Optimization of Chemistry and Process Parameters for Control of Intermetallic Formation in Mg Sludges

Yintian Fu
University of Windsor

Follow this and additional works at: https://scholar.uwindsor.ca/etd

Part of the Materials Science and Engineering Commons

Recommended Citation
Fu, Yintian, "Optimization of Chemistry and Process Parameters for Control of Intermetallic Formation in Mg Sludges" (2021). Electronic Theses and Dissertations. 8889.
https://scholar.uwindsor.ca/etd/8889

This online database contains the full-text of PhD dissertations and Masters' theses of University of Windsor students from 1954 forward. These documents are made available for personal study and research purposes only, in accordance with the Canadian Copyright Act and the Creative Commons license—CC BY-NC-ND (Attribution, Non-Commercial, No Derivative Works). Under this license, works must always be attributed to the copyright holder (original author), cannot be used for any commercial purposes, and may not be altered. Any other use would require the permission of the copyright holder. Students may inquire about withdrawing their dissertation and/or thesis from this database. For additional inquiries, please contact the repository administrator via email (scholarship@uwindsor.ca) or by telephone at 519-253-3000ext. 3208.
Optimization of Chemistry and Process Parameters for Control of Intermetallic Formation in Mg Sludges

By

Yintian Fu

A Thesis
Submitted to the Faculty of Graduate Studies
through the Department of Mechanical, Automotive & Materials Engineering
in Partial Fulfillment of the Requirements for
the Degree of Master of Applied Science
at the University of Windsor

Windsor, Ontario, Canada

2021

© 2021 Yintian Fu
Optimization of Chemistry and Process Parameters for Control of Intermetallic Formation in Mg Sludges

by

Yintian Fu

APPROVED BY:

______________________________________________
T. Bolisetti
Department of Civil & Environmental Engineering

______________________________________________
X. Nie
Department of Mechanical, Automotive & Materials Engineering

______________________________________________
H. Hu, Advisor
Department of Mechanical, Automotive & Materials Engineering

September 8, 2021
DECLARATION OF ORIGINALITY

I hereby certify that I am the sole author of this thesis and that no part of this thesis has been published or submitted for publication.

I certify that, to the best of my knowledge, my thesis does not infringe upon anyone’s copyright nor violate any proprietary rights and that any ideas, techniques, quotations, or any other material from the work of other people included in my thesis, published or otherwise, are fully acknowledged in accordance with the standard referencing practices. Furthermore, to the extent that I have included copyrighted material that surpasses the bounds of fair dealing within the meaning of the Canada Copyright Act, I certify that I have obtained a written permission from the copyright owner(s) to include such material(s) in my thesis and have included copies of such copyright clearances to my appendix.

I declare that this is a true copy of my thesis, including any final revisions, as approved by my thesis committee and the Graduate Studies office, and that this thesis has not been submitted for a higher degree to any other University or Institution.
ABSTRACT

Intermetallic formation in sludge during magnesium (Mg) melting, holding and high pressure die casting practices is a very important issue. But, very often it is overlooked by academia, original equipment manufacturers (OEM), metal ingot producers and even die casters. The aim of this study was to minimize the intermetallic formation in Mg sludge via the optimization of the chemistry and process parameters. Through the analyses of the commercial sludges, it was found that AZ91D recycling ingot sludge, and AZ91D, AM60B and AE44 die casting sludge contained intermetallic of 2.77wt.%, 10.33wt.%, 34.07wt.% and 44.81 wt.%, respectively. The Al₈Mn₅ intermetallic particles were identified by the microstructure analysis based on the Al and Mn ratio. The design of experiment (DOE) technique, Taguchi method, was employed to minimize the intermetallic formation in the sludge of Mg alloys with various chemical compositions of Al, Mn, Fe, and different process parameters, holding temperature and holding time. The sludge yield (SY) and intermetallic size (IS) was selected as two responses. The optimum combination of the levels in terms of minimizing the intermetallic formation were 9wt.% Al, 0.15wt.%Mn, 0.001wt.% (10 ppm) Fe, 690°C for the holding temperature and holding at 30 mins for the holding time, respectively. The best combination for smallest intermetallic size were 9wt.% Al, 0.15wt.%Mn, 0.001wt.% (10 ppm) Fe, 630°C for the holding temperature and holding at 60 mins for the holding time, respectively.
DEDICATION

To my Mom and Dad,

Yaping Li and Yelu Fu

Without their endless support and love,

none of my success would be possible.

To my Dear,

Yuxian Li

Thanks for your endless love, supports and encouragement.
ACKNOWLEDGEMENTS

I gratefully acknowledge every group and person who provides me with generous help and support. Without their help, this thesis would never have completed. Firstly, Meridian Lightweight Technologies Inc for funding my research.

Secondly, I would like to express my sincere gratitude to my supervisors, Dr. H. Hu for their selfless help, support, and academic guidance throughout the study at the University of Windsor.

Thirdly, I would like to thank my committee members (Dr. Xueyuan Nie and Dr. Tirupati Bolisetti) for their helpful comments and careful review of this work.

Finally, I would like to thank Mr. Andrew Jenner, Miss. Yuxian Li and Mr. Sufeng Liu from University of Windsor for their assistance with the experiments. And also support me whenever I meet difficulties.
TABLE OF CONTENTS

DECLARATION OF ORIGINALITY ................................................................. iii

ABSTRACT ................................................................................................. iv

DEDICATION .............................................................................................. v

ACKNOWLEDGEMENTS ............................................................................. vi

LIST OF TABLES ......................................................................................... xi

LIST OF FIGURES ....................................................................................... xiv

CHAPTER 1 Introduction ................................................................................. 1

1.1 Background ............................................................................................. 1

1.2 Objective ................................................................................................ 1

1.3 Thesis Layout .......................................................................................... 2

CHAPTER 2 Literature Review ....................................................................... 5

2.1 Introduction ............................................................................................. 5

2.2 Sludge Formation in Aluminum Alloys .................................................... 6

2.2.1 Sludge Factor .................................................................................... 7

2.2.2 Role of Iron, Manganese, and Chromium ........................................ 8

2.2.3 Determination of Sludge Factor ....................................................... 8

2.2.4 Effect of Holding Temperature on Sludge Formation .................... 10
2.2.5 Effect of Cooling Rate on Sludge Formation .............................................15

2.3 Control, Characterization and Assessment of Sludge in Die Cast Mg Alloys .........17

2.3.1 Metallurgical Principles for Control of Sludge in Ingot Production and Die Casting of Mg Alloys ..............................................................17

