °C (85)
3.12 SOLUBILITY OF OXIDES IN SALTS

Matiasovsky and Malinovsky\(^{(140)}\) studied the effect of sodium chloride addition on the properties of cryolite-alumina melts. The addition of NaCl lowered the liquidus temperature considerably and increased the electrical conductivity. The solubility of alumina was lowered due to the addition of sodium chloride. A continuous feed of alumina into the electrolyte cell made it possible to keep the alumina concentration in the electrolyte constant between 5-8%.

Shkuryakov et al.\(^{(141)}\) studied the effect of MgF\(_2\) and CaF\(_2\) additions on the solubility of alumina in a cryolite melt. A thermodynamic analysis at 1250 K showed that MgF\(_2\) is more effective in enhancing alumina solubility than CaF\(_2\) in cryolite. The dissolution rate of alumina is also increased by adding MgF\(_2\) to the melt.

Volodin and Danilova\(^{(142)}\) measured the solubility of Al\(_2\)O\(_3\) and SiO\(_2\) in a molten equimolar mixture of NaCl and KCl. Solubilities determined by an isothermal saturation method are given by

\[
\log X_{\text{Al}_2\text{O}_3} = (-950/T) - 1.95 \quad (995-1215 \text{ K})
\]

(3.69)

Alumina was found to react with NaCl by following reaction.

\[
\text{Al}_2\text{O}_3 + 2 \text{NaCl} = 2 \text{AlOCl} + \text{Na}_2\text{O}
\]

(3.70)

Inyushkina et al.\(^{(143)}\) measured the solubility of MgO in a melt of alkali metal chlorides. The solubility varied between 0.5 - 1.5 x 10\(^{-7}\) in NaCl at 850\(^{\circ}\)C.
1100 °C, between 2.0 - 11.8 x 10^{-7} in KCl at 820°-1000 °C and between 1.5 - 31.0 x 10^{-7} in RbCl at 750°-900 °C.

Barsukova and Ivanova(144) measured the solubility of beryllium, aluminum, iron and silicon oxides in NaCl and KCl melts. The isothermal saturation in an Argon atmosphere was used to determine the following solubility values at 900 °C in NaCl and KCl:
Fe_2O_3: 0.0036 and 0.0051 % and SiO_2: 0.0018 and 0.0017 %
Fe_2O_3 solubility increased by a factor of 10 with an increase of temperature to 1100 °C
SiO_2 solubility increased by 1.5 with an increase of temperature to 1100 °C
Al_2O_3: 10^{-6} % at 900°-1100 °C and BeO: 10^{-4} % at 900°-1100 °C

Inman et al.(145) conducted a potentiometric study of alumina solubility and the influence of complexing by fluoride ions in LiCl-KCl. The solubility of alumina was increased by the addition of F^- and from a plot of the log of solubility of alumina vs. F^- concentration, extrapolated to zero, the solubility of alumina in pure LiCl-KCl at 500 °C was estimated to be about 3 x 10^{-6} mol/L. Equilibrium potential measurements showed that complexing by F^- tended to reach a limit as the concentration of F^- was increased. As a consequence, the solubility of alumina also seemed to reach a limit with increasing concentration of F^-.

3.13 CHEMICAL REACTIONS

Masson and Taghiei(146) reported that KMgF3 or K_2NaAlF_6 was formed at the interface of Al-Mg alloy and NaCl-KCl-10 % KF. It is not clear whether formation of KMgF3 or K_2NaAlF_6 results from reaction of salt with
metal or with oxide. Schamm et al. (147) reported that deposition of K2ZrF6 on SiC facilitated the infiltration of liquid Al by disrupting and dissolving the oxide layer. The alumina film covering aluminum was disrupted due to reaction of K2ZrF6 with alumina to form "6KF-4AlF3". Moriguchi et al. (148) studied the reaction between alumina and different fluorides. Alumina was coated with LiF, NaF, KF or CsF and heated in a furnace. The following reaction was proposed to occur:

\[
6 \text{MF} + 2 \text{Al}_2\text{O}_3 = 3 \text{MAIO}_2 + \text{M}_3\text{AlF}_6
\]

(3.71)

In a similar study by Duke and Miller (149), alumina was coated with NaF, KF, CsF and RbF and heated. Formation of M3AlF6 was observed. The following reaction was proposed to take place between KF and Al2O3:

\[
12 \text{KF} + \text{Al}_2\text{O}_3 = 3 \text{K}_2\text{O} + 2 \text{K}_3\text{AlF}_6
\]

(3.72)

Mobin et al. (150) studied high temperature interactions of metal oxides with NaCl. Dried and powdered NaCl and alumina were mixed in a 1:1 molar ratio and pressed into compact tablets and oxidized at 1100 °C for 24 hours. Constituents identified in the reaction product by XRD analysis were NaCl, Al2O3 and NaAlO2.

3.14 OXIDATION OF ALUMINUM AND ALUMINUM ALLOYS

Aluminum is a very reactive metal, which forms a thin protective oxide layer. Oxide films on aluminum can be produced by exposure to air or by anodizing. Hass (151) stated that the thin oxide film on aluminum stops growth after one month, having attained a thickness of 45 Å at room temperature. The thickness of oxide films formed on various metals at room
temperature is shown in Figure 3.18 (152). A logarithmic growth rate is followed.

The oxidation of aluminum at 350 - 475 °C follows a parabolic rate law, but at 500 - 550 °C, the rate becomes linear (153). Oxide films formed on aluminum are amorphous up to 600 °C and become crystalline above this temperature (154). Impey et al. (155) studied the formation of oxide on molten aluminum at 750 °C. Initially γ-Al2O3 forms on liquid aluminum, which has a cubic spinel structure. Later this oxide transforms to α-Al2O3, which has a rhombohedral structure.

In contrast with aluminum, which oxidizes slowly and forms a protective oxide layer, Al-Mg alloy oxidizes rapidly and forms MgO and MgAl2O4 (156). The oxidation of aluminum containing 2.4 - 8 % Mg was studied by De Brouckere (157). Crystalline γ-Al2O3 formed between 120 - 350 °C. MgO formed preferentially above 350 °C. The films were yellow, brown or black in color. Duplex films consisting of MgO over Al2O3 formed if the alloy was heated at 250 °C first and then heated to 400 °C. An aluminum alloy containing up to 8 % Mg developed a thick film of MgO after melting.

### 3.15 SKIM FORMATION AND METAL LOSS

Generation of skim, the material found floating on a metal bath, is inevitable during melting of aluminum or during molten metal transfer. The appearance of skim varies from that of a thickened metallic layer to a nonmetallic layer (158). When Al scrap is melted, the amount of skim generated is much greater than what can be accounted for by oxidation. A large amount of metal is trapped in the oxide layer, which prevents it from
Figure 3.18 Thickness of oxide films formed on various metals at room temperature (152)
joining the metal bath. The incorporation of metal inside the oxide layer
gives rise to the formation of skim.

Stewart et al. (159) studied the metal loss during melting of Al alloys.
Figure 3.19 shows the effect of thickness of Al alloy AA 1100 on metal loss. As
is evident from the Figure 3.19, metal loss increases rapidly as the thickness of
alloy decreases. The increase in metal loss results from an increase in surface
area to volume ratio. Metal loss increased with increased magnesium content
as well. Coatings on Al scrap also increased metal loss.

Rossel (1) studied the effect of scrap thickness, alloying element, time
and temperature on metal loss. Metal loss increased exponentially with
decrease in scrap thickness. Higher temperatures and longer melting times
increased metal loss as well. Metal loss increased for alloys containing Mg.
Figure 3.20 shows the effect of alloying element on metal loss. Ye (160)
measured the metal loss in ternary salts based on equimolar NaCl-KCl. An
increase in metal loss was correlated with a decrease in interfacial tension
between metal and salt.

3.16 COALESCENCE OF METAL DROPS IN SALT FLUX

In general, coalescence is comprised of two processes, the collision of
droplets and the removal of the thin layer of fluid between the droplets (161).
The effect of salt flux additives on aluminum drop coalescence was studied by
Peterson (2). A reflective furnace was used to heat a quartz sample tube
containing 50 grams of salt. The salt solutions contained 5 weight % ternary
salt additions to 50 weight % NaCl and 50 weight % KCl binary. The salt was
melted and 5 grams of aluminum shot, of approximately 1-2 mm diameter
Figure 3.19 Effect of alloy thickness on metal loss (159)
Figure 3.20  Effect of alloying element on metal loss$^{(1)}$
was added to the molten salt flux. The time required for coalescence in a single pool was noted. After 10 minutes, the furnace was shut off. For the case of no addition to NaCl and KCl, Al droplets did not coalesce. However, this flux coalesces Al in industrial process due to stirring and mixing of the salt, which results in disruption of the oxide film. The coalescence was poor in chloride salts, but all the fluoride salts improved coalescence to some extent. Based on the degree of coalescence and the speed of coalescence, the salts were divided in three categories: superior, good and moderate. Peterson explained that the coalescence ability of the salt did not match the ability of the salt to reduce interfacial tension between Al and salt. The coalescence ability of the salt could not be correlated well with the free energy of formation of the oxides. Peterson suggested that the coalescence ability of the salt is probably related to the solubility of alumina in the salt. Johnston and Peterson(8) studied the effect of magnesium on coalescence ability of salt. They found that formation of oxides increased in the presence of magnesium, which increased the flux density and decreased the recovery.

Van Linden and Stewart(12) studied the effect of addition of fluoride salts on the coalescence of metal drops. 200 grams of salt was melted and 100 gram of AA5182 chips were added in small increments. The salt was frozen after the final addition. Coalescence increased with increasing fluoride concentration up to 10 wt. % fluoride addition at 760-800 °C. At 760 °C, coalescence decreased for greater than 10 wt. % addition of MgF₂ or CaF₂, but remained constant for NaF and KF. Between 3-10 wt. % addition of fluorides, coalescence was slightly better for NaF and KF than MgF₂ or CaF₂ at 760 °C. Figure 3.21 shows these results.
Figure 3.21  Effect of fluoride concentration and temperature on recovery (12)
Chapter IV

EXPERIMENTAL METHODS

Several properties of the metal-oxide-salt system were measured during the course of this research. Experimental methods used for these measurements are described in this chapter. The specifications of the materials used in the experiments conducted are listed in Table 8.

4.1 INTERFACIAL TENSION MEASUREMENT

The methods to measure interfacial tension have been described in section 3.2.1. The drop detachment method was used to measure the interfacial tension between the UBC alloy and molten salt. This method was used initially for the measurement of surface tension of organic liquids\(^{(49)}\). Later this method was applied for the measurement of interfacial tension between steel and slags by El Gammel et al.\(^{(46)}\). Figure 4.1 shows the forces acting on a detaching drop: the interfacial tension force \((F_i)\), the gravitational force \((F_g)\) and the buoyancy force \((F_b)\). The weight of the drop is supported by the interfacial tension force. The drop detaches from the orifice when the interfacial tension force can not support the weight of the drop. Therefore, at the point of detachment, an equilibrium is reached between interfacial
Table 8  Materials used in experiments

<table>
<thead>
<tr>
<th>Materials</th>
<th>Specifications</th>
<th>Provider</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure Al</td>
<td>99.999%</td>
<td>Alcoa</td>
</tr>
<tr>
<td>UBC alloy</td>
<td>1.91 % Mg, 0.79 % Mn</td>
<td>Alcoa</td>
</tr>
<tr>
<td></td>
<td>0.16 % Si, 0.35 % Fe</td>
<td></td>
</tr>
<tr>
<td>NaCl</td>
<td>Reagent grade</td>
<td>Jenneil Chem.</td>
</tr>
<tr>
<td>KCl</td>
<td>Reagent grade</td>
<td>Jenneil Chem.</td>
</tr>
<tr>
<td>NaF</td>
<td>Reagent grade</td>
<td>J. T. Baker</td>
</tr>
<tr>
<td>KF</td>
<td>Reagent grade</td>
<td>Aldrich</td>
</tr>
<tr>
<td>LiF</td>
<td>Reagent grade</td>
<td>Aldrich</td>
</tr>
<tr>
<td>CaF₂</td>
<td>Reagent grade</td>
<td>Aldrich</td>
</tr>
<tr>
<td>MgF₂</td>
<td>Reagent grade</td>
<td>Aldrich</td>
</tr>
<tr>
<td>Na₃AlF₆</td>
<td>Reagent grade</td>
<td>Aldrich</td>
</tr>
<tr>
<td>AlF₃</td>
<td>Reagent grade</td>
<td>Aldrich</td>
</tr>
<tr>
<td>LiCl</td>
<td>Reagent grade</td>
<td>J. T. Baker</td>
</tr>
<tr>
<td>CaCl₂</td>
<td>Reagent grade</td>
<td>J. T. Baker</td>
</tr>
<tr>
<td>MgCl₂</td>
<td>Reagent grade</td>
<td>J. T. Baker</td>
</tr>
</tbody>
</table>
Figure 4.1 Forces acting on a drop detaching from the orifice
tension force, the gravitational force, and the buoyancy force. The expression for these forces is given by the following equations:

\[ F_i = 2 \pi r \gamma_{m/s} \]  \hspace{1cm} (4.1)  
\[ F_g = V \rho_m g \]  \hspace{1cm} (4.2)  
\[ F_b = V \rho_s g \]  \hspace{1cm} (4.3)  

where, \( r \) is the radius of the orifice, \( \gamma_{m/s} \) the interfacial tension between the metal and salt, \( V \) the volume of the metal drop, \( \rho_m \) the density of metal, \( \rho_s \) the density of salt, and \( g \) the acceleration due to gravity. Above formulation is valid, when the metal drop does not wet the capillary. When the metal drop wets the capillary, \( r \) is the outer radius of the capillary.

