http://researchspace.auckland.ac.nz

ResearchSpace@Auckland

Copyright Statement

The digital copy of this thesis is protected by the Copyright Act 1994 (New Zealand).

This thesis may be consulted by you, provided you comply with the provisions of the Act and the following conditions of use:

- Any use you make of these documents or images must be for research or private study purposes only, and you may not make them available to any other person.
- Authors control the copyright of their thesis. You will recognise the author's right to be identified as the author of this thesis, and due acknowledgement will be made to the author where appropriate.
- You will obtain the author's permission before publishing any material from their thesis.

To request permissions please use the Feedback form on our webpage. http://researchspace.auckland.ac.nz/feedback

General copyright and disclaimer

In addition to the above conditions, authors give their consent for the digital copy of their work to be used subject to the conditions specified on the Library Thesis Consent Form.
INTERMETALLIC PHASES FORMED DURING GALFANIZING

Zhan Wen CHEN

Thesis submitted for the degree of Doctor of Philosophy at the School of Engineering, The University of Auckland, New Zealand.

November 1989
Galfan (5 wt% Al-Zn plus 0.05 wt% mischmetal or 0.1 wt% Mg) is a coating which in recent years has undergone many industrial studies and trials. The aim with Galfan is to produce a coating which has no intermetallic phases in the coating but this condition is not always achieved. Though it is important, the nature of the intermetallic phases and the mechanisms of their formation and growth during Galfanizing are far from fully understood.

The overall objective of this investigation was to identify the intermetallic phases which form and grow during Galfanizing.

At 450°C, the formation of the intermetallic phases was in the form of a local outburst and the intermetallic phases then grew in a breakaway morphology. The previously reported structure and composition of the intermetallic phases were found to be either incorrect or incomplete. The intermetallic local outburst was determined to be mainly Fe7Al4-Zn, with the outer part next to the eutectic being FeAl1-Zn,. The breakaway phase was FeAl1-Zn, and another phase next to the interface was Fe2Al5-Zn,. The intermetallic growth is characterized by the growth of Fe7Al4-Zn, towards the substrate with a <001> growth direction, following a reaction path of α (substrate) - Fe7Al4-Zn, - FeAl1-Zn, - Galfan (melt).

When the dipping temperature was increased, the rates of intermetallic formation and growth were greatly increased. The intermetallic morphology was shown to change from predominantly breakaway at 450°C to predominantly layered at temperatures higher than 490°C resulting from a fast growth of Fe7Al4-Zn,. The degree of the preferred orientation of Fe7Al4-Zn, increased at higher dipping temperatures. It was shown that the lattice parameters and therefore the interplanar spacings of Fe7Al4-Zn, formed during Galfanizing were dependent on the dipping temperatures. The same reaction path as that described for 450°C was also followed at higher temperatures. However, when the substrate is dipped at high temperatures and when the Fe7Al4-Zn, grows to a considerably thickness, the limited diffusion rate of aluminium across a thick Fe7Al4-Zn, layer resulted in the formation of FeZn10-Al14.
lic formation was much lengthened and the growth of $\text{Fe}_2\text{Al}_5$-$\text{Zn}_x$ and therefore the whole intermetallic layer became considerably slower. When silicon was present in the melt, the intermetallic phases did not grow to any noticeable extent at 450°C and 470°C. However, at 490°C and above though the nucleation time of the intermetallic was also delayed, once nucleated the growth was fast resulting in a highly localized growth.

It was found that the existing data on the interplanar spacings of $\text{Fe}_2\text{Al}_5$-$\text{Zn}_x$ were incorrect. The two most intense peaks were shown to be due to diffraction from 221 and 311 rather than from 002 and 130. A new list of interplanar spacings was proposed. It was shown that the lattice parameters and therefore interplanar spacings of $\text{Fe}_2\text{Al}_5$-$\text{Zn}_x$ formed during galvanizing were dependent on the aluminium content of the bath.

The compositions of intermetallic phases determined in this study were not consistent with those expected from previously published ternary phase diagrams. At 450°C, the solubility of zinc was found to be 5.3 wt% in $\text{FeAl}_5$, 20.9 wt% in $\text{Fe}_2\text{Al}_5$, and 2.0 wt% in $\text{FeAl}$ at 450°C. Based on these results, a new version of the Fe-Al-Zn ternary phase diagram at 450°C was proposed.
CONTENTS

ABSTRACT ii
ACKNOWLEDGEMENTS iv
CONTENTS v
LIST OF FIGURES viii
LIST OF TABLES xviii

1 INTRODUCTION AND REVIEW OF THE LITERATURE 1

1.1 HOT DIP GALFANIZING - a General Comment 1

1.2 PRETREATMENT OF SUBSTRATE 3
   1.2.1 The Concept of Wetting 3
   1.2.2 Surface Treatment 4

1.3 GALVANIZING 5
   1.3.1 The Fe-Zn System 5
   1.3.2 Reaction during Hot Dipping 6
   1.3.3 The Effect of Silicon in the Substrate 10
   1.3.4 The Addition of Aluminium into the Bath 12