2.3.2 Characterization of Mg Sludge .................................................................26

2.3.2.1 Chemical compositions of Mg die-casting alloys and sludge ................. 26

2.3.2.2 Characterization of die-casting sludge ................................................. 28

2.3.2.2.1 Morphology and sizes of intermetallics in die-casting sludge .......... 28

2.3.2.2.2 Chemical composition of intermetallics in die-casting sludge ......... 30

2.3.3 Al-Mn(-Fe) Intermetallic Formation and Thermodynamic Assessment .......33

2.3.3.1 Al-Mn(-Fe) intermetallic formation and interaction with oxide .......... 33

2.3.3.2 Thermodynamic assessment of Mg-Al-Mn system ................................ 36

2.3.4 Rapid Assessment of Mg Oxide and Intermetallic in Mg Alloys .................38

2.3.4.1 Spectroscopic technique ................................................................. 39

2.3.4.2 Fracture test ..................................................................................... 40

2.3.4.2.1 K-Mold ..................................................................................... 40

2.3.4.2.2 Light reflectance ........................................................................ 41

2.3.4.3 Filtration ......................................................................................... 42

2.3.4.4 Hybrid ............................................................................................ 44

2.4 Summary ................................................................................................. 47

CHAPTER 3 Experimental Procedure ....................................................................49
3.1 Materials.....................................................................................................................................49

3.1.1 Recycling Sludge and High Pressure Die Casting Sludge .................................................49

3.1.2 Aluminum and Magnesium Ingots, and Master Alloys.......................................................50

3.2 Melt Preparation.........................................................................................................................52

3.2.1 Protective Gas and Melting Unit .........................................................................................53

3.2.2 Tool Preheating ....................................................................................................................54

3.2.3 Ingot Preheating .................................................................................................................55

3.2.4 Melting Process ....................................................................................................................56

3.3 Microstructure Analysis ............................................................................................................59

3.3.1 Specimen preparation ...........................................................................................................59

3.3.2 Optical Microscopy (OM) and Scanning Electron Microscopy (SEM) .........................61

CHAPTER 4 Design of Experiment by Taguchi Method ...............................................................63

4.1 Design of Experiments Technique .........................................................................................63

4.2 Design of Orthogonal Array and Signal-to-Noise Analysis .................................................65

4.3 Determination of Sludge Yield ..............................................................................................69

4.4 Analysis of variance (ANOVA) .............................................................................................72

CHAPTER 5 Characterization of Mn and/or RE containing Intermetallics in AZ91D Recycling Ingot Sludge, and AZ91D, AM60 and AE44 Die Casting Sludges..............75

5.1 Characterization of Mn-containing Intermetallics in AZ91D Recycling Ingot Sludge .................................................................................................................................75

5.2 Characterization of Mn-containing Intermetallics in AZ91D Die Casting Sludge..92
5.3 Characterization of Mn-containing Intermetallics in AM60B Die Casting Sludge .................................................................108

5.4 Characterization of Mn-containing Intermetallics in AE44 Die Casting Sludge .................................................................124

5.5 Factors influencing intermetallic formation in sludge .........................146

CHAPTER 6 Control of Intermetallic Formation in Sludge of Mg Alloys by Taguchi Method .................................................................................................................................................................................................149

6.1 Determination of optimal levels for sludge yield........................................149

   6.1.1 Factor Contributions .......................................................................156

   6.1.2 Confirmation Experiment .................................................................158

   6.1.3 Summary for sludge Yield .................................................................162

6.2 Determination of optimal levels for intermetallic size ............................162

   6.2.1 Factor Contribution .......................................................................170

   6.2.2 Summary for Intermetallic Size .......................................................171

6.3 Chemical, Process and Comprehensive Sludge Factors for Al-containing Mg Alloys .................................................................................................................................173

CHAPTER 7 Conclusions .............................................................................179

CHAPTER 8 Future Work ............................................................................182

REFERENCES .................................................................................................183

VITA AUCTORIS .........................................................................................188
LIST OF TABLES

Table 2-1 Chemical composition of Al-Si-Cu alloys tested by Makhlouf and Apelian [9].

................................................................. 13

Table 2-2 Sludge factors for the alloys tested by Makhlouf and Apelian [9]. ............... 13

Table 2-3 Chemical compositions of ASTM B93 and B94 standards for automotive Mg alloys AZ91D, AM60B and AM50A for ingots and die castings, respectively [16, 17]. 20

Table 2-4 Die casting process, Mg alloys and casting temperatures for sludge generation [18]. .................................................................................................................. 27

Table 2-5 ICP results for melt compositions (wt%) taken from spectrometer discs [18]. 28

Table 2-6 Metallic sludge composition [18]. ........................................................................ 28

Table 2-7 Fe contents of intermetallic particles in sludge [18]. ....................................... 32

Table 2-8 Oxygen and MgO contents in primary AZ and AM ingots [30]. .................... 46

Table 2-9 Contents of MgO and Al-Mn intermetallic compounds in recycled AZ91 Ingots [30]. .................................................................................................................. 47

Table 3-1 Chemical composition of raw metallic materials.............................................. 50

Table 3-2 Densities of different gases. .............................................................................. 53

Table 3-3 The dimensions of the graphite crucible. ......................................................... 56

Table 4-1 Design factors and levels.................................................................................. 65

Table 4-2 Designed experiment plans.............................................................................. 66
Table 5-1 Elements in analyzed α-Mg matrix, Mn-containing intermetallic phase and MgO of Spot 5 shown in Figure 5-2........................................................................................................83

Table 5-2 Elements in analyzed α-Mg matrix, Mn-containing intermetallic phase and MgO of Spot 7 shown in Figures 5-4........................................................................................................................................89

Table 5-3 Volume Fractions and weight Percentages of Al₈Mn₅ intermetallic phases in AZ91D recycling ingot sludge ........................................................................................................................................91

Table 5-4 Elements in analyzed α-Mg matrix, Mn-containing intermetallic phase and MgO of Spot 4 shown in Figure 5-9........................................................................................................................................100

Table 5-5 Elements in analyzed α-Mg matrix, Mn-containing intermetallic phase and MgO of Spot 8 shown in Figures 5-11(a)........................................................................................................................................105

Table 5-6 Volume Fractions and weight Percentages of Al₈Mn₅ intermetallic phases in AZ91D die casting sludge ........................................................................................................................................107

Table 5-7 Elements in analyzed α-Mg matrix, Mn-containing intermetallic phase and MgO of Spot 2 shown in Figure 5-15........................................................................................................................................116

Table 5-8 Elements in analyzed α-Mg matrix, Mn-containing intermetallic phase and MgO of Spot 4 shown in Figures 5-17 (a)........................................................................................................................................121