At the point of detachment,

\[ F_i = F_g - F_b \]  \hspace{1cm} (4.4)  
\[ \text{or,} \quad 2 \pi r \gamma_{m/s} = V (\rho_m - \rho_s) g \]  \hspace{1cm} (4.5)  

Figure 4.2 shows a typical drop weight vs. time curve during formation and detachment of a drop. Section (a) denotes the period before the formation of the drop. Weight reading is constant before the formation of the drop, and is equal to the weight of crucible with salt, crucible stand and weight of submerged capillary. Section (b) corresponds to the formation and growth of the drop and section (c) corresponds to the detachment of the drop. \( W_1 \) is the change in weight during formation and growth of the drop and \( W_2 \) is the change in weight of the drop at the point of detachment. Change in weight of the drop at the point of detachment is given by,
Figure 4.2  Typical drop weight vs. time curve during formation and detachment of a drop
\[ W_2 = V (\rho_m - \rho_s) g \]  

(4.6)

Thus,

\[ \gamma_{s/m} = \frac{W_2}{2\pi r} \]  

(4.7)

However, equation (4.7) needs a correction due to the fact that a small portion of the drop remains attached to the orifice after the drop has detached. Harkins and Brown\(^{49}\) performed refined calculations to show that surface tension can be calculated correctly by applying a correction factor to equation (4.7)

\[ \gamma_{s/m} = \frac{W_2}{2\pi r \psi} \]  

(4.8)

where \( \psi \) is a correction factor dependent on the value of drop volume, radius of the orifice and density of molten metal. The value of correction factor can be obtained from tabulated or plotted values in the literature\(^{49-52}\).

Figure 4.3 shows the schematic of the apparatus used for this study. Prepurified Ar gas was passed through a copper chip furnace operating at 550 °C to remove residual oxygen. Salts were dried for more than 24 hours at 450 °C in furnace and mixed in the required proportion. Salt of the given composition was melted in a quartz crucible. The quartz crucible does not react with salts to a significant extent\(^{1}\). A gold-plated resistance heated furnace was used for this purpose, which became semi-transparent at the experimental temperature of 740 °C. A Keithley TRMS 179A multimeter for millivolt reading of the K-type thermocouple output and an electronic icepoint for temperature measurement were used to ensure precision.
Figure 4.3  Schematic of apparatus used for interfacial tension measurement

a. Copper furnace,  b. Boron nitride tube/capillary
c. Quartz crucible/holder, d. furnace, e. balance
temperature reading. The quartz crucible was fitted on a holder, which was placed on a sensitive electronic balance. The electronic balance was placed on a Jiffy Jack. During the experiment, a boron nitride capillary containing UBC alloy was lowered into the molten salt. This boron nitride capillary was connected to a boron nitride tube by a boron nitride linkage unit. Prepurified argon gas was blown through boron nitride tube and boron nitride linkage unit over molten UBC alloy in boron nitride capillary to maintain an inert atmosphere. After the UBC alloy was melted in the boron nitride capillary, molten UBC alloy droplet formed at the orifice. The weight data from the balance was fed to an IBM-PC during the formation and detachment of the drop and recorded on a floppy disk. The formation and detachment of the metal drop was observed through the semi-transparent furnace. After the experiment, the quartz crucible was lowered by lowering the Jiffy Jack, so that the boron nitride capillary was no longer touching the crucible and the furnace was switched off. Interfacial tension was calculated using Equation (4.8).

4.2 MEASUREMENT OF Na AND K CONTENT OF METAL

Thirty grams of following mixed salts were dried for more than 24 hours at 450 °C: equimolar NaCl-KCl and equimolar NaCl-KCl containing 5 wt. % NaF. The salts were melted in the quartz crucible, and a solid Al sample weighing approximately 1.0 gram was immersed in the molten salt at 740 °C and left for 4 hours. Subsequently, crucible was quenched in water. The salt was washed and Al was separated. Solid Al was mounted using phenolic resin and polished. The sample was analyzed for sodium and potassium content using Electron Microprobe Analysis (EMPA). In Electron Microprobe
Analysis, the sample is bombarded with electrons to generate X-rays. The concentration of the elements is estimated from the wavelength and the intensity of the lines in the X-ray spectrum. The sensitivity of Electron Microprobe Analysis is of the order of 10 ppm. Two samples were prepared for each salt and sodium and potassium contents in Al were measured at three different points selected at random.

4.3 CONTACT ANGLE MEASUREMENT

The methods to measure contact angle have been described in section 3.3.4. The sessile drop method was used to measure the contact angle between aluminum and alumina immersed in molten salt. The measurement of the contact angle consists in taking a picture of an aluminum droplet resting on an alumina layer immersed in molten salt, scanning and analyzing the picture.

Figure 4.4 shows the experimental setup. The Al₂O₃ single crystal and the crucible were rinsed with acetone and dried for 12 hours at 450 °C. The salts were also dried for same period. The alumina single crystal was placed at the bottom of crucible then covered with the flux. The crucible was put in a furnace at 800 °C till the salt flux melted. The temperature was then set at 740 °C. An Al sample weighing about 1.0 gram was immersed in the liquid flux. The pictures of the immersed droplet were taken when the metal was melted for 30 minutes. A scanner from Hewlett Packard (ScanJet IIC) and a Macintosh IIci were used for scanning the photographs and storing the scanned image. Software named Image was used for image processing and measurement of contact angle. Scanned image was first thresholded. The aim of thresholding
Figure 4.4  Set-up for contact angle measurement

Figure 4.5  Measurement of contact angle
is to change the scanned image to a binary format, the drop becoming completely black, while the surrounding are completely white. Contact angle was measured on the thresholded image manually as shown in Figure 4.5.

4.4 VISCOSITY MEASUREMENT

The methods to measure viscosity have been described in section 3.9.1. To measure the viscosity of molten salts, a gravity-type capillary viscometer made of quartz was used. For a gravity-type viscometer, kinematic viscosity can be related to time for flow of a fixed volume of liquid by the following equation (162):

\[ v = A t - B / t \]  

(4.9)

The constants A and B are determined by observing the times of flow of two or more liquids of known kinematic viscosity. Surface tension correction is not critical for glass capillary viscometers, because it is less than 1% of the viscosity value (163). A solution of KOH and water was used for this purpose. Since a capillary of shorter length is convenient for the experiments, capillaries of three different lengths (25 cm, 15 cm, and 11 cm) were used to check whether the variation of viscosity with time followed equation (4.9). The following five solutions were used: water, and 10, 20, 30, and 40 wt. % KOH. To determine the values of constants A and B, equation (4.9) can be rewritten as

\[ \nu t = A t^2 - B \]  

(4.10)

Values of "\( \nu t \)" were plotted against "t^2" for five solutions and a line of best fit was drawn through these points. The slope of the line is A and the
intercept is B. A good fit between 5 points was obtained for all three capillary lengths and hence the capillary of length 11 cm was chosen for further experiments. Figure 4.6 shows the plot of "vt" vs. "t^2" for the capillary of length 11 cm. With the constants A and B known, the viscometer was used to measure the kinematic viscosity of molten salts. Figure 4.7 shows the experimental setup. To measure the time of flow, three tungsten wires were kept in the molten salt and a potential of 0.5 V was applied using a potentiostat. A standard resistor was added to the electrical circuit and the voltage across the standard resistor was measured using a multimeter. When the salt touched the wires, current flowed through the circuit and a non-zero reading was displayed on multimeter. When salt level dropped below the lower end of wire, current stopped flowing and reading on multimeter became zero. The time for flow of a fixed volume of salt was measured using a stop-watch.

4.5 DENSITY MEASUREMENT

The density of the salts was measured using Archimedean method. The density of salt, ρ, is given by

\[ ρ = [(W_A - W_S) + S]/[(V + v)g] \]  

(4.11)

where \( W_A \) and \( W_S \) are the weight of sinker and immersed wire in air and salt, respectively, \( S \) the surface tension correction, \( V \) the volume of sinker, \( v \) the volume of immersed wire and \( g \) the acceleration due to gravity.

The sinker (alumina rod) and wire were weighed in air and in distilled water to determine the volume of sinker and immersed wire. Figure 4.8 shows the experimental setup for measurement of density. Salts were dried in
Figure 4.6 Variation of "vt" with "t²" for KOH solutions

\[ y = -66.890 + 1.2999 \times 10^{-2} x \quad R^2 = 0.999 \]
Figure 4.7  Schematic of apparatus used for viscosity measurement
Figure 4.8  Schematic of apparatus used for measurement of density
the furnace for 24 hours at 450 °C. Salt of the desired composition was melted in a quartz crucible. A gold-plated resistance heated furnace was used for this purpose, which became semi-transparent at the experimental temperature of 740 °C. The quartz crucible was fitted on a holder, which was placed on a Jiffy Jack. Sinker and wire were suspended from the balance. Sensitivity of the balance was 0.001 gram. The crucible and holder were raised by raising the jack until the sinker was immersed completely in salt. Reading on the balance decreased sharply as the sinker was immersed in salt. Once the sinker was completely inside the salt, further change in weight was negligible when the jack was raised slowly. This reading was recorded as the weight of sinker and immersed wire in salt. Equation (4.11) was used to calculate the density of the salts.

4.6 COALESCEENCE TEST

Figure 4.9 illustrates the test for coalescence of metal drops in salts. Salts were dried in furnace for 24 hours at 450 °C. Salt of desired composition was melted in a quartz crucible with a round bottom to ensure that chips were in contact inside the molten salt. The following salts were used: equimolar NaCl-KCl or equimolar NaCl-KCl containing 5 wt. % of MX, where MX was one of the following salts: LiCl, CaCl₂, MgCl₂, NaF, KF, LiF, MgF₂, CaF₂, Na₃AlF₆, and AlF₃. The weight of salt was 20 grams; 100 Al or UBC alloy chips weighing about 2.0 grams total were charged into the molten salt. Salts containing the charge were frozen after specific time intervals. The time interval varied between one minute to several hours. Salts were rinsed and
Figure 4.9  Test for coalescence of metal drops in salts
coalescence behavior of aluminum drops was analyzed by counting the number of drops.

4.7 STUDY OF OXIDE REMOVAL USING INTERFERENCE MICROSCOPY

The oxide layer on aluminum is transparent, so it can not be observed in an ordinary light microscope\(^{(163)}\). However, stripping of the oxide layer can be studied using interference microscopy. A partially detached oxide film can be seen by means of interference fringes developed by the gap between oxide and metal. Jordan and Milner\(^{(5)}\) have studied the removal of oxide from Al by fluxes used in welding.