1.4 ALUMINIZING 14
   1.4.1 The Fe-Al System 14
   1.4.2 Reaction during Hot Dipping 15
   1.4.3 The Effect of Silicon 15

1.5 HOT DIPPING IN Al-Zn ALLOY BATHS 17
   1.5.1 The Al-Zn and Fe-Al-Zn Systems 18
   1.5.2 Hot Dipping in 45, 55 and 75 wt% Al-Zn Baths 20
   1.5.3 Galvalume Hot Dipping 22

1.6 REACTION DURING GALFANIZING 25

1.7 THE SCOPE OF THIS RESEARCH 32

2 EXPERIMENTAL PROCEDURE AND PRELIMINARY STUDY 34

2.1 PRETREATMENT PROBLEM 34
   2.1.1 Preliminary Experiment 35
   2.1.2 Observation 36
   2.1.3 Conclusion 48
ACKNOWLEDGEMENTS

I would first of all like to thank my supervisors, Professor R.M. Sharp and Dr. J.T. Gregory for their guidance, support and patience during the course of this research project.

I wish to thank Dr. N. Clark, General Manager of Planning and Technology of New Zealand Steel Limited, for suggesting this research project and many discussions during the past four years.

Financial support from New Zealand Steel Limited is gratefully acknowledged. Galfan ingots were supplied by New Zealand Steel Limited.

Thanks to the technicians in the Department of Chemical and Materials Engineering, staff of purchasing office, library, Engineering Workshop, administration and custodial office of Engineering School, and staff of grassblower at the University of Auckland for their help and co-operation.

The assistance from Miss M. Short in the early stage of the writing of this thesis is very much appreciated.

I would also like to, once again, express my gratitude to Professor R.M. Sharp for his advice and inspiration in the course of this research, and his assistance in the preparation and critical reading of this final thesis.
2.2 GALFANIZING
   2.2.1 Materials
   2.2.2 Apparatus
   2.2.3 Hot Dipping Procedure

2.3 METALLOGRAPHY

2.4 X-RAY DIFFRACTION
   2.4.1 Specimen and Diffractometer
   2.4.2 Error Estimation
   2.4.3 Standards and the Study of the Fe₃Al₅ File
   2.4.4 Method of Data Analysis

2.5 EDS COMPOSITIONAL ANALYSIS
   2.5.1 Method of EDS Analysis
   2.5.2 Existing Data for the Fe-Al-Zn phase diagram
   2.5.3 Preliminary Experiment
   2.5.4 Results and Discussion

3 GROWTH MORPHOLOGY OF INTERMETALLIC PHASES
   3.1 LOW CARBON STEEL SUBSTRATE DIPPED AT 450°C
      3.1.1 Early Stages of Growth
      3.1.2 Breakaway growth
   3.2 THE EFFECT OF DIPPING TEMPERATURE
      3.2.1 Intermetallic Coverage
      3.2.2 Growth at 460°C-510°C
      3.2.3 Growth at 520°C and Above
      3.2.4 Overall Processes of Growth
   3.3 THE EFFECT OF QUENCHING
   3.4 THE EFFECT OF SILICON IN THE SUBSTRATE
      3.4.1 Intermetallic Nucleation
      3.4.2 Intermetallic Growth
   3.5 THE EFFECT OF SILICON IN THE MELT

4 STRUCTURAL IDENTIFICATION OF INTERMETALLIC PHASES
   4.1 DIPPING TEMPERATURE: 450°C
      4.1.1 Two Fe-Al-Zn Intermetallic Phases
      4.1.2 Preferred Orientation of Fe₃Al₅-Znₓ
      4.1.3 The Effect of Quenching
4.1.4 Summary of the Results

4.2 LATTICE PARAMETERS OF Fe₃Al₃-Zn₄
   4.2.1 Data Comparison
   4.2.2 Calculation of the Lattice Parameters

4.3 INCREASING THE DIPPING TEMPERATURE
   4.3.1 X-Ray Diffraction Data
   4.3.2 Three Fe-Al-Zn Intermetallic Phases
   4.3.3 Preferred Growth of Fe₃Al₃-Zn₄
   4.3.4 Lattice Parameters of Fe₃Al₃-Zn₄
   4.3.5 Summary of the Results