Table 5-9 Volume Fractions and weight Percentages of Al₈Mn₅ intermetallic phases in AM60B die casting sludge ........................................................................................................................................123

Table 5-10 Elements in analyzed α-Mg matrix, Mn and RE containing intermetallic phase and MgO of Spot 1 shown in Figure 5-22. ........................................................................................................135
Table 5-11 Elements in analyzed α-Mg matrix, Mn and RE containing intermetallic phase and MgO of Spot 2 shown in Figure 5-23. ................................................................. 143

Table 5-12 Volume Fractions and weight Percentages of intermetallic phases in AE44 die casting sludge........................................................... 145

Table 5-13 Chemical compositions of the analyzed Mg alloys, AZ91, AM60 and AE44 alloys in ingot and die casting forms. .................................................. 147

Table 5-14 Comparison of melt holding temperatures for sludge generation. .......... 148

Table 6-1 The S/N ratios calculated from the determined sludge yield relevant to the experiments designed by the Taguchi method..............................................152

Table 6-2 The mean factor response of sludge yield................................................ 153

Table 6-3 Results of the ANOVA for sludge yield.................................................... 158

Table 6-4 The S/N ratios calculated from the determined intermetallic size relevant to the experiments designed by the Taguchi method........................................ 166

Table 6-5 The factor response of size of intermetallic. ............................................. 167

Table 6-6 Results of the ANOVA for intermetallic size............................................. 172
LIST OF FIGURES

Figure 2-1 Calculation of the sludge factor with the SF formula [5]................................. 9

Figure 2-2 Sludge factor vs. Furnace temperature ( °C = ( °F -32) x5/9 )[5]. ....................... 9

Figure 2-3 An example showing the selection of the holding furnace temperature (660 – 663°C), i.e., (1200-1250 °F), for an A380 melt with a SF of 1.8 [5]............................... 10

Figure 2-4 Temperature vs sludge factor for the studied alloys [9]................................. 11

Figure 2-5 Optical microstructure of alloy A380, melt was held at 670°C for 3 hrs, cast in a copper wedge mold, at wall thickness of 0.36” (fast cooling). T-Star-like, B-Blocky particle [9]........................................................................................................................................ 14

Figure 2-6 Optical microstructure of alloy A380, melt was held at 720°C for 3 hrs, cast in a copper wedge mold, at wall thickness of 0.36” (fast cooling). T-Star-like, B-Blocky particle [9]........................................................................................................................................ 14

Figure 2-7 Fe-rich needle and polyhedral particle surrounded by the primary Si in alloy #3 (slow cooling). S-Primary Si, P-Polyhedral, N-Needle (or Platelet) [9]. ....................... 16

Figure 2-8 Microstructure of alloy #1, melt was held at 670°C for 3 hrs, cast in a copper mold, at wall thickness of 4.3 mm (fast cooling). T-Star-like, N-Needle (or Platelet), S-Primary Si [9]........................................................................................................................................ 16

Figure 2-9 Temperature-dependent mutual solubilities of Fe and Mn in in Mg alloys (a) AZ91, (b) AM60 and (c) AM50 [14]........................................................................................................ 22

Figure 2-10 Solubility of Mn in Mg-Al alloys, AZ91, AM60 and AM50 [15]............... 23
Figure 2-11 Magnesium-rich corner of the Mg-Al-Mn phase diagram, (a) 660 and (b) 700 °C [14].

Figure 2-12 Typical sludge as seen (a) and (b) in AZ91D, (c) AM60B, and (d) AM50A [18].

Figure 2-13 Probe results indicating that the majority of the particles could be Al$_8$(MnFe)$_5$ [14, 18].

Figure 2-14 EDS mapping of an AZ91D intermetallic. Elements appeared evenly distributed [18].

Figure 2-15 Typical cross-sections of primary Al-Mn(-Fe) particles in AZ91 after 4 h isothermal holding at 700 oC in (a) an Al2O3 crucible and (b) a mild steel crucible. In (a) and (b), the top are BSE-SEM images, the middle are corresponding EBSD phase maps and the bottom are IPF-X maps. (c) Pole figures for two families of planes from the sample in (a) showing cyclic twinning [3].

Figure 2-16 Typical 3D morphologies of primary Al$_8$Mn$_5$ particles nucleating on the oxide in AZ91 [3].

Figure 2-17 Calculated vertical sections of the Mg–Al–Mn–Zn phase diagram and the experimental data of Ref. [20] for the fixed 9.5 wt.% Al and 0.84 wt.% Zn alloy.

Figure 2-18 Optical micrographs showing massive presence of Al$_8$Mn$_5$ particles in Mg–10 wt.% Al–2.5 wt.%Mn alloy processed at 850 °C, (a) low and (b) high magnifications [22].

Figure 2-19 K-mould method [23, 25].
Figure 2-20 Optical micrographs showing as-polished (a) a lacy oxide network in cast AM60, and (b) a snaky oxide film associated with a surface defect in cast AM60 [24]. 41

Figure 2-21 Schematic diagram showing the principle of a brightimeter [26, 27]. 42

Figure 2-22 Norsk Hydro's magnesium inclusion assessment method (HMIAM) [23, 28, 29]. 43

Figure 3-1 Photographs showing sludge blocks generated from (a) the recycling process of AZ91D Mg alloy, and (b) the HPDC production process of AZ91D and AM60 Mg alloys. 49

Figure 3-2 Pure aluminum, (a) original ingot, and (b) sectioned pieces. 51

Figure 3-3 Pure magnesium, (a) original ingot, and (b) sectioned pieces. 51

Figure 3-4 Mg-2 wt.% Mn master alloy, (a) original ingot, and (b) sectioned pieces. 51

Figure 3-5 Al-10wt.% Fe master alloy, (a) original ingot, and (b) sectioned pieces. 52

Figure 3-6 SF6 protective gas system and melting furnace. 54

Figure 3-7 (a) a graphite crucible used for lab experiments, and (b) dimensions of the graphite crucible. 55

Figure 3-8 Flow chart showing the melt preparation procedure of lab experiments. 58

Figure 3-9 Photographs showing (a) the marking lines for sectioning of a sludge block, and (b) the sectioned specimens for metallographic analysis. 60
Figure 3-10 Photographs showing (a) an air-cooled cast cylindrical DOE Mg alloy sample prepared by the graphite crucible, and (b) the locations from which specimens were sectioned for metallographic analysis................................................................. 60

Figure 3-11 Buehler Optical Image Analyzer Model 2002. ................................................. 62

Figure 3-12 Scanning electron microscope (Hitachi Tabletop Microscope TM3000). .... 62