The study of oxide removal from Al by salts was done using an interference microscope. A "Carl Zeiss" interference microscope was used for examining the interference patterns. The interference microscope utilizes interference phenomena of light for observation of surface profile. Figure 4.10 shows the schematic surface of a specimen, and Figure 4.11 shows the corresponding interference fringe pattern\(^{(164)}\). Monochromatic light produced by thallium lamp was used for producing the interference. The wavelength of the monochromatic light was 5400 Å. Interference bands are produced by superimposing the monochromatic light beams reflected from the specimen and a standard mirror.

An Al sample was cut and ground to 120 grit followed by grinding at 240, 320, 400, and 600 grit. Then the sample was electropolished using a mixture of perchloric acid and ethanol as the electrolyte. A beaker was kept in an ice bath, because the temperature of electrolyte should not exceed 25 °C. Temperature was continuously monitored while perchloric acid was slowly
Figure 4.10 Schematic profile of the surface (164)

Figure 4.11 Interference fringe pattern corresponding to the profile in figure 4.9 (164)
added to ethanol. 50 ml of perchloric acid was added to 250 ml of ethanol, and
the electrolyte was stirred by a magnet during electropolishing. The Al sample
polished to 600 grit was used as anode and a steel sheet was used as cathode.
Electropolishing was done at 10 volts. The electropolished Al sample was
oxidized in furnace at 500 °C for 15 hours. An interference pattern from
electropolished and oxidized Al sample was observed. Subsequently, Al
samples were immersed in equimolar NaCl-KCl for 1.5 minutes and in
equimolar NaCl-KCl containing 5 wt. % NaF for 0.5, 1.5, 2.5, and 3.5 minutes at
740 °C. The samples were washed in hot water after immersion in salt.
Interference pattern was observed on surface of sample without any further
surface preparation. Interference photographs were taken for all the samples
except the sample immersed in salt for 3.5 minutes. The sample immersed for
3.5 minutes melted and changed shape during the immersion.

4.8 METAL LOSS MEASUREMENT

UBC alloy samples were weighed before the experiment. Salts were
dried in the furnace for 24 hours at 450 °C. Salt of the desired composition
was melted in an alumina crucible. The weight of salt was 30 grams. UBC
alloy samples were charged into the molten salt. Salts containing the charge
were frozen after six hours. Salts were rinsed and UBC alloy drops were
recovered. The UBC alloy drops were weighed subsequently on an electronic
balance. The difference in weight of UBC alloy before and after the
experiment is the metal loss in the salt.
Chapter V

RESULTS AND DISCUSSION

5.1 INTERFACIAL TENSION

Interfacial tension between UBC alloy and salts of varying composition based on equimolar NaCl-KCl ratio was measured as a function of various additives. Figures 5.1 to 5.3 show the variation of interfacial tension as a function of wt. % halide addition in equimolar NaCl-KCl. Results varied up to ±10% from average value. For equimolar NaCl-KCl, the interfacial tension measured was 511 mN/m and this value decreased sharply as NaF or KF was added. The value of interfacial tension between pure aluminum and equimolar NaCl-KCl was found to be 710 mN/m by Ho and Sahai (165). The surface tension of Al decreases sharply as magnesium is added to it. At 700 ºC, the surface tension of Al alloy drops by more than 200 mN/m for the addition of about 1.9 wt. % Mg (166). The observed difference in interfacial tension between Al/salt and UBC/salt is the result of the relatively lower surface tension of the UBC alloy compared to surface tension of pure Al. However, the adsorption of sodium and potassium at the interface of UBC alloy and equimolar NaCl-KCl salt may also contribute to this.
Figure 5.1 Variation of interfacial tension between UBC alloy and salt as a function of additives in equimolar NaCl-KCl salt solution
Figure 5.2  Variation of interfacial tension between UBC alloy and salt as a function of additives in equimolar NaCl-KCl salt solution
Figure 5.3  Variation of interfacial tension between UBC alloy and salt as a function of LiCl in equimolar NaCl-KCl salt solution
Figure 5.4 shows the variation of interfacial tension between pure aluminum and salt containing equimolar NaCl-KCl and NaF as a function of wt. % NaF added. The reason for variation of interfacial tension between pure Al and equimolar NaCl-KCl can be understood in terms of activity of sodium in the system. Dewing and Desclaux first proposed that sodium acts as a surface active element and adsorbs at the interface between Al and cryolite on the basis of interfacial tension measurements. Interfacial tension was found to decrease as the NaF/AlF₃ ratio increased. Utigard et al. have developed a model based on Girifalco and Good's equation, which relates interfacial tension to the activity of the surface active element. The calculated values of interfacial tension are in good agreement with the experimentally measured values. As the activity of sodium increases, fractional surface coverage of sodium at the interface also increases. This results in a decrease in the interfacial tension between aluminum and cryolite as NaF/AlF₃ ratio increases. For the case of pure aluminum in equilibrium with equimolar NaCl-KCl, the activity of sodium is governed by the following equilibrium

\[ 3 \text{NaCl} + \text{Al} = \text{AlCl}_3 + 3 \text{Na}, \]  

(5.1)

with the equilibrium constant at 740 °C,

\[ K_{eq} = 8.34 \times 10^{-24} \]  

(5.2)

\[ a_{\text{Na}} = K_{eq}^{1/3} \left( \frac{a_{\text{NaCl}}}{(a_{\text{AlCl}})_3} \right)^{1/3} \]  

(5.3)

where the activity of aluminum is omitted since it is near unity. The value of the equilibrium constant was calculated from the JANAF thermochemical tables. The amount of sodium in aluminum can be estimated from
Figure 5.4  Variation of interfacial tension between Al and salt as a function of NaF in equimolar NaCl-KCl salt solution\(^{(69)}\)
equations (5.1) to (5.3) using an activity coefficient for sodium in aluminum of 405 at 740 °C (168). The activity coefficient of sodium chloride and aluminum chloride is assumed to be one. Based on equation (5.1), the mole fraction of sodium is assumed to be three times the mole fraction of aluminum chloride. Then, from equation (5.3), the mole fraction of sodium in aluminum is calculated to be $1.4 \times 10^{-8}$.

The activity of potassium is governed by the equilibrium:

$$3 \text{ KCl} + \text{Al} = \text{AlCl}_3 + 3 \text{ K},$$ (5.4)

with the equilibrium constant at 740 °C,

$$K_{eq} = 3.28 \times 10^{-27}$$ (5.5)

$$a_K = K_{eq}^{1/3} \left[ a_{\text{KCl}} / (a_{\text{AlCl}_3})^{1/3} \right]$$ (5.6)

The activities of sodium and potassium both are extremely low in this case, and it can be assumed that adsorption of sodium or potassium does not take place to a significant extent. The validity of this assumption is discussed below.

The interfacial tension can be related to surface tension of the constituent phases by Girifalco and Good's equation (65)

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2\phi(\gamma_1\gamma_2)^{1/2}$$ (5.7)

where $\gamma_1$ is the surface tension of phase 1, $\gamma_2$ is the surface tension of phase 2, $\gamma_{12}$ is the interfacial tension between the two phases and $\phi$ is a constant characteristic of the system. Utigard et al. (64) have used the value of $\phi = 0.41$.
for the interfacial tension between aluminum and cryolite. Here the same value of $\phi = 0.41$ is assumed for the interfacial tension between aluminum and equimolar NaCl-KCl, because $\phi$ is a function of intermolecular forces acting between the two phases and type of intermolecular forces acting in cryolite and equimolar NaCl-KCl are similar. The surface tension of aluminum is 886 mN/m at 740 °C (169) and surface tension of equimolar NaCl-KCl is 106 mN/m at 740 °C (170). Substituting these values in equation (5.7), the value of 740 mN/m is obtained. This matches reasonably well with the experimentally measured value of 710 mN/m by Ho and Sahai (165). Thus the assumption that the adsorption of sodium or potassium does not take place to a significant amount in aluminum/equimolar NaCl-KCl appears valid.

Consider the system aluminum/equimolar NaCl-KCl with the addition of NaF. When NaF is added to equimolar NaCl-KCl, the activity of sodium changes. The activity of sodium is governed by the equilibrium of equation (5.1) and equation (5.8) in the presence of NaF.

$$3 \text{NaF} + \text{Al} = \text{AlF}_3 + 3 \text{Na},$$

(5.8)

$$K_{eq} = 3.90 \times 10^{-9}$$

(5.9)

$$a_{Na} = K_{eq}^{1/3} \left[ a_{NaF} / (a_{AlF_3})^{1/3} \right]$$

(5.10)

The amount of sodium in aluminum can be estimated from equations (5.8) to (5.10). Activity coefficient of sodium in aluminum is 405 at 740 °C (168). The activity coefficients for sodium chloride and aluminum fluoride are assumed to be one. Based on equation (5.8), mole fraction of sodium is assumed to be three times the mole fraction of aluminum fluoride. Then,
from equation (5.10), the mole fraction of sodium in aluminum is calculated to be $1.7 \times 10^{-5}$.

The equilibrium constant for reaction (5.8) is many orders of magnitude higher than the equilibrium constant for reaction (5.1). As a result, the activity of sodium increases by many orders of magnitude and the adsorption of sodium at the interface increases significantly when NaF is added to equimolar NaCl-KCl. The adsorption of sodium is not the only factor that contributes to the observed decrease in interfacial tension. Adsorption of potassium also takes place at the interface, because the activity of potassium is also increased by the following mechanism. NaF reacts with KCl to form KF and NaCl. The KF, in turn, reacts with aluminum to increase the activity of potassium. Thus, following reactions also take place due to addition of NaF in equimolar NaCl-KCl.

$$\text{NaF} + \text{KCl} = \text{NaCl} + \text{KF}$$  \hspace{1cm} (5.11)

$$K_{eq} = [a_{\text{NaCl}} \cdot a_{\text{KF}}] / [a_{\text{NaF}} \cdot a_{\text{KCl}}] = 4.072 \times 10^{-2}$$  \hspace{1cm} (5.12)

and,

$$\text{Al} + 3 \text{KF} = \text{AlF}_3 + 3 \text{K},$$  \hspace{1cm} (5.13)

$$K_{eq} = 2.28 \times 10^{-8}$$  \hspace{1cm} (5.14)

$$a_K = K_{eq}^{1/3} \left[ a_{\text{KF}} / (a_{\text{AlF}_3})^{1/3} \right]$$  \hspace{1cm} (5.15)

The adsorption of sodium and potassium due to the addition of NaF in equimolar NaCl-KCl results in the observed decrease in interfacial tension. As amount of NaF addition increases, activity of sodium and potassium also
increases. Thus fractional surface coverages of sodium and potassium also increase, resulting in further decrease in interfacial tension.

The same principles described above can be applied to understand the variation of interfacial tension between the UBC alloy and equimolar NaCl-KCl as a function of additives. Figure 5.1 shows the variation of interfacial tension between UBC alloy and salt flux as a function of NaF, KF and AlF₃ additions. The activity of sodium and potassium increases most for the additions of NaF and KF, and this results in the decrease in interfacial tension. For AlF₃ addition, adsorption of surface-active elements does not take place to the same extent and interfacial tension decreases by a negligible amount. The activity of surface active elements in case of the UBC alloy/salt system is affected by the equilibrium of other reactions as well. The reactions between Mg and the salt also affect the activity of surface active elements. The following reactions should also be considered for the case of interfacial tension between UBC alloy and equimolar NaCl-KCl in addition to the reactions between aluminum and salt.

\[2 \text{NaCl} + \text{Mg} = \text{MgCl}_2 + 2 \text{Na},\]  
\[K_{eq} = 9.94 \times 10^{-9}\]  
\[a_{\text{Na}} = K_{eq}^{1/2} [a_{\text{NaCl}} x (a_{\text{Mg}})^{1/2}/(a_{\text{MgCl}_2})^{1/2}]\]  

and,

\[2 \text{KCl} + \text{Mg} = \text{MgCl}_2 + 2 \text{K},\]  
\[K_{eq} = 5.34 \times 10^{-11}\]
Since the equilibrium constants for the reactions between Mg and salt are significantly higher than the equilibrium constants for corresponding reactions between aluminum and salt, the activities of Na and K are higher in case of UBC/equimolar NaCl-KCl than in case of pure aluminum/equimolar NaCl-KCl. Thus the difference in interfacial tension between aluminum/equimolar NaCl-KCl and UBC alloy/equimolar NaCl-KCl may not be entirely due to the decrease in surface tension of Al by the addition of Mg, but may also be due to adsorption of sodium and potassium at the interface of UBC alloy and salt.