4.4 THE EFFECT OF SILICON IN THE SUBSTRATE
   4.4.1 X-Ray Diffraction Data
   4.4.2 Two Intermetallic Phases

5 COMPOSITIONAL ANALYSIS OF INTERMETALLIC PHASES
   5.1 DIPPING TEMPERATURE: 450°C
      5.1.1 Data of Compositional Analysis
      5.1.2 Intermetallic Local Outburst
      5.1.3 The Two Phases in Breakaway Growth
   5.2 DIPPING TEMPERATURE: 490°C-510°C
   5.3 DIPPING TEMPERATURE: 520°C AND HIGHER
   5.4 OVERALL REACTION PATHS
   5.5 SUMMARY OF THE RESULTS

6 CONCLUSIONS

APPENDICES
   A.1 Published Data of interplanar spacing and Intensity
   A.2 Error Estimation for X-ray Diffraction Experiment
   A.3 Calculation of interplanar spacings of Fe₃Al₃
   A.4 Results of the Study on the Fe-Al-Zn Phase Diagram at 450°C

REFERENCES
## LIST OF FIGURES

<table>
<thead>
<tr>
<th>Fig.</th>
<th>Description</th>
<th>Pg</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>The balance of interfacial tensions acting around periphery of a droplet of liquid at equilibrium</td>
<td>3</td>
</tr>
<tr>
<td>1.2</td>
<td>Fe-Zn phase diagram (7)</td>
<td>5</td>
</tr>
<tr>
<td>1.3</td>
<td>Microstructures of iron specimens galvanized for 20 minutes at the indicated temperatures (14)</td>
<td>6</td>
</tr>
<tr>
<td>1.4</td>
<td>Modes of formation and growth of the phases in solid iron and solid zinc couple at 410°C (15)</td>
<td>7</td>
</tr>
<tr>
<td>1.5</td>
<td>Rate of reaction between iron and liquid zinc as a function of temperature (7)</td>
<td>8</td>
</tr>
<tr>
<td>1.6</td>
<td>Rate of growth of $\Gamma$, $\delta$, and $\zeta$ at 457°C (7,17)</td>
<td>8</td>
</tr>
<tr>
<td>1.7</td>
<td>A qualitative drawing of the $\Delta G/T$ curves for Fe-Zn system (24)</td>
<td>9</td>
</tr>
<tr>
<td>1.8</td>
<td>Variation of average coating thickness as a function of silicon content of steel hot dipping for 15 minutes (24)</td>
<td>11</td>
</tr>
<tr>
<td>1.9</td>
<td>Microstructures of coatings dipped in 0.25 wt% Al-Zn bath at 450°C (35)</td>
<td>13</td>
</tr>
<tr>
<td>1.10</td>
<td>Fe-Al phase diagram (38,39,40)</td>
<td>14</td>
</tr>
<tr>
<td>1.11</td>
<td>Microstructure of aluminized layer of pure iron dipped in pure aluminium bath for 1 minute at 700°C (44)</td>
<td>15</td>
</tr>
<tr>
<td>1.12</td>
<td>Microstructures of aluminized layers of steel containing 1.58 wt% silicon dipped in pure aluminium bath and pure iron dipped in 4 wt% Si-Al bath for 1 minute at 700°C (44)</td>
<td>16</td>
</tr>
</tbody>
</table>
1.13 Relation between thickness of intermetallic layer in the aluminized coatings and dipping time (50)

1.14 Al-Zn phase diagram (51,52,53,54)

1.15 Ternary Fe-Al-Zn phase diagrams (54,57,58)

1.16 Microstructures of coatings of pure iron dipped in 45, 55 and 75 wt% Al-Zn baths (59)

1.17 Schematic diffusion path given by Selverian et al for hot dipping of pure iron in 45, 55 and 75 wt% Al-Zn baths at temperatures between 570 and 655°C (59)

1.18 Microstructures of coatings of steel dipped into Galvalume bath for 4, 900 and 1800 seconds (60)

1.19 Reaction path for steel dipped for 1800 seconds in Galvalume bath plotted in the modified Fe-Al-Si system at 610°C (60)

1.20 Galfan coating produced by continuous hot dipping (61)

1.21 Reaction paths in (5-10) wt% Al-Zn baths at 450, 525, 560 and 590°C given by Ghuman and Goldstein (35)

1.22 Reaction paths followed when hot dipping in (1-10) wt% Al-Zn baths at temperature >600°C given by Ghuman and Goldstein (35)

1.23 Two compositional fields of intermetallic phases present in coating dipped in a 5 wt% Al-Zn bath given by Makimattila (65)

2.1 Appearances of Galfanized coatings. Pickling: HCl-Water-Ethanol, no fluxing, Hot dipping: T=440°C, t as indicated

2.2 Appearances of Galfanized coatings. Pickling: HCl-Water-Ethanol, no fluxing, Hot dipping: T=460°C, t as indicated
2.3 Appearances of Galfanized coatings. Pickling: HCl-Water-Ethanol, no fluxing, Hot dipping: T=480°C, t as indicated