Figure 4-1 Procedures for the Taguchi method [33].........................................................64

Figure 4-2 Schematical illustration showing a Mg cylinder casting with an Al-Mn intermetallic-free area and an Al-Mn intermetallic-concentrated layer............................. 72

Figure 5-1 SEM micrographs at low magnification showing a microstructure panoramic view of the AZ91D recycling ingot sludge with seven spots selected for EDS analyses........................................................................................................78

Figure 5-2 EDS results for Spot 5 in the AZ91D recycling ingot sludge: (a) SEM micrograph in BSE mode, and elemental maps for (b) all detected elements, (c) Mg, (d) Al, (e) Mn, (f) Fe and (g) O. ............................................................... 81

Figure 5-3 EDS spectra (a), (b) and (c) for the areas containing α-Mg matrix (dark), and Mn-containing intermetallic phases (gray), and MgO inclusion (black) for points 1-3 as shown in Figure 5-2 (a), respectively. ......................................................... 83

Figure 5-4 SEM micrograph showing microstructure of Spot 7................................. 84
Figure 5-5 EDS results for Spot 7 in the AZ91D recycling ingot sludge: (a) SEM micrograph in BSE mode, and elemental maps for (b) overall detected elements, (c) Mg, (d) Al, (e) Mn, (f) Fe and (g) O. .......................................................... 87

Figure 5-6 EDS spectra (a), (b) and (c) for the areas containing α-Mg matrix (dark), and Mn-containing intermetallic phases (gray), and MgO inclusion (black) for Point 4, 5 and 7 as shown in Figure 5-4, respectively. .................................................................................. 89

Figure 5-7 Binary black and white images showing the volume fraction of Al₈Mn₅ intermetallic phases in (a) Spot 5 and (b) Spot 7 of the AZ91D recycling ingot sludge. . 90

Figure 5-8 SEM micrographs at low magnification showing a microstructure panoramic view of the AZ91D die casting sludge with six spots selected for EDS analyses.......... 94

Figure 5-9 EDS results for Spot 12 in the AZ91D die casting sludge: (a) SEM micrograph in BSE mode, and elemental maps for (b) all detected elements, (c) Mg, (d) Al, (e) Mn, (f) Fe and (g) O. ........................................................................................................ 98

Figure 5-10 EDS spectra (a), (b) and (c) for the areas containing α-Mg matrix (dark), and Mn-containing intermetallic phases (gray), and MgO inclusion (black) for points 8-10 as shown in Figure 5-9 (a), respectively. ................................................................. 99

Figure 5-11 EDS results for Spot 8 in the AZ91D die casting sludge: (a) SEM micrograph in BSE mode, and elemental maps for (b) all detected elements, (c) Mg, (d) Al, (e) Mn, (f) Fe and (g) O. ........................................................................................................... 103
Figure 5-12 EDS spectra (a), (b) and (c) for the areas containing α-Mg matrix (dark), and Mn-containing intermetallic phases (gray), and MgO inclusion (black) for points 11-13 as shown in Figure 5-11 (a), respectively. ................................................................. 105

Figure 5-13 Binary black and white images showing the volume fraction of Al₈Mn₅ intermetallic phases in (a) Spot 12 and (b) Spot 8 of the AZ91D die casting sludge. 106

Figure 5-14 SEM micrographs at low magnification showing a microstructure panoramic view of the AM60B die casting sludge with six spots selected for EDS analyses. 110

Figure 5-15 results for Spot 16 in the AM60B die casting sludge: (a) SEM micrograph in BSE mode, and elemental maps for (b) all detected elements, (c) Mg, (d) Al, (e) Mn, (f) Fe and (g) O. ................................................................. 114

Figure 5-16 EDS spectra (a), (b) and (c) for the areas containing α-Mg matrix (dark), and Mn-containing intermetallic phases (gray), and MgO inclusion (black) for points 14-16 as shown in Figure 5-15 (a), respectively. ................................................................. 115

Figure 5-17 EDS results for Spot 18 in the AM60B die casting sludge: (a) SEM micrograph in BSE mode, and elemental maps for (b) all detected elements, (c) Mg, (d) Al, (e) Mn, (f) Fe and (g) O. ................................................................. 119

Figure 5-18 EDS spectra (a), (b) and (c) for the areas containing α-Mg matrix (dark), and Mn-containing intermetallic phases (gray), and MgO inclusion (black) for points 17-19 as shown in Figure 5-17 (a), respectively. ................................................................. 121

Figure 5-19 Binary black and white images showing the volume fraction of Al₈Mn₅ intermetallic phases in (a) Spot 16 and (b) Spot 18 of the AM60B die casting sludge. 122
Figure 5-20 SEM micrographs at low magnification showing a microstructure panoramic view of the AE44 die casting sludge with five spots selected for EDS analyses. .......... 127

Figure 5-21 EDS results for Spot 22 in the AE44 die casting sludge: (a) SEM micrograph in BSE mode, and elemental maps for (b) all detected elements, (c) Mg, (d) Al, (e) Mn, (f) O, (g) Ce, (h) Pr, (i) La and (j) Nd. .............................................................. 132

Figure 5-22 EDS spectra (a), (b), (c) and (d) for the areas containing α-Mg matrix (dark), and intermetallic phases contain RE and Mn (dark gray), and RE-containing intermetallic phases (bright grey), and MgO inclusion (black) for points 20-23 as shown in Figure 5-21 (a), respectively ................................................................. 134

Figure 5-23 EDS results for Spot 21 in the AE44 die casting sludge: (a) SEM micrograph in BSE mode, and elemental maps for (b) all detected elements, (c) Mg, (d) Al, (e) Mn, (f) O, (g) Ce, (h) Pr, (i) La and (j) Nd. .............................................................. 140

Figure 5-24 EDS spectra (a), (b), (c) and (d) for the areas containing α-Mg matrix (dark), and intermetallic phases contain RE and Mn (dark gray), and RE-containing intermetallic phases (light grey), and MgO inclusion (black) for points 24-27 as shown in Figure 5-23(a), respectively ................................................................. 142

Figure 5-25 Binary black and white images showing the volume fraction of AlMnRE and AlRE intermetallic phases in (a) Point 22 and (b) Point 21 of the AE44 die casting sludge. ................................................................. 144

Figure 6-1 Effect of Al content on the mean S/N ratio .................................................. 153

Figure 6-2 Effect of Mn content on the mean S/N ratio .................................................. 154
Figure 6-3 Effect of Fe content on the mean S/N ratio........................................... 154

Figure 6-4 Effect of Holding Temperature on the mean S/N ratio......................... 155