5.2 SODIUM AND POTASSIUM CONTENT OF ALUMINUM

In the previous section it was described that surface active elements are adsorbed at the interface between metal and salt. It was also stated that adsorption of surface active elements is increased when salt contains fluoride additives. Surface active elements are produced by reaction between metal and salt, and these elements are then distributed at the interface, and metal and salt phases. If adsorption of surface active elements is increased when salt contains fluoride additives, then amount of surface active elements in the metal phase will also be increased. Thus a verification of the proposed mechanism can be performed by analyzing the metal or salt sample.

The sodium and potassium content of aluminum was measured using EMPA. Table 9 shows the amount of sodium and potassium in aluminum after it was charged in equimolar NaCl-KCl and equimolar NaCl-KCl containing 5 wt. % NaF. The amount of sodium and potassium in aluminum
increased ten-fold when the salt contained 5 wt. % sodium fluoride compared to equimolar NaCl-KCl, which is in general agreement with the increased adsorption of sodium and potassium in aluminum in salt containing fluorides. Table 10 compares the experimentally measured amount of sodium in aluminum with calculated values. The discrepancy between measured and calculated values is large for equimolar NaCl-KCl. The reason for this discrepancy could be the pick-up of sodium by the sample during mounting and polishing of the sample.

5.3 COALESCENCE OF ALUMINUM CHIPS

The coalescence ability of salts is a very important factor in selection of salts suitable for use as flux in recycling of aluminum scrap. Better coalescence of metal drops in salt will result in better yield for the process. Coalescence of metal drops results in an increase in resulting drop diameter, which increases the probability of separation of the metal drop from the salt flux. On the other hand, a smaller drop is more likely to be entrapped in salt flux.

The coalescence of aluminum chips in salts based on equimolar NaCl-KCl composition was observed as a function of time to evaluate the coalescence ability of different salts. The following salts were used: equimolar NaCl-KCl or equimolar NaCl-KCl containing 5 wt. % of MX, where MX was one of the following salts: LiCl, CaCl₂, MgCl₂, NaF, KF, LiF, MgF₂, CaF₂, Na₃AlF₆, and AlF₃. All ternary salts showed improved ability to coalesce aluminum drops.
Table 9  
Amount of sodium and potassium in aluminum

<table>
<thead>
<tr>
<th>Salt</th>
<th>equimolar NaCl-KCl</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium (wt. %)</td>
<td>Sample 1</td>
<td>0.018</td>
<td>0.000</td>
<td>0.011</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sample 2</td>
<td>0.003</td>
<td>0.000</td>
<td>0.005</td>
<td></td>
</tr>
<tr>
<td>Average :</td>
<td>0.006 wt. %,</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>standard deviation : 0.006 wt. %</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Potassium (wt. %)</td>
<td>Sample 1</td>
<td>0.015</td>
<td>0.020</td>
<td>0.015</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sample 2</td>
<td>0.000</td>
<td>0.009</td>
<td>0.000</td>
<td></td>
</tr>
<tr>
<td>Average :</td>
<td>0.010 wt. %,</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>standard deviation : 0.008 wt. %</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Salt</th>
<th>equimolar NaCl-KCl- 5 wt. % NaF</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium (wt. %)</td>
<td>Sample 1</td>
<td>0.080</td>
<td>0.070</td>
<td>0.038</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sample 2</td>
<td>0.062</td>
<td>0.071</td>
<td>0.050</td>
<td></td>
</tr>
<tr>
<td>Average :</td>
<td>0.062 wt. %,</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>standard deviation : 0.014 wt. %</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Potassium (wt. %)</td>
<td>Sample 1</td>
<td>0.136</td>
<td>0.081</td>
<td>0.067</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sample 2</td>
<td>0.109</td>
<td>0.133</td>
<td>0.119</td>
<td></td>
</tr>
<tr>
<td>Average :</td>
<td>0.108 wt. %,</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>standard deviation : 0.025 wt. %</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 10  
Comparison of amount of sodium in aluminum

<table>
<thead>
<tr>
<th>Salt</th>
<th>Experimental</th>
<th>Calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(Mole fraction)</td>
<td>(Mole fraction)</td>
</tr>
<tr>
<td>equimolar NaCl-KCl</td>
<td>$7.1 \times 10^{-5}$</td>
<td>$1.4 \times 10^{-8}$</td>
</tr>
<tr>
<td>equimolar NaCl-KCl- 5 wt. % NaF</td>
<td>$7.3 \times 10^{-4}$</td>
<td>$1.7 \times 10^{-5}$</td>
</tr>
</tbody>
</table>
The progress of coalescence in salts based on equimolar NaCl-KCl is shown in Figures 5.5-5.7. Figure 5.5 shows the aluminum chips before they are charged in salt. Figure 5.6 shows the progress of coalescence in salts containing fluorides, while Figure 5.7 shows the progress of coalescence in salts consisting of chlorides only as a function of time. Figure 5.8 shows the number of drops remaining as a function of time for salts consisting of chlorides only.

The end result of charging the metal chips is the formation of a single drop of metal in all salts. However, the time taken for formation of a single drop of metal is significantly different for different salts. Aluminum drops coalesced in salts containing fluorides as well as chlorides, however, the behavior of salts consisting of chlorides only was significantly different from salts containing fluorides. A single pool of aluminum formed in less than two minutes for all salts containing fluorides with the exception of MgF$_2$, which took less than 3 minutes to form a single pool of aluminum. Coalescence in salts consisting of chlorides only took significantly longer time compared to salts containing fluorides. A single pool of aluminum formed in equimolar NaCl-KCl in less than 12 hours.

From these figures, the chips join before they have melted completely in salts containing fluorides, while in salts consisting of chlorides only, chips form individual drops first, then join together in a larger drop. Number of drops keeps decreasing as drops coalesce and increase in size. In salts consisting of chlorides only, the coalescence of metal drops is very slow. Partial coalescence of two metal drops can be seen in Figure 5.7. The reason
Figure 5.5  Aluminum chips before the experiment

Figure 5.6  Coalescence of aluminum drops in NaCl-KCl-5 wt. % NaF
Figure 5.7  Coalescence of aluminum drops in Equimolar NaCl-KCl
Figure 5.8  Progress of coalescence with time in equimolar NaCl-KCl plus addition of chlorides
for the poor coalescence ability of salts consisting of chlorides only is their inability to strip the oxide layer covering the metal.

The results of observation of progress of coalescence of aluminum drops in salt fluxes can be summarized as follows:
1. Coalescence of aluminum drops took place in all salts studied.
2. Complete coalescence in salts containing fluorides took 2-3 minutes, while complete coalescence in salts containing only chlorides took many hours.
3. In salts containing fluorides, all aluminum chips joined together before each chip had individually become a liquid drop.
4. There is no significant difference between the coalescence ability of salts containing various fluorides.
5. In salts containing only chlorides, many individual drops formed, which coalesced as time proceeded.

5.4 COALESCENCE OF UBC ALLOY CHIPS

Progress of coalescence of UBC alloy chips was observed as a function of time in salts based on equimolar NaCl-KCl. Following salts were used: equimolar NaCl-KCl or equimolar NaCl-KCl containing 5 wt. % of MX, where MX was one of the following salts: NaF, KF, LiF, MgF₂, CaF₂, Na₃AlF₆, and AlF₃. The results of coalescence measurement are shown in Tables 11-12 and Figures 5.9-5.12. Figures 5.13-5.16 show the number of drops remaining as a function of time for different salts.

Coalescence of UBC alloy drops was more difficult than coalescence of aluminum drops. UBC alloy contains magnesium, which makes UBC alloy to oxidize more severely than aluminum. Thus UBC alloy is covered with an
Table 11  Coalescence of UBC alloy chips in equimolar NaCl-KCl

<table>
<thead>
<tr>
<th>Time (hrs)</th>
<th># of non-spherical particles</th>
<th># of spherical particles</th>
<th>Total # of particles</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>40</td>
<td>36</td>
<td>76</td>
</tr>
<tr>
<td>24</td>
<td>28</td>
<td>25</td>
<td>53</td>
</tr>
<tr>
<td>48</td>
<td>15</td>
<td>28</td>
<td>43</td>
</tr>
<tr>
<td>72</td>
<td>14</td>
<td>18</td>
<td>32</td>
</tr>
<tr>
<td>96</td>
<td>3</td>
<td>14</td>
<td>17</td>
</tr>
</tbody>
</table>

Table 12  Progress of coalescence of UBC chips in NaCl-KCl with 5 wt. % fluorides as a function of time

<table>
<thead>
<tr>
<th>Fluoride</th>
<th>1 min</th>
<th>2 min</th>
<th>3 min</th>
<th>5 min</th>
<th>10 min</th>
<th>30 min</th>
<th>60 min</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaF</td>
<td>1</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LiF</td>
<td>1</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na₃AlF₆</td>
<td>1</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KF</td>
<td>4</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaF₂</td>
<td>91</td>
<td>71</td>
<td>57</td>
<td>25</td>
<td>6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MgF₂</td>
<td>93</td>
<td>90</td>
<td>83</td>
<td>40</td>
<td>16</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AlF₃</td>
<td>100</td>
<td>99</td>
<td>93</td>
<td>96</td>
<td>95</td>
<td>82</td>
<td>76</td>
</tr>
</tbody>
</table>
Figure 5.9  Coalescence of UBC alloy drops in NaCl-KCl-5 wt. % NaF

Figure 5.10  Coalescence of UBC alloy drops in NaCl-KCl-5 wt. % CaF₂

Figure 5.11  Coalescence of UBC alloy drops in NaCl-KCl-5 wt. % AlF₃
Figure 5.12 Coalescence of UBC alloy drops in Equimolar NaCl-KCl
Figure 5.13  Progress of coalescence of UBC alloy drops as a function of time in equimolar NaCl-KCl
Figure 5.14 Progress of coalescence of UBC alloy drops as a function of time in equimolar NaCl-KCl plus addition of fluorides.
Figure 5.15  Progress of coalescence of UBC alloy drops as a function of time in equimolar NaCl-KCl plus addition of fluorides
Figure 5.16  Progress of coalescence of UBC alloy drops as a function of time in equimolar NaCl-KCl plus addition of NaF/AlF₃
oxide layer that is much thicker than the oxide layer covering aluminum and therefore it is more difficult to strip oxide layer from UBC alloy compared to aluminum.

Extent of coalescence differed for various fluorides used. Complete or nearly complete coalescence was observed for salts containing NaF, KF, LiF and Na₃AlF₆ after 2 minutes, while formation of large number of drops was observed for salts containing MgF₂, CaF₂ and AlF₃. Though coalescence of Al chips was found to be similar for all salts containing fluorides, significant difference was observed for coalescence of UBC alloy chips in different salts containing fluorides. The thick oxide layer on UBC alloy chips is more difficult to strip and the difference in coalescence ability of salts containing fluorides can be seen in the experiments.

It can be seen that coalescence of UBC alloy chips in equimolar NaCl-KCl takes much longer compared to coalescence of Al chips in equimolar NaCl-KCl. What is striking is that UBC chips took a very long time to change their shape to spherical drops. It was also observed that surface of UBC alloy drops looked very dull and rough because surface of UBC alloy drops was covered with a thick layer of oxide. Though UBC alloy drops coalesced as time progressed, the coalescence was extremely slow. The coalescence was not complete even after the UBC alloy chips were immersed in equimolar NaCl-KCl for 96 hours. Thus it can be concluded that salt takes longer time to decrease the strength of oxide layer on UBC alloy than pure Al.

Based on these experiments salts can be classified in four categories depending on their coalescence ability:
1. Excellent: NaF, KF, LiF, Na$_3$AlF$_6$

2. Good: CaF$_2$, MgF$_2$

3. Moderate: AlF$_3$

4. Poor: NaCl-KCl

The results of observation of progress of coalescence of UBC alloy drops in salt fluxes can be summarized as follows:

1. Coalescence of UBC alloy drops took place in all salts studied.

2. Complete coalescence in salts containing NaF, KF, LiF and Na$_3$AlF$_6$ took 2-3 minutes, while complete coalescence in salts containing other fluorides took longer.