2.4 Microstructures of a Galfanized coating. Pickling: HCl-Water-Ethanol, no fluxing, Hot dipping: T=460°C, t=900 s

2.5 Microstructures of two Galfanized coatings. Pickling: HCl-Water-Ethanol, no fluxing, Hot dipping: T=480°C, t: A-400 s, B-600 s

2.6 Microstructures of a Galfanized coating at high magnification, Pickling: HCl-Water-Ethanol, no fluxing, Hot dipping: T=480°C, t=600 s

2.7 Appearances of Galfanized coatings. Pickling as indicated, no fluxing, Hot dipping: T=460°C, t=160 s

2.8 Appearance of Galfanized coatings. Pickling: HCl, no fluxing, Hot dipping: T=440°C, t as indicated

2.9 Microstructures of Galfanized coatings. Pickling: HCl, no fluxing, Hot dipping: T=440°C, t; A-30 s, B-60 s, C-100 s

2.10 Appearances of Galfanized coatings. Pickling: a. HCl-Water-Ethanol, b. HCl, c. and d. HCl-Water, Fluxing as indicated, Hot dipping: T=440°C, t=60 s

2.11 Microstructures of the four steel substrates

2.12 Apparatus for hot dip Galfanizing

2.13 Schematic drawing of the furnace and bath used in hot dip Galfanizing

2.14 Features of Galfanized coatings

2.15 The system of the diffractometer measurement

2.16 The penetration depth of X-ray in X-ray diffraction experiment
2.17 Systematic error of the X-ray diffraction experiment

2.18 Random error of the X-ray diffraction experiment

2.19 Schematic diffraction patterns for a Galfanized coating produced when a low carbon steel substrate is hot dipped for 35 seconds in a bath held at 490°C

2.20 Temperature-time history for vacuum heating, vacuum melting and annealing of the five alloys

2.21 Microstructures of specimens showing the phases identified

2.22 Results of EDS analysis plotted in Urednicek and Kirkaldy's Fe-Al-Zn ternary section at 450°C

2.23 The modified Fe-Al-Zn ternary phase diagram at 450°C

3.1 Microstructures of Galfanized coatings of low carbon steel dipped at 450°C for times as indicated

3.2 The Nucleation processes

3.3 Diffusion coefficients of Fe and Al in Fe₅Al, and FeAl, plotted against 1/T

3.4 Relation between ln(t) and 1/T where t is the dipping time for the intermetallic to cover the whole substrate surface and T is the dipping temperature

3.5 Microstructures of Galfanized coatings of low carbon steel dipped at 460°C for times as indicated

3.6 Microstructures of Galfanized coatings of low carbon steel dipped at 480°C for times as indicated

3.7 Microstructures of Galfanized coatings of low carbon steel dipped at 490°C for times as indicated
3.8 Microstructures of Galfanized coatings of low carbon steel dipped at 500°C for times as indicated

3.9 Microstructures of Galfanized coatings of low carbon steel dipped at 510°C for times as indicated

3.10 Microstructures of Galfanized coatings of low carbon steel dipped at 520°C for times as indicated

3.11 Microstructures of Galfanized coatings of low carbon steel dipped at 575°C for times as indicated

3.12 Intermetallic layer thickness as a function of dipping time

3.13 Relation between (a) x and $\sqrt{t}$, and (b) $\log(x)$ and $\log(t)$, where x is the intermetallic layer thickness and t is the dipping time.

3.14 Microstructures of Galfanized coatings of low carbon steel dipped at 450°C for times as indicated and quenched in ice water after dipping

3.15 Microstructures of Galfanized coatings of low carbon steel dipped at 490°C for times as indicated and quenched in ice water after dipping

3.16 Microstructures of Galfanized coatings of low carbon steel dipped at 520°C for times as indicated and quenched in ice water after dipping

3.17 Microstructures of Galfanized coatings of low carbon steel dipped at 575°C for times as indicated and quenched in ice water after dipping

3.18 Microstructures of Galfanized coatings of 0.1 wt% Si steel dipped at 450°C for time as indicated

3.19 Microstructures of Galfanized coatings of 0.1 wt% Si steel dipped at 490°C for time as indicated
3.20 Microstructures of Galfanized coatings of 0.1 wt% Si steel dipped at 520°C for time as indicated

3.21 Microstructures of Galfanized coatings of 0.5 wt% Si steel dipped at 450°C for time as indicated

3.22 Microstructures of Galfanized coatings of 0.5 wt% Si steel dipped at 490°C for time as indicated

3.23 Microstructures of Galfanized coatings of 0.5 wt% Si steel dipped at 520°C for time as indicated

3.24 Microstructures of Galfanized coatings of 1.58 wt% Si steel dipped at 450°C for time as indicated

3.25 Microstructures of Galfanized coatings of 1.58 wt% Si steel dipped at 490°C for time as indicated

3.26 Microstructures of Galfanized coatings of 1.58 wt% Si steel dipped at 520°C for time as indicated

3.27 Microstructures of Galfanized coatings of 1.58 wt% Si steel dipped at 490°C for time as indicated. Specimens were heavily etched.