Figure 6-5 Effect of Holding Temperature on the mean S/N ratio......................... 155

Figure 6-6 Single response signal-to-noise graph for case the only considering only the sludge yield................................................................. 156

Figure 6-7 SEM micrographs showing the Al-Mn intermetallic-free zone and the Al-Mn intermetallic-concentrated layer of the alloys with least sludge yield from the confirmation experiment............................................................................................. 160

Figure 6-8 SEM micrographs showing the Al-Mn intermetallic-free zone and the Al-Mn intermetallic-concentrated layer of the alloy with most sludge yield from the confirmation experiment............................................................................................. 161

Figure 6-9 Effect of Al content on the mean S/N ratio........................................... 167

Figure 6-10 Effect of Mn content on the mean S/N ratio........................................... 168

Figure 6-11 Effect of Fe content on the mean S/N ratio........................................... 168

Figure 6-12 Effect of Holding Temperature content on the mean S/N ratio............ 169

Figure 6-13 Effect of Holding Time content on the mean S/N ratio......................... 169

Figure 6-14 Single response signal-to-noise graph for case only consider intermetallic size. ................................................................................................................. 170
Figure 6-15 Regression coefficients $R^2$ with standard errors for six developed SFs. CSFSY, PSFSY, CPSFSY, CSFIS, PSFIS, and CPSFIS stand for the sludge factors of CSF$^{SY}$, PSF$^{SY}$, CPSF$^{SY}$, CSF$^{IS}$, PSF$^{IS}$, and CPSF$^{IS}$, respectively ................................................................. 176

Figure 6-16 Comparison of predicted sludge yields and intermetallic sizes with the experimental measurements for the confirmation experiment with the least sludge formation........................................................................................................................................... 178

Figure 6-17 Comparison of predicted sludge yields and intermetallic sizes with the experimental measurements for the confirmation experiment with the most sludge formation........................................................................................................................................... 178
CHAPTER 1
Introduction

1.1 Background

Sludge containing intermetallic particles is the residue settled at the bottom of the crucibles during metal melting and holding processes. Sludge formation in Mg die casting foundry is often overlooked because it seems to be disconnected with original equipment manufacturers (OEMs), ingot producers and even design engineers of die casters. Therefore, there is a lack of general knowledge on sludge formation mechanisms. However, sludge formation in Mg foundry is a very important topic because the improper handling of sludge could degrade product quality. The excessive sludge formation impacts metal delivery system, contributes around 50% of total metal loss in the melting process, and acts a thermal barrier which could result in significant metal temperature fluctuation in a die casting furnace. Such metal temperature fluctuation negatively influences normal casting production from production stoppage (if metal temperature is too low) to Fe pick-up (if metal temperature is too high). Also, the magnesium melting, holding and handling practices in the casting industry showed such metal fluctuation could shorten crucible life due to thermal shock and excessive heating of the crucible steel. Therefore, it is very important to characterize Mg sludges and minimize their formation as much as possible.

1.2 Objective

In this work, the major effort was to minimize the intermetallic formation in the sludges resulting from the melting and holding of Mg alloys during die casting operation. Intermetallic particles $\text{Al}_x\text{(Mn)}_y$ originated from the primary and secondary Mg ingots play an important role as precipitation sites for Fe in lowering the level of dissolved Fe and
increasing the overall corrosion resistance of the castings. Sludge intermetallic generation for die casting of magnesium alloys has a direct impact on the casting product quality. To understand the characteristics of Mg die casing sludge and to control the intermetallic formation Mg sludge, several objectives were aimed to be achieved:

1. To characterize intermetallic particles in the sludge generated from the commercial Mg alloys;
2. To design experiment Mg alloys with chemical elements of Al, Mn and Fe by using the Taguchi method;
3. To mimic industrial practices by melting and holding the designed experimental alloys at a desired temperature for a fix time based on the Taguchi design;
4. To quantify the sludge yield (SY) based on the measured volume fraction of intermetallic phase;
5. To determine the intermetallic size (IS) based on microstructure analyses:
6. To obtain the optimum combination of chemical composition and process parameters holding temperature and times for SY and IS; and
7. To develop the sludge factors as a function of the chemical composition and process parameters by using the multivariate linear regression.

1.3 Thesis Layout

This thesis is a partial fulfillment of the requirement for the degree of Maters of Applied Science. It is divided into eight chapters. Chapter 1 presents a general background conducted in this study as an introduction and the outline of the work was presented.

In Chapter 2, a literature review related to this study was carried out. characteristics and possible control of Mg die casting sludge, based on the established knowledge of
sludge formation and factor in Al die casting alloys, were reviewed. Metallurgical principles for control of sludge in ingot production in association with die casting of Mg alloys were discussed. Rapid assessment of Mg oxide and intermetallics relevant to sludge formation in Mg alloys was highlighted.

In Chapter 3, there were the outlines of the methodology for the overall experimentation. A systematic experimental procedure was described for evaluation of sludge yield and microstructural characterization.

In Chapter 4, a design of experiment (DOE) technique, the Taguchi method, was reviewed. The design of orthogonal array, signal-to-noise analysis, and analysis of variance (ANOVA) were introduced.

In Chapter 5, the characterization of the commercial Mg alloys sludge, including the AZ91D recycling ingot sludge, AZ91D, AM60B and AE44 die casting sludges was revealed and discussed.

In Chapter 6, a design of experiment (DOE) technique, the Taguchi method, was used to optimally control the sludge intermetallic formation in the sludge generated from the designed experimental alloys with different the chemical compositions of Al, Mn and Fe processed at various holding temperatures and times. During the optimization, the SY and IS were employed as two individual responses. The results of the response analysis were used to derive the optimal level combinations. To develop the Sludge Factors for the designed Mg alloys, multivariate linear regression analyses were carried out with the DOE results. Six Sludge Factor equations for the sludge yield and intermetallic size were established as a function of the chemical compositions and/or the processing parameters.
Finally, the conclusions of this study were summarized in Chapter 7 and the future work was proposed in Chapter 8.
CHAPTER 2
Literature Review

2.1 Introduction

Magnesium alloys as the lightest weight metals which have been increasingly desired hugely in the automotive related manufacturing industry, because they possess high strength-to-weight ratios, good ductility, low density and excellent corrosion resistance [1, 2].