3. In salts containing NaF, KF, LiF and Na$_3$AlF$_6$ all UBC alloy chips joined together before each chip has individually become a liquid drop. In other salts, many individual drops formed, which coalesced as time proceeded.

4. There is significant difference between the coalescence ability of salts containing various fluorides as well as between the salts containing fluorides and equimolar NaCl-KCl.

5.5 STUDY OF OXIDE REMOVAL USING INTERFERENCE MICROSCOPY

The study of oxide removal from Al by salts was performed using interference microscopy. Electropolished Al samples were immersed in equimolar NaCl-KCl for 1.5 minutes and in equimolar NaCl-KCl containing 5 wt. % NaF for 0.5, 1.5, and 2.5 minutes. Interference photographs were taken for all samples. Interference patterns from the Al samples are shown in Figures 5.17-5.21.
Figure 5.17  Interference pattern from electropolished Al surface oxidized for 15 hours at 500 °C
Figure 5.18  Interference pattern from electropolished Al surface immersed in equimolar NaCl-KCl for 1.5 minutes at 740 °C
Figure 5.19  Interference pattern from electropolished Al surface immersed in equimolar NaCl-KCl containing 5 wt. % NaF for 0.5 minutes
Figure 5.20  Interference pattern from electropolished Al surface immersed in equimolar NaCl-KCl containing 5 wt. % NaF for 1.5 minutes
Figure 5.21  Interference pattern from electropolished Al surface immersed in equimolar NaCl-KCl containing 5 wt. % NaF for 2.5 minutes
Figure 5.17 shows the interference fringe pattern from an oxidized electropolished aluminum sample. The fringe pattern consists of parallel dark and bright fringes. This type of fringe pattern is characteristic of a plane surface. When the surface is not plane, then the fringes bend. In this case, if the oxide layer is partly stripped from the surface, the fringes will bend.

Figure 5.18 shows the interference pattern from an oxidized electropolished sample immersed in equimolar NaCl-KCl for 1.5 minutes. The fringe pattern consists of parallel lines, which indicates that removal of oxide layer from Al surface has not taken place. The Figure 5.18 also shows cracks formed in the oxide layer due to thermal stresses that generate between aluminum and oxide due to heating.

The interference fringe pattern from sample immersed in equimolar NaCl-KCl containing 5 wt. % NaF for 0.5 minutes is shown in Figure 5.19. Al sample was coated with solidified salt, when the sample was taken out of salt. When the Al sample is immersed in the salt, the salt first solidifies around the sample and then starts to melt as temperature of sample increases. The interference pattern from this sample shows set of parallel lines, which indicates that removal of the oxide layer from the Al surface has not started. Once the salt has melted around Al sample, then the oxide layer is stripped from the surface rapidly. This can be seen from the interference patterns from the sample immersed in equimolar NaCl-KCl containing 5 wt. % NaF for 1.5 minutes as seen in Figure 5.20. The interference pattern from sample immersed in equimolar NaCl-KCl containing 5 wt. % NaF for 2.5 minutes shows that the stripping of the oxide layer is still in progress as seen in Figure 5.21. Thus the removal of the oxide layer from the Al surface does not take
place in equimolar NaCl-KCl, while removal of oxide layer from Al surface in equimolar NaCl-KCl containing 5 wt. % NaF is very rapid and part of the oxide layer is removed even before aluminum has completely melted. This is in agreement with the observation of progress of coalescence in salts consisting of chlorides and salts containing fluorides.

5.6 PROCESS OF OXIDE REMOVAL AND COALESCENCE

The aluminum alloy is covered with a thin layer of oxide, and the oxide layer is compact and strong prior to being charged in salt. When the metal inside the oxide layer melts, it tends to assume its equilibrium shape of a sphere. However, the oxide layer restricts this deformation. Aluminum expands due to melting. Change in volume on melting of aluminum is between 5.71-7.59 % (171). The oxide layer is weakened by expansion in volume of aluminum due to melting and chemical attack by the salt. When the oxide layer is no longer compact, the metal can deform to spherical shape even though the oxide layer is attached to it at several places.

The process of oxide removal from the Al alloy drops can be understood by the mechanism proposed by Jordan and Milner (5). When Al alloy covered with thin layer of oxide is charged in the salt, oxide layer is stripped by a three-step process as shown in Figure 5.22.

1. Openings develop in oxide layer

2. Salt penetrates between oxide and metal

3. Oxide layer is stripped.
Process of oxide removal

Oxide layer is compact before charging

Openings develop in oxide layer due to chemical attack or crack formation

Strength decreases, drop becomes spherical

Oxide is stripped as salt penetrates between metal and oxide

Figure 5.22 Process of oxide removal
There are three important time intervals determining the progress of coalescence.

1. Time for melting of metal chip ($t_m$)

2. Time for weakening of strength of oxide layer ($t_w$)

3. Time for stripping of significant fraction of oxide layer ($t_s$)

The progress of coalescence of Al and UBC alloy chips in different salts can be illustrated by the relative values of these three time intervals.

5.6.1 Coalescence of Al drops in Fluorides

In this case, the coalescence of drops is very fast. The progress of coalescence is illustrated by Figure 5.23 in this case. Aluminum chips join together before the chips have melted completely. Thus in this case, the oxide layer has weakened and a significant fraction of oxide layer has been stripped even before the chips have melted completely. The following relation holds between the three time intervals

$$t_w, t_s < t_m \quad (5.22)$$

5.6.2 Coalescence of aluminum drops in chlorides

In this case coalescence of drops is very slow. Chips melt completely and form metal drops and then these drops keep coalescing with progress of time. Progress of coalescence is illustrated by Figure 5.24 in this case. Oxide layer is not stripped to a significant extent in this case, but cracks develop due to thermal stresses. When drops come into contact, they start coalescing with
the metal inside the oxide layer joining along the cracks. Coalescence is favored by a decrease in free energy due to the reduction in surface area. Thus melting of metal chips is faster than stripping of the oxide layer and

\[ t_m' t_w < t_s \]  \hspace{1cm} (5.23)

5.6.3 Coalescence of UBC alloy drops in fluorides

Coalescence of UBC alloy drops in salts containing 5 wt. % of NaF, KF, LiF and Na₃AlF₆ was found to be very fast and therefore \( t_w, t_s < t_m \) for these salts. The process of coalescence proceeds as in Figure 5.23. For salts containing MgF₂, CaF₂, and AlF₃, multiple drops formed, which coalesced with the progress of time. Process of coalescence proceeds as in Figure 5.25 and in this case,

\[ t_m' t_w < t_s \]  \hspace{1cm} (5.24)

5.6.4 Coalescence of UBC alloy drops in chlorides

From Figures 5.12, UBC alloy chips could not deform to spherical shape even after being immersed in molten salts for many hours. The reason for this behavior is that the molten metal inside is being restricted from assuming a spherical shape by a tenacious oxide layer. Thus time for weakening the oxide layer is large in this case. The process of coalescence proceeds as in Figure 5.24. For coalescence of UBC alloy drops in equimolar NaCl-KCl,

\[ t_m < t_w < t_s \]  \hspace{1cm} (5.25)
Process of coalescence

(1) Oxide + Metal with partially detached oxide layer

Metal with partially detached oxide layer

Figure 5.23  Process of coalescence
Process of coalescence

(2) Metal coated with oxide + Metal coated with oxide

Metal coated with oxide

Figure 5.24 Process of coalescence (continued)
Process of coalescence

Metal drops with partially detached oxide layer

Oxide

Metal with partially detached oxide layer

Figure 5.25 Process of coalescence (continued)
5.7 CONTACT ANGLE AND WORK OF ADHESION

The results of measurements of contact angle between aluminum and salt flux of different compositions using single crystal alumina are shown in Table 13. Results varied up to ± 5° from the average value.

Alumina-salt interfacial tension for different salts can be calculated from these results using equation (5.26), provided that interfacial tension between aluminum and alumina as well as interfacial tension between aluminum and salt is known.

\[ \gamma_{\text{Al/alumina}} + \gamma_{\text{Al/salt}} \cos \theta = \gamma_{\text{alumina/salt}} \]  

(5.26)

where \( \gamma_{\text{alumina/salt}} \) is the interfacial tension between alumina and salt, \( \gamma_{\text{Al/alumina}} \) is the interfacial tension between Al and alumina, \( \gamma_{\text{Al/salt}} \) is the interfacial tension between Al and salt, and \( \theta \) is the contact angle between Al and alumina.

Interfacial tension between Al and salt has been measured by Ho and Sahai (165). Interfacial tension between aluminum and alumina can be calculated from equation (5.27).

\[ \gamma_{\text{Al/alumina}} + \gamma_{\text{Al}} \cos \theta = \gamma_{\text{alumina}} \]  

(5.27)

where \( \gamma_{\text{alumina}} \) is the surface tension of alumina, \( \gamma_{\text{Al}} \) is the surface tension of Al, and \( \theta \) is the contact angle between Al and alumina in vacuum. Surface tension of alumina compiled from various sources by Impey et al. (38) is shown in Figure 3.3. Surface tension of alumina is estimated as 1520 mN/m at 740 °C from Figure 3.3. The contact angle between molten Al and alumina
Table 13  Contact angle between aluminum and alumina in salt flux

<table>
<thead>
<tr>
<th>Salt flux</th>
<th>Contact angle (degrees)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equimolar NaCl-KCl</td>
<td>132</td>
</tr>
<tr>
<td>Equimolar NaCl-KCl</td>
<td>134</td>
</tr>
<tr>
<td>+ 1 wt. % sodium fluoride</td>
<td></td>
</tr>
<tr>
<td>Equimolar NaCl-KCl</td>
<td>138</td>
</tr>
<tr>
<td>+ 1 wt. % Cryolite</td>
<td></td>
</tr>
<tr>
<td>Equimolar NaCl-KCl + 1 wt. % aluminum fluoride</td>
<td>140</td>
</tr>
<tr>
<td>Equimolar NaCl-KCl</td>
<td>132</td>
</tr>
<tr>
<td>+ 1 wt. % potassium fluoride</td>
<td></td>
</tr>
<tr>
<td>Equimolar NaCl-KCl</td>
<td>132</td>
</tr>
<tr>
<td>+ 1 wt. % lithium fluoride</td>
<td></td>
</tr>
<tr>
<td>Equimolar NaCl-KCl</td>
<td>134</td>
</tr>
<tr>
<td>+ 1 wt. % calcium fluoride</td>
<td></td>
</tr>
</tbody>
</table>
in vacuum is 99° (172). Surface tension of Al is 886 mN/m at 740 °C (30). The interfacial tension between Al and alumina is thus calculated to be 1659 mN/m at 740 °C. The calculated value of interfacial tension between alumina and salt are shown in Table 14.

The change in free energy due to oxide film removal based on Sully's criterion (7) is given by equation 5.28.

$$\Delta G = S \left( \gamma_{\text{metal/flux}} + \gamma_{\text{oxide/flux}} - \gamma_{\text{metal/oxide}} \right)$$ \hspace{1cm} (5.28)

Equation 5.28 has been used to calculate the change in free energy per unit area for alumina film removal in various fluxes as shown in Table 15. From Table 15, the free energy change for oxide removal is positive for all salts and does not show a wide range of variation for different salt fluxes. Thus interfacial tension considerations alone are not sufficient to explain the observations relating to coalescence ability of salt fluxes containing fluorides. Another way to look at the data of interfacial tension is the construction of a ternary interfacial energy diagram. Consider aluminum as phase 1, salt as phase 2 and alumina as phase three.