3.28 Microstructures of Galfanized coatings of 0.1 wt% Si steel dipped at 490°C for time as indicated. Specimens were heavily etched.

3.29 Microstructures of Galfanized coatings of 0.5 wt% Si steel dipped at 490°C for time as indicated. Specimens were heavily etched.

3.30 Microstructures of Galfanized coatings of low carbon steel dipped in Galfan bath containing silicon at 450°C for times as indicated.
3.31 Microstructures of Galfanized coatings of low carbon steel dipped in Galfan bath containing silicon at 470°C for times as indicated

3.32 Microstructures of Galfanized coatings of low carbon steel dipped in Galfan bath containing silicon at 490°C for times as indicated

3.33 Microstructures of Galfanized coatings of low carbon steel dipped in Galfan bath containing silicon at 520°C for times as indicated

3.34 Microstructures of Galfanized coatings of low carbon steel dipped in Galfan bath containing silicon at 575°C for times as indicated

4.1 Intensity ratios as a function of the angle between various planes and (002) of Fe₃Al₃-Znₓ present in coatings dipped at 450°C for times as indicated

4.2 Intensity ratio as a function of the angle between various planes and (002) of Fe₃Al₃-Znₓ present in coatings dipped at 450°C for times as indicated and quenched after dipping

4.3 Intensity ratios as a function of the angle between various planes and (002) of Fe₃Al₃-Znₓ present in coating dipped at 460°C for 185 s. The Fe₃Al₃-Znₓ is present further away from the Fe₃Al₃-Znₓ-substrate interface in grinding 3 than 4 and 5

4.4 Intensity ratios as a function of the angle between various planes and (002) of Fe₃Al₃-Znₓ present in coating dipped at 490°C for 30 s. The Fe₃Al₃-Znₓ is present further away from the Fe₃Al₃-Znₓ-substrate interface in Grinding 1 than 2 and 3

4.5 Intensity ratios as a function of the angle between various planes and (002) of Fe₃Al₃-Znₓ present in coatings dipped at 490°C for times as indicated
4.6 Intensity ratios as a function of the angle between various planes and (002) of Fe₅Al₃-Znₓ present in coatings dipped at 520°C for times as indicated

4.7 Intensity ratio as a function of the angle between various planes and (002) of Fe₅Al₃-Znₓ present in coatings dipped at 575°C for times as indicated

4.8 Intensity ratios as a function of the angle between various planes and (002) of Fe₅Al₃-Znₓ present in coatings dipped at 490, 500, 510°C for 20 s

4.9 Intensity ratios as a function of the angle between various planes and (002) of Fe₅Al₃-Znₓ present in coatings dipped for prolonged dipping times

4.10 d-spacings (3.82 Å) of Fe₅Al₃-Znₓ present in coatings of low carbon steel as a function of dipping temperature

4.11 d-spacings (3.21 Å) of Fe₅Al₃-Znₓ present in coatings of low carbon steel as a function of dipping temperature

4.12 d-spacings (2.36 Å) of Fe₅Al₃-Znₓ present in coatings of low carbon steel as a function of dipping temperature

4.13 d-spacings (2.118 Å) of Fe₅Al₃-Znₓ present in coatings of low carbon steel as a function of dipping temperature

4.14 d-spacings (2.064 Å) of Fe₅Al₃-Znₓ present in coatings of low carbon steel as a function of dipping temperature

4.15 d-spacings (1.944 Å) of Fe₅Al₃-Znₓ present in coatings of low carbon steel as a function of dipping temperature

4.16 d-spacings (1.769 Å) of Fe₅Al₃-Znₓ present in coatings of low carbon steel as a function of dipping temperature

4.17 d-spacings (1.478 Å) of Fe₅Al₃-Znₓ present in coatings of low carbon steel as a function of dipping temperature
4.18 d-spacings (1.358 Å) of Fe₃Al₃–Znₓ present in coatings of low carbon steel as a function of dipping temperature

4.19 d-spacings (1.225 Å) of Fe₃Al₃–Znₓ present in coatings of low carbon steel as a function of dipping temperature

4.20 d-spacings (1.213 Å) of Fe₃Al₃–Znₓ present in coatings of low carbon steel as a function of dipping temperature

4.21 d-spacings (2.026 Å) of the substrate plotted against the dipping temperature

5.1 Compositions of intermetallic phases present in coatings dipped at 450°C for 64 and 128 seconds plotted in the Fe-Al-Zn phase diagram