Currently, the most widely used commercial magnesium alloys, such as AM60B and AZ91, are based on Mg–Al system. All the current magnesium die casting alloys are based upon aluminum as the main alloying element. In the Mg-Al alloys, Al₈Mn₅ intermetallic particles form as primary solidification phases, which are important for ensuring adequate corrosion resistance. However, the presence of the excessive Al₈Mn₅ particles interacting with magnesium oxide inclusions above the α-Mg liquidus temperature leads to sludge formation and sedimentation. The interaction between the Al₈Mn₅ particles and oxide films generates deleterious casting defects [3, 4]. The sludge during the die casting operation often experiences a buildup of solid heavy-element compounds at the bottom of a melting and holding furnace. The sludge buildup can cause the damage to the furnace, the “hardspot” inclusions in casting and the restriction of metal flow filling the die cavity. The sludge contributes around 50% of total metal loss in the Mg melting and casting process. In addition, the formation of excessive sludge acting a thermal barrier could result in significant melt temperature fluctuation in the die casting furnace. The melt temperature fluctuation impacts normal casting operation. The very low melt temperature could stop the casting production, while the melt picks up easily iron from the steel crucible at the
high temperature to generate additional sludge. Therefore, sludge formation in the die casting furnace is a very important subject, but very often is overlooked by academia, OEMs, ingot producers and even die casters. It is essential to understand Mg sludge formation and minimize it as much as possible.

Compared with that in the Mg alloys, the sludge formation in Al die casting alloys has been well understood. A Sludge Factor relating to metal chemistry is proposed and proven to be useful to determine sludge formation tendency of and quantity of a specific alloy chemistry. The work had been performed to relate sludge formation with the Sludge Factor and the Al melt holding temperature [5-11]. However, similar studies on the formation and control of sludge in die casting Mg alloys are limited.

This Chapter intends to give an overview of formation, characteristics and control of Mg die-casting sludge, based on the established knowledge of sludge formation and factor in Al die casting alloys. Previous work on characterization and assessment of sludge in die cast Mg alloys are reviewed. Metallurgical principles for control of sludge in ingot production in association with die casting of Mg alloys are discussed. Rapid assessment of Mg oxide and intermetallics relevant to sludge formation in Mg alloys are highlighted.

**2.2 Sludge Formation in Aluminum Alloys**

In-depth studies on metallurgical aspects of aluminum alloys, in particular, mechanisms of sludge formation, have been extensively carried out. This is because aluminum foundries, and especially aluminum die casting operation, usually experience a buildup on the floor of melting and holding furnaces, commonly called “sludge”. Sludge is made of primary crystals that contain aluminum and silicon, and are also rich in iron,
manganese, and chromium. These crystals have high melting points and high specific gravity, which cause them to settle to the bottom of the melt. The precipitation of sludge crystals often occurs only in the melt having sufficiently large amounts of iron, manganese, and/or chromium in relation to the furnace operation temperature [9].

2.2.1 Sludge Factor

Sludge formation depends on not only the chemical composition of Al alloys, but also the process parameters such as melting and holding temperatures, and holding time of the melt. To reveal the effect of the chemical composition on the sludge formation, Jorstad [5] and Groteke [6] defined a Sludge Factor (SF) for die casting Al alloy A380. This factor is calculated from the Fe, Mn, and Cr contents of the alloys as follows:

\[
\text{Sludge Factor (SF)} = (1 \times \text{wt\%Fe}) + (2 \times \text{wt\%Mn}) + (3 \times \text{wt\%Cr})
\] (1)

To minimize the sludge formation, a small SF needs to be maintained for the A380 alloy, when the furnace holding temperature is low. Shabestari, and Gruzleski [7] studied the influence of chemical composition, holding temperature and cooling rate on sludge formation in Al-12.7 wt% Si alloys. They found that the Fe, Mn and Cr contents of the alloy as well as the cooling rate significantly affected the morphology, quantity, and size of the sludge particles. Sludge was unable to form until a specific temperature was reached for a given Fe content, and the sludge forming temperature depended on the Fe content of the alloy. The following relationship was proposed to describe the dependence of sludge forming temperature on the iron content:

\[
\text{Temperature (°C)} = 645.7 + 34.2 (\text{wt\%Fe})
\] (2)

It was found that the sludge crystals consisted mainly of Fe, Mn and Cr-rich compounds.
2.2.2 Role of Iron, Manganese, and Chromium

To prevent molten Al alloys from soldering die steel, iron is introduced into die casting aluminum alloys as a desirable element. Most casting Al alloys contain about 0.8 wt%. The Al alloys containing the Fe content above this amount exhibit almost no tendency to dissolve die steel, while the two materials are in intimate contact. For this reason, most aluminum die casters desire that their alloys contain between 0.8% and 1.1% [5]. Manganese and chromium present in the aluminum alloys as secondary impurities, which are beneficial to their mechanical properties. Jorstad [5] found that Mn and Cr changed the morphology of the Fe-rich phase from acicular to cubic form. Consequently, the ductility and strength of cast components were improved.

2.2.3 Determination of Sludge Factor

Figure 2-1 illustrates the calculation of the sludge factor which determines the tolerable limits by using the simple and straightforward formula. The SF value is 1.83 for the melt containing 0.89 wt% Fe, 0.35% Mn and 0.08 wt% Cr. Figure 2-2 presents the tolerable sludge factor vs temperature chart, which can be used to determine a minimum holding furnace temperature for a given melt of the A380 alloy to avoid sludge formation during the die casting operation. The holding furnace temperature should increase with increasing the SF values for the A380 melt. If the temperature for the melt with the high SF was insufficient high to prevent all the heavy-element phase precipitating from solution, the sludge buildup could take place. For instance, as shown in Figure 2-3, the furnace temperature of 660-663°C (1200-1250°F) needs to be selected for the A380 melt with a SF of 1.8.
“Sludge” Factor = 
\[(1 \times \%\text{Fe}) + (2 \times \%\text{Mn}) + (3 \times \%\text{Cr})\]

Example
0.89% Fe \times 1 = 0.89
0.35% Mn \times 2 = 0.70
0.08% Cr \times 3 = 0.24

“Sludge” Factor = 1.83

Figure 2-1 Calculation of the sludge factor with the SF formula [5].

Figure 2-2 Sludge factor vs. Furnace temperature \((^\circ C = (^\circ F - 32) \times 5/9))\) [5].
Figure 2-3 An example showing the selection of the holding furnace temperature (660 – 663°C), i.e., (1200-1250 °F), for an A380 melt with a SF of 1.8 [5].