Let,

$$\Sigma = \gamma_{\text{metal/flux}} + \gamma_{\text{oxide/flux}} + \gamma_{\text{metal/oxide}}$$ \hspace{1cm} (5.29)

$$x = \frac{\gamma_{\text{metal/flux}}}{\Sigma}$$

$$y = \frac{\gamma_{\text{oxide/flux}}}{\Sigma}$$

$$z = \frac{\gamma_{\text{metal/oxide}}}{\Sigma}$$ \hspace{1cm} (5.30)
Table 14  Interfacial tension in aluminum, alumina and salt system

<table>
<thead>
<tr>
<th>Salt flux</th>
<th>$\gamma_{Al/salt}$ $^{(mN/m)}$</th>
<th>$\gamma_{Alumina/salt}$ $^{(mN/m)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equimolar NaCl-KCl</td>
<td>710</td>
<td>1183</td>
</tr>
<tr>
<td>Equimolar NaCl-KCl</td>
<td>659</td>
<td>1201</td>
</tr>
<tr>
<td>+ 1 wt. % sodium fluoride</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Equimolar NaCl-KCl +</td>
<td>686</td>
<td>1149</td>
</tr>
<tr>
<td>+ 1 wt. % Cryolite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Equimolar NaCl-KCl + 1 wt. %</td>
<td>706</td>
<td>1118</td>
</tr>
<tr>
<td>aluminum fluoride</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Equimolar NaCl-KCl</td>
<td>624</td>
<td>1241</td>
</tr>
<tr>
<td>+ 1 wt. % potassium fluoride</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Equimolar NaCl-KCl</td>
<td>686</td>
<td>1200</td>
</tr>
<tr>
<td>+ 1 wt. % lithium fluoride</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Equimolar NaCl-KCl</td>
<td>681</td>
<td>1186</td>
</tr>
<tr>
<td>+ 1 wt. % calcium fluoride</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 15  Free energy change for oxide removal

<table>
<thead>
<tr>
<th>Salt flux</th>
<th>Free energy change per unit area (mJ/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equimolar NaCl-KCl</td>
<td>234</td>
</tr>
<tr>
<td>Equimolar NaCl-KCl + 1 wt. % sodium fluoride</td>
<td>201</td>
</tr>
<tr>
<td>Equimolar NaCl-KCl + 1 wt. % Cryolite</td>
<td>176</td>
</tr>
<tr>
<td>Equimolar NaCl-KCl + 1 wt. % aluminum fluoride</td>
<td>165</td>
</tr>
<tr>
<td>Equimolar NaCl-KCl + 1 wt. % potassium fluoride</td>
<td>206</td>
</tr>
<tr>
<td>Equimolar NaCl-KCl + 1 wt. % lithium fluoride</td>
<td>227</td>
</tr>
<tr>
<td>Equimolar NaCl-KCl + 1 wt. % calcium fluoride</td>
<td>208</td>
</tr>
</tbody>
</table>
x, y and z can have a maximum value of one and they are related by equation (5.31)

\[ x + y + z = 1 \]  \hspace{1cm} (5.31)

The values of x, y and z for different salts are given in Table 16. Figure 5.26 shows the ternary interfacial energy diagram for aluminum-salt-alumina system. Line AB corresponds to contact angle of 0° and line BC corresponds to contact angle of 180°. The region BCZ represents the region in which oxide film removal is spontaneous.

All the points corresponding to different salts are very close. These are shown by a single point O in Figure 5.26. Although the point O falls in the region where oxide film removal is not spontaneous, it is very close to the boundary where oxide film removal becomes spontaneous. Thus only a small amount of energy is needed to remove the oxide layer.

5.8 MECHANISM OF OXIDE REMOVAL

The solubility of alumina in salts is considerable in fluorides and negligible in chlorides. Salts consisting of chlorides only were found to be least effective in coalescing aluminum drops, and salts containing different fluorides were found to be highly effective. For many years it was thought that salts actually dissolved the oxide to produce the desired result. For this reason West(4) decided to measure the solubility of alumina in different fluxes to evaluate the efficiency of these fluxes. To his surprise, West(4) found that alumina was virtually insoluble in fluxes, and proposed that the oxide was detached by the formation of volatile aluminum chloride at the oxide
Table 16  Data for ternary interfacial energy diagram

<table>
<thead>
<tr>
<th>Salt flux</th>
<th>x</th>
<th>y</th>
<th>z</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equimolar NaCl-KCl</td>
<td>0.20</td>
<td>0.33</td>
<td>0.47</td>
</tr>
<tr>
<td>Equimolar NaCl-KCl + 1 wt. % sodium fluoride</td>
<td>0.19</td>
<td>0.34</td>
<td>0.47</td>
</tr>
<tr>
<td>Equimolar NaCl-KCl + 1 wt. % Cryolite</td>
<td>0.20</td>
<td>0.33</td>
<td>0.47</td>
</tr>
<tr>
<td>Equimolar NaCl-KCl + 1 wt. % aluminum fluoride</td>
<td>0.20</td>
<td>0.32</td>
<td>0.48</td>
</tr>
<tr>
<td>Equimolar NaCl-KCl + 1 wt. % potassium fluoride</td>
<td>0.18</td>
<td>0.35</td>
<td>0.47</td>
</tr>
<tr>
<td>Equimolar NaCl-KCl + 1 wt. % lithium fluoride</td>
<td>0.19</td>
<td>0.34</td>
<td>0.47</td>
</tr>
<tr>
<td>Equimolar NaCl-KCl + 1 wt. % calcium fluoride</td>
<td>0.19</td>
<td>0.34</td>
<td>0.47</td>
</tr>
</tbody>
</table>
Figure 5.26  Ternary interfacial energy diagram for aluminum-oxide-salt system
metal interface. Mechanism proposed by West\(^4\) is shown in Figure 5.27. However, this explanation is not plausible, because salts consisting of chlorides only are not very efficient in stripping the oxide layer from metal. Also, reaction of aluminum with chlorides is unlikely from free energy consideration. In a work conducted at Alcoa Research Laboratories, alumina windows, produced by stripping away the metal substrate from anodized aluminum samples, were immersed in molten flux\(^6\). No thinning of oxide windows was reported. Thus there remains little doubt that salt fluxes do not dissolve oxide to any appreciable extent.

Sully et al.\(^7\) gave an alternative criterion shown in Figure 5.28 based on interfacial tension characteristics. According to them, the oxide layer was detached from metal, when following criterion was satisfied

\[
\gamma_{\text{metal/flux}} + \gamma_{\text{oxide/flux}} < \gamma_{\text{metal/oxide}} 
\]

which is equivalent to saying that change in free energy due to detachment of oxide from metal, i.e. work of adhesion between metal and oxide, is negative. The change in free energy due to oxide film removal is given by equation 5.33.

\[
\Delta G = S \left( \gamma_{\text{metal/flux}} + \gamma_{\text{oxide/flux}} - \gamma_{\text{metal/oxide}} \right) 
\]

when \(\Delta G\) is negative, equation (5.32) is satisfied. However, measurement of interfacial tension and contact angle has shown that the change in free energy due to oxide film removal is positive for salt fluxes and equation (5.32) is not satisfied by any of the salt fluxes.
Jordan and Milner(5) proposed another mechanism shown in Figure 5.29 for detachment of oxide from metal by salt fluxes. According to their explanation, detachment of oxide from metal is electrochemical in nature with the aluminum acting as an anode, the oxide acting as a cathode and salt flux acting as an electrolyte. Aluminum goes into the solution as Al$^{3+}$ ions undermining the oxide film and salt penetrates between aluminum and oxide. Storchai(173) has also proposed that detachment of oxide film from metal by fluxes is of electrochemical nature.

Terril et al. (6) have suggested that the moisture content of the salt plays an important role in this mechanism. Every molten salt contains chemically combined moisture in varying amount. In salts containing fluorides, fluorides react with dissolved moisture to generate hydrogen fluoride. Hydrogen fluoride penetrates oxide film at weak spots and combines with aluminum to liberate hydrogen and oxide film is removed by the hydrogen.

From the calculation of work of adhesion between aluminum and alumina immersed in molten salt, the work of adhesion is positive. Thus extra energy is needed for the process to be spontaneous. This extra energy is provided by mechanical energy induced by interfacial tension gradient and electrochemical energy due to dissolution of metal in salt(160). Another contribution can result from chemical reactions in the system. Pask et al. (174-175) have proposed that the free energy of the reaction at the interface contributes to the driving force for wetting. However, it is unlikely that chemical reactions contribute to the energy for oxide removal in aluminum-oxide-salt system, which will be evident from the following discussion.
Figure 5.27 Oxide removal mechanism proposed by West

$$\gamma_{\text{Al/Alumina}} > \gamma_{\text{Alumina/Salt}} + \gamma_{\text{Al/Salt}}$$

Figure 5.28 Oxide removal mechanism proposed by Sully et al.

Figure 5.29 Oxide removal mechanism proposed by Jordan and Milner
Table 17 shows the free energy of formation per halide ion of different salts at 1000 K\(^7\). It is clear from table that coalescence ability of salts can not be related to the free energy of formation.

Coalescence ability of salts can not be related to their reactions with oxide either. It is not certain which chemical species are formed when salts react with alumina. Peterson\(^2\) has assumed the formation of AlOF when salts react with alumina. Assuming that AlOCl forms when NaCl reacts with alumina, equations 5.34-5.39 show the reaction and standard free energy of those reactions. The standard free energy of reactions are positive and the order does not correspond to the coalescence ability of corresponding salts.

\[
\begin{align*}
2 \text{NaCl} + \text{Al}_2\text{O}_3 &= 2 \text{AlOCl} + \text{Na}_2\text{O}, \Delta G^0 = +1000 \text{ KJ/mol} \quad (5.34) \\
2 \text{NaF} + \text{Al}_2\text{O}_3 &= 2 \text{AlOF} + \text{Na}_2\text{O}, \Delta G^0 = +835 \text{ KJ/mol} \quad (5.35) \\
2 \text{KF} + \text{Al}_2\text{O}_3 &= 2 \text{AlOF} + \text{K}_2\text{O}, \Delta G^0 = +888 \text{ KJ/mol} \quad (5.36) \\
2 \text{LiF} + \text{Al}_2\text{O}_3 &= 2 \text{AlOF} + \text{Li}_2\text{O}, \Delta G^0 = +750 \text{ KJ/mol} \quad (5.37) \\
\text{MgF}_2 + \text{Al}_2\text{O}_3 &= 2 \text{AlOF} + \text{MgO}, \Delta G^0 = +634 \text{ KJ/mol} \quad (5.38) \\
\text{AlF}_3 + \text{Al}_2\text{O}_3 &= 3 \text{AlOF}, \Delta G^0 = +844 \text{ KJ/mol} \quad (5.39)
\end{align*}
\]

Terril et al.\(^6\) have suggested that salts react with retained moisture to form hydrogen fluoride, which reacts with aluminum to form hydrogen. The corresponding reactions and standard free energy of reactions are shown in equations (5.40) - (5.48). Again the standard free energy of reactions do not match the observed coalescence ability of corresponding salts.
Table 17  Free energy of formation of salts (167)

<table>
<thead>
<tr>
<th>Salt</th>
<th>Free energy of formation per halide ion at 1000 K (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>-319</td>
</tr>
<tr>
<td>KCl</td>
<td>-341</td>
</tr>
<tr>
<td>LiCl</td>
<td>-327</td>
</tr>
<tr>
<td>CaCl$_2$</td>
<td>-321</td>
</tr>
<tr>
<td>MgCl$_2$</td>
<td>-241</td>
</tr>
<tr>
<td>AlCl$_3$</td>
<td>-169</td>
</tr>
<tr>
<td>NaF</td>
<td>-471</td>
</tr>
<tr>
<td>KF</td>
<td>-467</td>
</tr>
<tr>
<td>LiF</td>
<td>-520</td>
</tr>
<tr>
<td>CaF$_2$</td>
<td>-529</td>
</tr>
<tr>
<td>MgF$_2$</td>
<td>-475</td>
</tr>
<tr>
<td>Na$_3$AlF$_6$</td>
<td>-461</td>
</tr>
<tr>
<td>AlF$_3$</td>
<td>-417</td>
</tr>
</tbody>
</table>
\[ 2 \text{NaCl} + \text{H}_2\text{O} = 2 \text{HCl} + \text{Na}_2\text{O}, \Delta G^\circ = +364 \text{KJ/mol} \quad (5.40) \]

\[ 6 \text{HCl} + 2 \text{Al} = 2 \text{AlCl}_3 + 3 \text{H}_2, \Delta G^\circ = -409 \text{KJ/mol} \quad (5.41) \]

\[ 2 \text{NaF} + \text{H}_2\text{O} = 2 \text{HF} + \text{Na}_2\text{O}, \Delta G^\circ = +313 \text{KJ/mol} \quad (5.42) \]

\[ 6 \text{HF} + 2 \text{Al} = 2 \text{AlF}_3 + 3 \text{H}_2, \Delta G^\circ = -829 \text{KJ/mol} \quad (5.43) \]

\[ 2 \text{KF} + \text{H}_2\text{O} = 2 \text{HF} + \text{K}_2\text{O}, \Delta G^\circ = +345 \text{KJ/mol} \quad (5.44) \]

\[ 2 \text{LiF} + \text{H}_2\text{O} = 2 \text{HF} + \text{Li}_2\text{O}, \Delta G^\circ = +236 \text{KJ/mol} \quad (5.45) \]

\[ \text{MgF}_2 + \text{H}_2\text{O} = 2 \text{HF} + \text{MgO}, \Delta G^\circ = +93 \text{KJ/mol} \quad (5.46) \]

\[ \text{CaF}_2 + \text{H}_2\text{O} = 2 \text{HF} + \text{CaO}, \Delta G^\circ = +162 \text{KJ/mol} \quad (5.47) \]

\[ 2 \text{AlF}_3 + 3 \text{H}_2\text{O} = 6 \text{HF} + \text{Al}_2\text{O}_3, \Delta G^\circ = +46 \text{KJ/mol} \quad (5.48) \]