5.2 Compositions of intermetallic phases present in coatings dipped at 450°C for 256 seconds plotted in the Fe-Al-Zn phase diagram

5.3 Compositions of intermetallic phases present in coatings dipped at 450°C for 1024 seconds plotted in the Fe-Al-Zn phase diagram

5.4 Compositions of intermetallic phases present in coatings dipped at 450°C for 4096 seconds plotted in the Fe-Al-Zn phase diagram

5.5 Schematic reaction path during Galfanizing at 450°C plotted in the Fe-Al-Zn phase diagram

5.6 Composition of intermetallic phases determined by Caceres et al and Ghuman and Goldstein

5.7 Compositions of intermetallic phases present in coatings dipped at 490°C for 5 seconds plotted in the Fe-Al-Zn phase diagram

5.8 Compositions of intermetallic phases present in coatings dipped at 490°C for 10 seconds plotted in the Fe-Al-Zn phase diagram
5.9 Compositions of intermetallic phases present in coatings dipped at 490°C for 300 seconds plotted in the Fe-Al-Zn phase diagram

5.10 Compositions of intermetallic phases present in coatings dipped at 500°C for 170 seconds plotted in the Fe-Al-Zn phase diagram

5.11 Compositions of intermetallic phases present in coatings dipped at 510°C for 90 seconds plotted in the Fe-Al-Zn phase diagram

5.12 Compositions of intermetallic phases present in coatings dipped at 520°C for 5 seconds plotted in the Fe-Al-Zn phase diagram

5.13 Compositions of intermetallic phases present in coatings dipped at 520°C for 15 seconds plotted in the Fe-Al-Zn phase diagram

5.14 Compositions of intermetallic phases present in coatings dipped at 520°C for 80 seconds plotted in the Fe-Al-Zn phase diagram

5.15 Compositions of intermetallic phases present in coatings dipped at 575°C for 3 seconds plotted in the Fe-Al-Zn phase diagram

5.16 Compositions of intermetallic phases present in coatings dipped at 575°C for 10 seconds plotted in the Fe-Al-Zn phase diagram

5.17 Compositions of intermetallic phases present in coatings dipped at 575°C for 40 seconds plotted in the Fe-Al-Zn phase diagram

5.18 Schematic reaction paths during Galfanizing at temperatures from 450°C to 575°C plotted in the Fe-Al-Zn ternary phase diagram
LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Pg</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Properties of Fe-Zn intermetallic compounds</td>
<td>6</td>
</tr>
<tr>
<td>1.2</td>
<td>Reported phases of the inhibiting layer during galvanizing</td>
<td>13</td>
</tr>
<tr>
<td>1.3</td>
<td>Properties of Fe-Al intermetallic compounds</td>
<td>14</td>
</tr>
<tr>
<td>1.4</td>
<td>Bath compositions and temperatures used by Selverian et al</td>
<td>20</td>
</tr>
<tr>
<td>1.5</td>
<td>Phases present in the alloy layers formed during hot dipping in Galvalume bath at 610°C as a function of time</td>
<td>24</td>
</tr>
<tr>
<td>1.6</td>
<td>Reported compositions of phases referred to Table 1.5</td>
<td>24</td>
</tr>
<tr>
<td>1.7</td>
<td>Various studies on coating-substrate interface and intermetallic phases in the coatings hot dipped in zinc baths containing around 5 wt% aluminium</td>
<td>27</td>
</tr>
<tr>
<td>2.1</td>
<td>Types of substrate surface treatment</td>
<td>35</td>
</tr>
<tr>
<td>2.2</td>
<td>Conditions of hot dip Galvanizing in the pre-treatment experiment</td>
<td>36</td>
</tr>
<tr>
<td>2.3</td>
<td>Chemical composition for four different steel substrates</td>
<td>50</td>
</tr>
<tr>
<td>2.4</td>
<td>Temperatures and dipping times for four different steel substrates</td>
<td>53</td>
</tr>
<tr>
<td>2.5</td>
<td>The mass absorption coefficients of Fe, Al and Zn</td>
<td>59</td>
</tr>
<tr>
<td>2.6</td>
<td>Standard d-spacings and intensities of Fe$_2$Al$_3$-Zn$_x$ based on Harvey and Mercer's data</td>
<td>68</td>
</tr>
</tbody>
</table>
2.7 The nine d-spacings of Fe₅Al₃-Znₓ and their intensities from the standard file (Table 2.6) compared to the nine d-spacings and their intensities from the X-ray diffraction of Galfanized coating as shown in Fig. 2.19