2.2.4 Effect of Holding Temperature on Sludge Formation

Despite fact that many studies were conducted on the mechanism of sludge formation in Al-based alloys, published results seem inconsistent. Jorstad [5] and Groteke [6] (Figure 4) predicted that, for a hypoeutectic Al-Si alloy containing 1% Fe, content, sludge could form when the holding temperature was below 600°C. But, Shabestari [7] predicted that, for the same iron content, sludge could be found only as the melt was held at a high temperature of 680°C (Figure 2-4).
The influence of holding temperature and time and alloy chemistry on sludge formation in Al-Si-Cu alloys was investigated by Flores et al [8]. It was found that, in Al-Si-Cu alloys with the composition exceeding 0.60% Fe, 0.50% Mn and 8% Si, sludge in the form of Al(Fe, Mn) Si formed at temperatures in the range 610-660°C. As the melt of a 7.5%Si, 1.2%Fe, 3.53%Cu, 0.60%Mn, 0%Cr alloy was held at a selected temperature for 50 minutes, the area percentage of Al(Fe, Mn) Si type sludge formed at a location 14 cm from the melt surface was approximately 2.4%, 8.2% and 1.1% for holding temperatures 630°C, 640°C, and 660°C, respectively. In addition, at 640°C, the area percent of the sludge increased significantly when the Cr content of the alloy was increased from 0% to 0.2%. Flores et al. [8] also reported that the average size of the sludge particles depended on the holding temperature and time. At 640°C, the average size of the sludge particles was over
40 μm after holding for one to two minutes, while at 630°C and 660°C, it was about 5 μm for the same holding time. These findings suggest that the Al(Fe, Mn)Si type sludge forms most readily at about 640°C.

Makhlouf and Apelian [9] investigated the effects of holding temperatures and chemical composition of five hypoeutectic and hypereutectic Al-Si experimental alloys with different contents of alloying and impurity elements, Si, Cu, Mg, Fe, Mn and Cr on sludge formation, in comparison with the commercial die casting alloy A380 (Table 2-1). The SF values of the tested alloys are listed in Table 2-2. The experiment alloys were prepared and melted in an electric resistance furnace at 850°C and held for 30 minutes from pure aluminum and Al-Si, Al-Fe, Al-Mg, master alloys. To evaluate the effect of holding temperatures, the melt temperature then was lowered to 720°C or 670°C for holding 3 hrs. Upon the completion of holding, the melt was moved out of the furnace and solidified quiescently in air for slow cooling, or was poured into a copper wedge mold for fast cooling.

Microstructure examination of the samples either slowly or fast cooled to resemble die-casing showed that the holding temperature (670°C vs. 720°C) appeared little influence on sludge formation in the experimental alloys with the SF ranging from 1.32 to 2.51. However, a few small star-like Fe-rich particles were found in samples from alloy A380 melts that were held at 670°C for 3 hours. This phase was not detected in A380 melts that were held at 720°C for 3 hours. The particles were small and might not contribute to sludge. This phenomenon became more important when the cooling rate became lower. It was also observed that, for fast cooling in a copper wedge mold, more and larger star-like Fe-rich particles were observed in the casting whose melt was held at 670°C than in the casting whose melt was held at 720°C, as shown in Figures 2-5 and 2-6. It was explained that
ingots and other charge material used to produce A380 alloy might contain intermetallic particles of high melting temperatures, which could dissolve in the melt at the high holding temperature, but not completely dissolve at the lower temperature. These intermetallic particles and their residues could act as nuclei for the sludge phases.

**Table 2-1** Chemical composition of Al-Si-Cu alloys tested by Makhlouf and Apelian [9].

<table>
<thead>
<tr>
<th>Alloy No.</th>
<th>Si</th>
<th>Cu</th>
<th>Fe</th>
<th>Mn</th>
<th>Mg</th>
<th>Ni</th>
<th>Cr</th>
<th>Zn</th>
<th>Ti</th>
<th>Sr</th>
<th>Others Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>13.0</td>
<td>5.0</td>
<td>1.6</td>
<td>0.25</td>
<td>0.50</td>
<td>0.25</td>
<td>0.05</td>
<td>3.0</td>
<td>0.20</td>
<td>&lt;0.02</td>
<td>0.50</td>
</tr>
<tr>
<td>2</td>
<td>7.0</td>
<td>1.25</td>
<td>0.7</td>
<td>0.50</td>
<td>0.05</td>
<td>0.05</td>
<td>0</td>
<td>3.0</td>
<td>0.20</td>
<td>0.02</td>
<td>0.50</td>
</tr>
<tr>
<td>3</td>
<td>13.0</td>
<td>5.0</td>
<td>1.2</td>
<td>0.50</td>
<td>0.25</td>
<td>0.25</td>
<td>0.05</td>
<td>3.0</td>
<td>0.20</td>
<td>&lt;0.02</td>
<td>0.50</td>
</tr>
<tr>
<td>4</td>
<td>7.0</td>
<td>1.25</td>
<td>0.7</td>
<td>0</td>
<td>0.05</td>
<td>0.25</td>
<td>0.15</td>
<td>0.50</td>
<td>0</td>
<td>&lt;0.02</td>
<td>0.50</td>
</tr>
<tr>
<td>5</td>
<td>7.0</td>
<td>1.25</td>
<td>0.7</td>
<td>0.25</td>
<td>0.05</td>
<td>0.05</td>
<td>0</td>
<td>3.0</td>
<td>&lt;0.2</td>
<td>&lt;0.02</td>
<td>0.50</td>
</tr>
<tr>
<td>A380.0</td>
<td>7.5-9.5</td>
<td>3.0-4.0</td>
<td>1.3</td>
<td>0.50</td>
<td>0.10</td>
<td>0.5</td>
<td>-</td>
<td>3.0</td>
<td>-</td>
<td>-</td>
<td>0.50</td>
</tr>
</tbody>
</table>

**Table 2-2** Sludge factors for the alloys tested by Makhlouf and Apelian [9].

<table>
<thead>
<tr>
<th>Alloy</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>A380.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Targeted</td>
<td>2.25</td>
<td>1.7</td>
<td>2.35</td>
<td>1.15</td>
<td>1.2</td>
<td>&lt;2.3</td>
</tr>
<tr>
<td>Achieved</td>
<td>2.51</td>
<td>1.86</td>
<td>2.54</td>
<td>1.27</td>
<td>1.32</td>
<td>1.7</td>
</tr>
</tbody>
</table>
**Figure 2-5** Optical microstructure of alloy A380, melt was held at 670°C for 3 hrs, cast in a copper wedge mold, at wall thickness of 0.36” (fast cooling). T-Star-like, B-Blocky particle [9].