Jordan and Milner\(^{(5)}\) have proposed that the removal of oxide is related to the electrochemical dissolution of aluminum. However, the removal of oxide can be understood based on chemical dissolution of aluminum. When aluminum is charged in salt, metal loss takes place due to displacement reactions described in section 5.1 and due to dissolution of aluminum in salt. Table 18 shows the metal loss of aluminum in different salts measured by Ye\(^{(160)}\). In Table 19, metal loss of UBC alloy in different salts is shown. An increase in metal loss results in better coalescence ability. The coalescence ability of salts matches well with metal loss in the salt. The coalescence ability of salts matches well with the interfacial tension between aluminum and salt as well. Addition of NaF or KF in equimolar NaCl-KCl decreases the interfacial tension the most, and these salts are found to have
excellent coalescence ability. Addition of CaF$_2$ or MgF$_2$ decreases interfacial tension to a lesser degree compared to addition of NaF or KF, and the coalescence ability also decreases. The addition of AlF$_3$ decreases the interfacial tension the least, and the coalescence ability of this salt is also worst among all the fluoride addition. This is not surprising, since interfacial tension is related to metal loss due to displacement reactions as described in section 5.1.

Table 18  Metal loss and coalescence of aluminum drops$^{(160)}$

<table>
<thead>
<tr>
<th>Salt</th>
<th>Metal loss (gram)</th>
<th>coalescence</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equimolar NaCl-KCl</td>
<td>0.001</td>
<td>Poor</td>
</tr>
<tr>
<td>Equimolar NaCl-KCl + 5 wt. % CaCl$_2$</td>
<td>0.002</td>
<td>Poor</td>
</tr>
<tr>
<td>Equimolar NaCl-KCl + 5 wt. % LiCl</td>
<td>0.003</td>
<td>Poor</td>
</tr>
<tr>
<td>Equimolar NaCl-KCl + 5 wt. % NaF</td>
<td>0.015</td>
<td>Good</td>
</tr>
<tr>
<td>Equimolar NaCl-KCl + 5 wt. % KF</td>
<td>0.014</td>
<td>Good</td>
</tr>
<tr>
<td>Equimolar NaCl-KCl + 5 wt. % Cryolite</td>
<td>0.007</td>
<td>Good</td>
</tr>
</tbody>
</table>
Table 19  Metal loss and coalescence of UBC alloy drops

<table>
<thead>
<tr>
<th>Salt</th>
<th>Metal loss (gram)</th>
<th>coalescence</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equimolar NaCl-KCl</td>
<td>0.002</td>
<td>Poor</td>
</tr>
<tr>
<td>Equimolar NaCl-KCl + 5 wt. % MgF&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0.010</td>
<td>Good</td>
</tr>
<tr>
<td>Equimolar NaCl-KCl + 5 wt. % CaF&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0.009</td>
<td>Good</td>
</tr>
<tr>
<td>Equimolar NaCl-KCl + 5 wt. % AlF&lt;sub&gt;3&lt;/sub&gt;</td>
<td>0.014</td>
<td>Moderate</td>
</tr>
<tr>
<td>Equimolar NaCl-KCl + 5 wt. % NaF</td>
<td>0.071</td>
<td>Excellent</td>
</tr>
<tr>
<td>Equimolar NaCl-KCl + 5 wt. % KF</td>
<td>0.028</td>
<td>Excellent</td>
</tr>
<tr>
<td>Equimolar NaCl-KCl + 5 wt. % LiF</td>
<td>0.045</td>
<td>Excellent</td>
</tr>
</tbody>
</table>
5.9 VISCOSITY OF SALTS

Viscosity of salt flux is an important property. Viscosity affects the coalescence of metal droplets in the salt. In general, coalescence is comprised of two processes, the collision of droplets and the removal of thin layer of fluid between the droplets\(^{(176)}\). In case of aluminum alloy droplets, it is proposed that the coalescence is comprised of three processes, collision of droplets, breakage of alumina layer covering aluminum alloy droplets and removal of thin layer of salt flux between the droplets. The viscosity of salt flux plays an important role in all three processes. Number of collisions of the droplets and momentum carried by droplets is decreased by an increase in viscosity. Breakage of alumina layer will be difficult for the collision of droplets which possess smaller value of momentum. Removal of thin layer of salt flux will also be difficult for a flux having higher viscosity. Thus the effect of increase in viscosity is to decrease the coalescence ability of flux and decrease the recovery.

An experiment with pure NaCl was conducted at 850 °C. The kinematic viscosity is calculated to be 0.80 cS and viscosity is calculated to be 1.23 cP. Corresponding values of viscosity from literature are 0.92 cP\(^{(177)}\), 1.12 cP\(^{(128)}\), 1.20 cP\(^{(133)}\) and 1.26 cP\(^{(178)}\).

The viscosity and density of equimolar NaCl-KCl were measured as a function of temperature. Figure 5.30 shows the density of equimolar NaCl-KCl as a function of temperature. Variation of viscosity with temperature is given by an Arrhenius-type equation of the form

\[
\eta = A \exp\left(\frac{E_{vis}}{RT}\right)
\]  

(5.49)
Figure 5.30 Variation of density of equimolar NaCl-KCl with temperature
where $\eta$ is the viscosity, $A$ a constant, $E_{\text{vis}}$ the energy of activation, and $T$ the temperature. Figure 5.31 shows the plot of $\ln \eta$ with $1/T$. The energy of activation can be calculated from the slope and is equal to 32.6 J/mol.

The variation of kinematic viscosity of equimolar NaCl-KCl as a function of addition of halides is shown in Figures 5.32-5.33 and listed in Table 20. Kinematic viscosity of salts varied between 0.71 to 0.96 cS at 740 °C and the reproducibility was ± 0.04 cS. The variation of viscosity with composition can not be correlated with the change in density or the melting point of the salt added to equimolar NaCl-KCl. The viscosity of a dilute electrolyte solution is composed of contributions from various factors:

$$\eta = \eta^o + \eta^C + \eta^E + \eta^A + \eta^D \quad (5.50)$$

where $\eta^o$ is the viscosity of the solvent, $\eta^C$ is the change in viscosity due to coulombic interactions, $\eta^E$ is the change in viscosity arising from shape and size of the ions, $\eta^A$ is the change in viscosity due to alignment or orientation of polar molecules by the ionic field and $\eta^D$ is the change in viscosity due to distortion of the solvent structure. If distortion opens up the structure, viscosity decreases. Since the solution is ionic, the contribution of $\eta^A$ is also zero. Thus, the change in viscosity is due to coulombic interactions, shape and size effect, and distortion of the solvent structure.
Figure 5.31  Variation of viscosity of equimolar NaCl-KCl with temperature
Figure 5.32  Variation of viscosity of equimolar NaCl-KCl with mole % additives
Figure 5.33  Variation of viscosity of equimolar NaCl-KCl with mole % additives
<table>
<thead>
<tr>
<th>Salt</th>
<th>Kinematic Viscosity (cS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl (850 °C)</td>
<td>0.80</td>
</tr>
<tr>
<td>Equimolar NaCl-KCl (700 °C)</td>
<td>0.96</td>
</tr>
<tr>
<td>Equimolar NaCl-KCl (740 °C)</td>
<td>0.83</td>
</tr>
<tr>
<td>Equimolar NaCl-KCl (800 °C)</td>
<td>0.72</td>
</tr>
<tr>
<td>Equimolar NaCl-KCl (850 °C)</td>
<td>0.58</td>
</tr>
<tr>
<td>NaCl-KCl-2.5 % NaF (740 °C)</td>
<td>0.77</td>
</tr>
<tr>
<td>NaCl-KCl-5 % NaF (740 °C)</td>
<td>0.76</td>
</tr>
<tr>
<td>NaCl-KCl-7.5 % NaF (740 °C)</td>
<td>0.79</td>
</tr>
<tr>
<td>NaCl-KCl-10 % NaF (740 °C)</td>
<td>0.92</td>
</tr>
<tr>
<td>NaCl-KCl-2.5 % KF (740 °C)</td>
<td>0.87</td>
</tr>
<tr>
<td>NaCl-KCl-5 % KF (740 °C)</td>
<td>0.96</td>
</tr>
<tr>
<td>NaCl-KCl-7.5 % KF (740 °C)</td>
<td>0.80</td>
</tr>
<tr>
<td>NaCl-KCl-10 % KF (740 °C)</td>
<td>0.80</td>
</tr>
<tr>
<td>NaCl-KCl-2.5 % LiF (740 °C)</td>
<td>0.78</td>
</tr>
<tr>
<td>NaCl-KCl-5 % LiF (740 °C)</td>
<td>0.83</td>
</tr>
<tr>
<td>NaCl-KCl-5 % MgF₂ (740 °C)</td>
<td>0.96</td>
</tr>
<tr>
<td>NaCl-KCl-2.5 % Cryolite (740 °C)</td>
<td>0.80</td>
</tr>
<tr>
<td>NaCl-KCl-5 % Cryolite (740 °C)</td>
<td>0.76</td>
</tr>
<tr>
<td>NaCl-KCl-2.5 % LiCl (740 °C)</td>
<td>0.71</td>
</tr>
</tbody>
</table>
From above discussion, the change in viscosity of equimolar NaCl-KCl with addition of ternary salt will depend on how the addition of ternary salt changes the structure existing in equimolar NaCl-KCl. One important factor in this regard is the ratio of ionic radii for the ternary salt. Ratio of anion radius to cation radius at room temperature for KF, NaF, LiF, and LiCl are 1.02, 1.43, 2.26, and 3.01 respectively\(^\text{178}\). Stilinger et al.\(^\text{180}\) have pointed out that for ions which do not differ much in size, it is almost exclusively opposite type of ions that come close enough into contact, while for ions which differ much in size, larger ions can be easily in contact with same type of ions. For 2.5 wt. % addition of ternary salt in equimolar NaCl-KCl, viscosity increases for addition of KF and decreases for addition of NaF, LiF and LiCl, the decrease being greatest for LiCl. From Table 17 the electrostatic attraction between cation and anion is stronger in KF than NaCl and KCl. Anion and cation of KF are of same size, so same type of ions do not come in close

<table>
<thead>
<tr>
<th>Salt</th>
<th>Kinematic Viscosity (cS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl-KCl-5 % LiCl (740 °C)</td>
<td>0.73</td>
</tr>
<tr>
<td>NaCl-KCl-5 % CaCl(_2) (740 °C)</td>
<td>0.92</td>
</tr>
<tr>
<td>NaCl-KCl-5 % MgCl(_2) (740 °C)</td>
<td>0.84</td>
</tr>
<tr>
<td>NaCl-KCl-2.5 % CaF(_2) (740 °C)</td>
<td>0.80</td>
</tr>
<tr>
<td>NaCl-KCl-5 % CaF(_2) (740 °C)</td>
<td>0.85</td>
</tr>
</tbody>
</table>
contact. Thus addition of KF in equimolar NaCl-KCl increases the electrostatic attraction between ions, thus increasing the resistance to flow, which results in increase of viscosity. NaF and LiF also have stronger electrostatic bond between ions compared to NaCl and KCl, but the cation and anion sizes are different for NaF and LiF, and same type of ions can come in contact resulting in electrostatic repulsion. The addition of NaF or LiF in equimolar NaCl-KCl decreases the net electrostatic attraction between the ions, which results in decrease in viscosity. From Table 17, it can be inferred that LiF is more strongly bound than NaF, but cation and anion sizes are more disparate in LiF than NaF. As a result addition of NaF and LiF decrease the viscosity to same degree. It can be inferred from Table 17 that electrostatic attraction between ions in LiCl is comparable to NaCl and KCl. Anion and cation sizes are very disparate in LiCl. Thus addition of LiCl results in greater electrostatic repulsion. Thus addition of LiCl in equimolar NaCl-KCl results in even greater decrease in viscosity compared to NaF and KF. It was found that increasing the addition of ternary salt resulted in restoring of viscosity value to that of equimolar NaCl-KCl. The reason for this is unclear. It is possible that with increase in concentration the ternary salt ions start occupying the normal sites occupied by NaCl-KCl ions by displacing them instead of going into interstices.