2.8 Hughes’s composition of alloy layer formed during galvanizing in Zn bath containing 1.5 wt% Al at 460°C

2.9 Raynor et al’s composition of FeAlₓ-Znₓ

2.10 Compositions of powder mixtures

2.11 Phases and their composition in the five alloys

2.12 Composition (wt% Al) of three Fe-Al phases compared with previously published analyses

2.13 Composition of the corners of the three phase region compared with the results of Urednicek and Kirkaldy

3.1 Diffusion coefficient of Fe and Al in FeₓAl₃ and FeAlₓ

3.2 Data for various temperatures for the time taken for the intermetallic to cover the substrate surface

3.3 Times for intermetallic formation as a function of substrate silicon content and temperature

4.1 d-spacings and X-ray diffraction (Cr Kα radiation) intensities for coating of low carbon steel dipped at 450°C for 128 s

4.2 d-spacings and X-ray diffraction (Cr Kα radiation) intensities for coating of low carbon steel dipped at 450°C for 256 s

4.3 d-spacings and X-ray diffraction (Co Kα radiation) intensities for coating of low carbon steel dipped at 450°C for 512 s
4.4 d-spacings and X-ray diffraction (Cr Kα radiation) intensities for coating of low carbon steel dipped at 450°C for 1024 s

4.5 d-spacings and X-ray diffraction (Co Kα radiation) intensities for coating of low carbon steel dipped at 450°C for 4096 s

4.6 Data of preferred orientation of Fe₃Al₃-Zn₄ based on G2 in Table 4.1 (450°C, 128 s)

4.7 Data of preferred orientation of Fe₃Al₃-Zn₄ based on G2 in Table 4.2 (450°C, 256 s)

4.8 Data of preferred orientation of Fe₃Al₃-Zn₄ based on G4 in Table 4.3 (450°C, 512 s)

4.9 Data of preferred orientation of Fe₃Al₃-Zn₄ based on G5 in Table 4.4 (450°C, 1024 s)

4.10 Data of preferred orientation of Fe₃Al₃-Zn₄ based on G2 in Table 4.5 (450°C, 4096 s)

4.11 d-spacings and X-ray diffraction (Co X-ray) intensities for coating of low carbon steel dipped at 450°C for 256 s and quenched after dipping

4.12 d-spacings and X-ray diffraction (Co X-ray) intensities for coating of low carbon steel dipped at 450°C for 512 s and quenched after dipping

4.13 hkl and d-spacings of Fe₃Al₃-Zn₄ from this experiment compared with calculated and previously published data

4.14 d-spacings of Fe₃Al₃-Zn₄ formed during hot dipping in zinc baths which contain aluminium

4.15 d-spacings and X-ray diffraction (Cr Kα radiation) intensities for coating of low carbon steel dipped at 460°C for 185 s
4.16 d-spacings and X-ray diffraction (Cr Kα radiation) intensities for coating of low carbon steel dipped at 480°C for 55 s

4.17 d-spacings and X-ray diffraction (Cr Kα radiation) intensities for coating of low carbon steel dipped at 490°C for 35 s

4.18 d-spacings and X-ray diffraction (Cr Kα radiation) intensities for coating of low carbon steel dipped at 490°C for 20 s

4.19 d-spacings and X-ray diffraction (Cr Kα radiation) intensities for coating of low carbon steel dipped at 500°C for 20 s

4.20 d-spacings and X-ray diffraction (Cr Kα radiation) intensities for coating of low carbon steel dipped at 510°C for 20 s

4.21 d-spacings and X-ray diffraction (Co Kα radiation) intensities for coating of low carbon steel dipped at 470°C for 900 s

4.22 d-spacings and X-ray diffraction (Co Kα radiation) intensities for coating of low carbon steel dipped at 490°C for 300 s

4.23 d-spacings and X-ray diffraction (Co Kα radiation) intensities for coating of low carbon steel dipped at 500°C for 170 s

4.24 d-spacings and X-ray diffraction (Co Kα radiation) intensities for coating of low carbon steel dipped at 510°C for 90 s

4.25 d-spacings and X-ray diffraction (Cr Kα radiation) intensities for coating of low carbon steel dipped at 520°C for 5 s

4.26 d-spacings and X-ray diffraction (Co Kα radiation) intensities for coating of low carbon steel dipped at 520°C for 15 s

4.27 d-spacings and X-ray diffraction (Cr Kα radiation) intensities for coating of low carbon steel dipped at 520°C for 20 s

4.28 d-spacings and X-ray diffraction (Cr Kα radiation) intensities for coating of low carbon steel dipped at 575°C for 7 s
4.29 d-spacings and X-ray diffraction (Cr Kα radiation) intensities for coating of low carbon steel dipped at 575°C for 10 s

4.30 d-spacings and X-ray diffraction (Co Kα radiation) intensities for coating of low carbon steel dipped at 575°C for 20 s

4.31 Dipping temperatures, dipping time and the intensity of a peak (d=2.190 Å) of FeZn10-Al,

4.32 d-spacings and X-ray diffraction intensities (Co Kα radiation) for coating of low carbon steel dipped at 490°C for 20 s and quenched after dipping