Theoretical determination of viscosity has been done for some simple salts, e.g. NaCl and RbCl, by Cicotti et al.\textsuperscript{(181)} using molecular dynamics calculations. Calculated values differ from experimental values by upto 14.6%. Theoretical determination of viscosity of ternary salts has not been done so far due to the complexity of calculations. Experimental measurement of viscosity is therefore very useful.
5.10 TERMINAL FALLING VELOCITY

The terminal falling velocity of aluminum drops in molten salt flux depends on the density and viscosity of molten salt and diameter of aluminum drop. The viscosity and density of salt keeps increasing as scrap is charged in the salt flux. The increase in viscosity and density of salt results from the suspension of the oxide films stripped from metal in the flux. As salt becomes more and more dense and viscous, more and more metal is entrapped in the salt, because the terminal falling velocity of aluminum drop decreases rapidly with increase in density and viscosity of molten salt. When terminal falling velocity becomes very small, the aluminum drop will be trapped in salt flux. The terminal falling velocity, $V_t$, of an aluminum drop falling in molten salt flux is given by following expression (182)

$$V_t = d_a^2 g (\rho_a - \rho_s)/18 \eta$$  \hspace{1cm} (5.51)

where, $d_a$ is the diameter of aluminum drop, $g$ is acceleration due to gravity, $\rho_a$ is density of molten aluminum, $\rho_s$ is density of molten salt flux and $\eta$ is the viscosity of molten salt flux. The effect of density and viscosity of molten salt and diameter of aluminum drop on terminal falling velocity of aluminum drop is shown in Figures 5.34 and 5.35. In Figure 5.34, density and diameter of aluminum drop is varied and viscosity is kept constant. Density of clean salt is approximately 1.55 gm/cm$^3$ at 740 °C, which can increase up to the density of aluminum as more and more oxide is suspended in salt. Therefore density is varied between 1.55 and 2.3 gm/cm$^3$. Viscosity of molten salt is assumed 1.29 cP. In Figure 5.35, viscosity and diameter of aluminum drop is varied and density is kept constant. Viscosity of equimolar NaCl-KCl
is 1.29 cP at 740 °C. Viscosity of molten salts can reach 500 cP as more and more oxide is suspended in salt\(^7\). Therefore viscosity is varied between 1 to 500 cP. Density of molten salt is assumed 1.55 gm/cm\(^3\). It can be seen from figures 5.34 and 5.35 that recovery of metal is easier if diameter of the drop is large, viscosity of salt is low, and density of salt is low. Therefore better coalescence results in increased recovery of metal.
Figure 5.34 Variation of terminal velocity of aluminum drops as a function of drop diameter and density of salt flux
Figure 5.35  Variation of terminal velocity of aluminum drops as a function of drop diameter and viscosity of salt flux
Chapter VI

SUMMARY AND CONCLUSIONS

The interfacial tension between UBC alloy and salts has been measured using the drop detachment method. The salts consisted of varying amount of NaF, KF, Na₃AlF₆, AlF₃, LiF, LiCl, and MgF₂ in equimolar NaCl-KCl. The interfacial tension between UBC alloy and equimolar NaCl-KCl was found to be 511 mN/m. Interfacial tension decreased for salt addition in equimolar NaCl-KCl in all cases. This variation can be qualitatively described in terms of adsorption of surface active elements in equilibrium with UBC alloy and salt. The adsorption of surface active elements Na and K does not take place to a significant extent in aluminum/equimolar NaCl-KCl, because the activities of Na and K are very low. Addition of NaF in equimolar NaCl-KCl increases the activity of Na and K. The adsorption of Na and K increases at the interface due to increase in their activities, which results in the observed decrease in interfacial tension. The addition of LiF to equimolar NaCl-KCl increases the activity of Na and K by formation of NaF and KF, respectively. Simultaneous adsorption of Na, K and Li is the reason for the observed decrease in interfacial tension in this case. The decrease in interfacial tension is more pronounced for the addition of metal fluorides than metal chlorides, because
the activity of surface active elements is higher for metal fluoride additions than for metal chlorides. These conclusions were verified by measurement of sodium and potassium content of aluminum after it was charged in salt flux. Amount of sodium and potassium in aluminum increased ten-fold when the salt containing 5 wt. % sodium fluoride was used instead of equimolar NaCl-KCl.

Progress of coalescence of aluminum chips was observed as a function of time in equimolar NaCl-KCl and equimolar NaCl-KCl containing LiCl, MgCl₂, CaCl₂, NaF, KF, LiF, MgF₂, CaF₂, Na₃AlF₆ and AlF₃. Following observations were made.

1. Coalescence of aluminum drops took place in all salts studied.
2. Complete coalescence in salts containing fluorides took 2-3 minutes, while complete coalescence in salts containing only chlorides took many hours.
3. In salts containing fluorides, all aluminum chips joined together before each chip has individually become a liquid drop.
4. No significant difference was observed between the coalescence ability of salts containing various fluorides.
5. In salts containing only chlorides, many individual drops formed, which coalesced as time proceeded.

Similar experiments were performed for UBC alloy chips. The progress of coalescence of UBC alloy chips was observed as a function of time in equimolar NaCl-KCl and in equimolar NaCl-KCl containing NaF, KF, LiF, MgF₂, CaF₂, Na₃AlF₆ and AlF₃. The extent of coalescence differed for various fluorides used. Complete or nearly complete coalescence was observed for salts containing NaF, KF, LiF and Na₃AlF₆ after 2 minutes, while formation
of a large number of drops was observed for salts containing MgF₂, CaF₂ and AlF₃. Though coalescence of Al chips was found to be similar for all salts containing fluoride, a significant difference was observed for the coalescence of UBC alloy chips in different salts containing fluorides. The thick oxide layer on UBC alloy chips is more difficult to strip and the difference in coalescence ability of salts for aluminum and UBC alloy results from this. Based on these experiments salts can be classified into four categories depending on their coalescence ability:

1. Excellent : NaF, KF, LiF, Na₃AlF₆
2. Good : CaF₂, MgF₂
3. Moderate : AlF₃
4. Poor : NaCl-KCl

Oxide layer is stripped by a three-step process.

1. Openings develop in oxide layer
2. Salt penetrates between oxide and metal
3. Oxide layer is stripped.

There are three important time intervals determining the progress of coalescence: time for melting of metal chip, time for weakening of strength of oxide layer and time for stripping of significant fraction of oxide layer. Progress of coalescence of aluminum and UBC alloy chips in different salts can be illustrated by the relative values of these three time intervals.
The measurement of contact angle between Al and alumina in the salt flux of different compositions was done using the sessile drop method. Oxide-flux interfacial tension for different salts were calculated from the measured value of contact angle. The interfacial tension between Al and alumina was estimated from the literature. The change in free energy due to oxide film removal was calculated for different salts. The free energy change for oxide removal is positive for all salts and does not show a wide range of variation for different salt fluxes. Thus interfacial tension considerations alone are not sufficient to explain the observations relating to coalescence ability of salt fluxes. The construction of ternary interfacial energy diagram showed that although oxide film removal is not spontaneous, the point corresponding to interfacial tension values is very close to the boundary where oxide film removal becomes spontaneous. Thus only a small amount of energy is needed to remove the oxide layer.

The mechanism of oxide removal was discussed. Coalescence ability of salts does not correlate with the free energy of formation of salts or standard Gibbs energy of reaction between the salt and the oxide. Coalescence ability matches well with the ability of the salt to dissolve Al.

The viscosity of salts was measured using a capillary viscometer. Viscosity of salts affects the coalescence of metal drops. Coalescence is comprised of three processes: contact between droplets, breakage of alumina layer covering aluminum alloy droplets and removal of thin layer of salt flux between the droplets. The viscosity of the salt flux plays an important role in all three processes. The number of collisions of the droplets and the momentum carried by droplets is decreased by an increase in viscosity.
Breakage of alumina layer will be difficult for the collision of droplets which possess smaller values of momentum. Removal of thin layer of salt flux will also be difficult for a flux having higher viscosity. Thus the effect of increase in viscosity is to decrease the coalescence ability of salt flux. Viscosity and density of equimolar NaCl-KCl was measured as a function of temperature. Energy of activation was calculated to be 32.61 J/mol. Kinematic viscosity of salts varied between 0.71 to 0.96 cS at 740 °C.

The terminal falling velocity of aluminum drops in molten salt flux depends on the density and viscosity of molten salt and diameter of aluminum drop. The viscosity and density of salt keeps increasing as scrap is charged in the salt flux. The increase in viscosity and density of the salt results from the suspension of the oxide films stripped from metal in the flux. As the salt becomes more and more dense and viscous, more and more metal is entrapped in the salt, because the terminal falling velocity of Al drop decreases rapidly with increase in density and viscosity of molten salt. When the terminal falling velocity becomes very small, the Al drop will be trapped in salt flux. Recovery of metal is easier if the diameter of the drop is large and therefore better coalescence results in increased recovery of metal.
REFERENCES


166


22. T. Young, Phil. Trans., Vol. 95, 1805, p. 65

23. P. S. De Laplace, Mechanique Celeste, Coureier, Paris, 1805

24. K. F. Gauss, Principae Generalia Theoreticae Figurae Fluidorum In Statu Aequilirii, Gottingen, 1830


37. J. Ye, Ph. D. Dissertation, The Ohio State University, 1994, p. 97


62. L. Jing Et Al., Jinshu Xuebao, 1990, 26(1), B6-B10 (Ch.)


69. F. K. Ho, M. S. Thesis, Materials Sc. and Engg., Ohio State University, 1990


72. F. Neumann, Vorlesungen Uber Die Theorie Der Capillaritat, B. G. Teubner, Leipzig, 1894

73. P. S. Laplace, Mecanique Celeste, Suppl. To Vol. X, Paris, 1806


75. W. A. Zisman, Advan. Chem. Ser., Vol. 43, 1964


86. R. Albett, Phil. Mag., Vol. 46, 1923, p. 244


93. R. J. Good and E. Elbing, In Chemistry and Physics of Interfaces Ii, Ed. Sydney Ross, American Chemical Society Publications, p. 71


110. E. C. Bingham, Fluidity And Plasticity, Mcgraw-Hill, New York, 1922, p. 65

111. H. Bloom, The Chemistry of Molten Salts, Published By W. A. Benjamin, Inc., 1967, p. 10


117. A. W. Francis, Physics, Vol. 4, 1933, p. 403


134. I. Votava and K. Matiasovsky, Chemicke Zvesty, Vol. 27, 1973, p. 582


136. J. Ye, Ph. D. Dissertation, The Ohio State University, 1994, p. 102


144. Z. S. Barsukova and I. D. Ivanova, Miner. Sy're, 1970, p. 19


155. S. A. Impey, D. J. Stephenson, and J. R. Nicholls, Materials Science and Technology, V. 4, 1988, p. 1126


160. J. Ye, Ph. D. Dissertation, The Ohio State University, 1994


164. Interference Microscope Manual, Carl Zeiss, West Germany


177. Janz et al., Physical Properties Data Compilations Relevant to Energy Storage, Part 2, 1979, p. 332