4.33 d-spacings and X-ray diffraction intensities (Co Kα radiation) for coating of low carbon steel dipped at 520°C for 10 s and quenched after dipping

4.34 d-spacings and X-ray diffraction intensities (Co Kα radiation) for coating of low carbon steel dipped at 575°C for 7 s and quenched after dipping

4.35 (hkl) and d-spacings of Fe₃Al₅-Zn₅ formed at two temperatures in Galfan bath

4.36 d-spacings and X-ray diffraction (Co Kα radiation) intensities for coating of 0.1 wt% Si steel dipped at 450°C for 2100 s

4.37 d-spacings and X-ray diffraction (Co Kα radiation) intensities for coating of 0.1 wt% Si steel dipped at 490°C for 720 s

4.38 d-spacings and X-ray diffraction (Co Kα radiation) intensities for coating of 0.1 wt% Si steel dipped at 520°C for 30 s

4.39 d-spacings and X-ray diffraction (Co Kα radiation) intensities for coating of 0.5 wt% Si steel dipped at 450°C for 2940 s

4.40 d-spacings and X-ray diffraction (Co Kα radiation) intensities for coating of 0.5 wt% Si steel dipped at 490°C for 840 s
4.41 d-spacings and X-ray diffraction (Co Kα radiation) intensities for coating of 0.5 wt% Si steel dipped at 520°C for 180 s

4.42 d-spacings and X-ray diffraction (Co Kα radiation) intensities for coating of 1.58 wt% Si steel dipped at 450°C for 1560 s

4.43 d-spacings and X-ray diffraction (Co Kα radiation) intensities for coating of 1.58 wt% Si steel dipped at 490°C for 1080 s

4.44 d-spacings and X-ray diffraction (Co Kα radiation) intensities for coating of 1.58 wt% Si steel dipped at 520°C for 180 s

5.1 Compositions of intermetallic phases determined by EDS quantitative analysis for coatings dipped at 450°C for times as indicated

5.2 Compositions of intermetallic phases determined by EDS quantitative analysis for coatings dipped at temperatures from 490°C for 300 s

5.3 Compositions of intermetallic phases determined by EDS quantitative analysis for coatings dipped at temperatures from 500°C for 170 s

5.4 Compositions of intermetallic phases determined by EDS quantitative analysis for coatings dipped at temperatures from 510°C for 90 s

5.5 Compositions of intermetallic phases determined by EDS quantitative analysis for coatings dipped at temperatures from 520°C for times as indicated

5.6 Compositions of intermetallic phases determined by EDS quantitative analysis for coatings dipped at temperatures from 575°C for times as indicated

A1.1 JCPDS file for Fe (70)
A1.2 JCPDS file for Al (70) 212
A1.3 JCPDS file for Zn (70) 213
A1.4 JCPDS file for FeAl, \( \text{Fe}_5\text{Al}_{13} \) (70) 213
A1.5 JCPDS file for Fe\(_2\)Al\(_5\) (70) 214
A1.6 JCPDS file for FeAl\(_2\) (70) 215
A1.7 JCPDS file for FeAl (70) 215
A1.8 X-ray diffraction data for Fe\(_2\)Al\(_5\) and Fe\(_2\)Al\(_5\)-Zn\(_x\) from Harvey and Mercer (37) 216
A1.9 X-ray diffraction data for Fe\(_2\)Al\(_5\) from Urednicek and Kirkaldy (36) 216
A1.10 X-ray diffraction data for coatings produced in zinc baths containing 0.12, 0.15, 0.22 and 1.1 wt% aluminium from Urednicek and Kirkaldy (36) 217
A1.11 X-ray diffraction data for FeZn\(_7\) from Gellings (12) 219
A1.12 X-ray diffraction data for FeZn\(_8\) from Gellings (11) 219
A1.13 JCPDS file for FeZn\(_7\) (70) 220
A1.14 JCPDS file for \( \text{Al}_{0.77}\text{Zn}_{0.23} \) (70) 220
A2.1 Data of error estimation for X-ray diffraction experiment 221
A3.1 Atom positions of Fe\(_2\)Al\(_5\) (73, 74) 224
A3.2 Possible diffracting planes and d-spacings for Fe\(_2\)Al\(_5\) 225
A3.3 Calculated d-spacings and intensities of Fe\(_2\)Al\(_5\) peaks compared with previously published data 227
A3.4 The corrected d-spacings data file for Fe$_2$Al$_3$

A4.1 X-ray diffraction data for specimen 1

A4.2 X-ray diffraction data for specimen 2

A4.3 X-ray diffraction data for specimen 3

A4.4 X-ray diffraction data for specimen 4

A4.5 X-ray diffraction data for specimen 5

A4.6 Compositions of phases and error