**Figure 2-6** Optical microstructure of alloy A380, melt was held at 720°C for 3 hrs, cast in a copper wedge mold, at wall thickness of 0.36” (fast cooling). T-Star-like, B-Blocky particle [9].
2.2.5 Effect of Cooling Rate on Sludge Formation

In the open literature, various opinions about the role of cooling rate in sludge formation are present. Most studies indicated that the morphology of the sludge is significantly affected by the cooling rate. The study by Ghomashchi [10] and Gustafsson et al. [11] showed that the polyhedral and Chinese script morphologies of the Al(Fe, Mn)Si type sludge were independent of cooling rate. Jorstad [5] failed to mention the cooling condition used to develop the SF formula (Eq. 1)

To reveal cooling rates (slow, medium, and fast) playing an important role in determining the amount, size and morphology of sludge, five hypoeutectic and hypereutectic Al-Si experimental alloys with different contents of alloying and impurity elements, Si, Cu, Mg, Fe, Mn and Cr and the high (2.54) and low (1.27) SFs on sludge formation, in comparison with the commercial die casting alloy A380 (SF=1.7) were studied by Makhlouf and Apelian [9]. They found that, as the melt was cooled slowly in the crucible after holding, the sludge formed in the alloys with both the high and low SFs in the form of large Chinese script, and polyhedral and blocky particles (Figures 2-7 and 2-8). The size of the sludge particles and the volume fraction of sludge decreased as the cooling rate increased. In the alloys with the low SFs, the Fe-rich phases form in the interdendritic regions, and they became so small which made no contribution to sludge. When the fast cooling was applied, almost no sludge was observed in the alloys. For alloy A380, it appeared that the holding temperatures had more influence on sludge formation than the cooling rate. More and larger sludge particles were present in the cast alloys, which were solidified under both the slow and fast cooling conditions after holding at a relatively
low temperature (670°C). There were fewer sludge particles in alloy A380 solidified after holding at a relatively high temperature (720°C) as shown in Figure 1-8.

![Image](image1.png)

**Figure 2-7** Fe-rich needle and polyhedral particle surrounded by the primary Si in alloy #3 (slow cooling). S-Primary Si, P-Polyhedral, N-Needle (or Platelet) [9].

![Image](image2.png)

**Figure 2-8** Microstructure of alloy #1, melt was held at 670°C for 3 hrs, cast in a copper mold, at wall thickness of 4.3 mm (fast cooling). T-Star-like, N-Needle (or Platelet), S-

Primary Si [9].

16
2.3 Control, Characterization and Assessment of Sludge in Die Cast Mg Alloys

2.3.1 Metallurgical Principles for Control of Sludge in Ingot Production and Die Casting of Mg Alloys

Magnesium alloys have been increasingly used in the automotive industry for the past two decades, owing to their high specific strength, good damping capacity, excellent castability, and superior machinability. Presently, the most popular automotive magnesium alloys, such as AM60 and AZ91, are based on the Mg-Al-Mn-Zn system, and contain primary $\alpha$-Mg and eutectic $\beta$-Mg$_{17}$Al$_{12}$ as the major constituent phases [1, 2]. The corrosion resistance of the automotive Mg alloys depends significantly on the iron (Fe) content. In the absence of manganese (Mn), Fe and Al can form precipitates, which act as effective micro-cathodes in the primary $\alpha$-Mg matrix to form galvanic corrosion. To maximize corrosion resistance, 0.3 wt. % Mn is usually added to wrap the impurity Fe in manganese aluminides. A particle of iron embedded in a particle of manganese aluminide is less detrimental to magnesium because the galvanic activity between manganese aluminide and $\alpha$-Mg is less than that between Mg and Fe [12]. The beneficial effect of Mn in reducing the Fe content needs to be counterbalanced by an increased quantity of Al-Mn(-Fe) intermetallic compounds in the melt during die casting practice. With the normal level of Mn addition, the intermetallic compounds form at a temperature above the $\alpha$-Mg liquidus temperature, and precipitate by gravitational sedimentation to the bottom of a crucible holding the alloy melt. However, excessive usage of Mn and improper temperature control might generate a large amount of sludge in the crucible, which could cause a deleterious effect on die casting operation and product quality [3, 4].
Thorvaldsen et al. [13] investigated the generation of sludge and dross during the melting and handling of Mg alloys, AZ91D, AM60 and AS41, in Mg die casting operations. As two main types of wastes, sludge was settled to the bottom of crucibles, while dross floated on the melt surface. The results revealed that the amount of sludge removed from the melting crucibles varied between 2 and 4% of the total metal input. There were three major constituents in the tested sludge, which are oxides (29% ± 14%), intermetallics (0.8% ± 0.8%) and entrapped metal (70% ± 14%). The oxide content was affected by process parameters, the agitation of melt surface, the melt temperature, and gas protection system, rather than to the low oxide level in the primary ingots. The low agitation level of the melt surface could be reducing the extent of oxidation by careful charge of ingots into the crucible and using automatic transfer systems instead of manual discharging. The low melt temperature near the liquidus temperature reduced the oxidation rate of molten Mg alloys. When applying the gas-protection system, the balance between the melt loss due to oxidation and the cost of the protective gases should be taken into consideration. Intermetallic particles (AlₓMnᵧ) originated from the primary ingots played an important role as precipitation sites for Fe in lowering the level of dissolved Fe and increasing the overall corrosion resistance of the castings. It was suggested that a reduction in the sludge formation by a factor of 10 might be achievable, while the oxidation of molten Mg alloys in the crucible was reduced and the Mg content of the primary ingot was kept at a low level.

To establish the optimum level of Mn in the Mg alloys AZ91, AM60 and AM50 (Table 2-3), Holta et al. [14] and Holta and Westengen [15] determined the temperature-dependent mutual solubility of Fe and Mn for each alloy as shown in Figure 2-9, which gave the production routes of the primary ingots for various Mn additions. Each curve in Figure 2-
9 represented a specific manganese addition and each data point gave the measured equilibrium contents of Fe and Mn. By fitting the data, the polynomial equations were determined, which were used to attain the desired iron by controlling the Mn content and the holding temperature of the melt. The empirical equations for AZ91, AM60 and AM50 are given below [14, 15]:

\[
[\% \text{Fe}] = 0.1772 - 5.95 \, T^{-4} \, (T) - 0.2924 \, (\% \text{Mn}) + 4.444 \, T^{-4} \, (T)(\% \text{Mn}) + 5.131 \times 10^{-7} \, (T)^2 - 0.104 \, (\text{Mn})^2
\]

for AZ91 \hspace{1cm} (3)

\[
[\% \text{Fe}] = [\% \text{Al}]^{0.0218} \exp \left( 6.91 - \frac{10987}{T(K)} \right) - 0.00371[\% \text{Al}] [\% \text{Mn}]
\]

for AM60 and AM50 \hspace{1cm} (4)

where T is the casting temperature (°C), and the element contents, [%Fe], [%Mn] and [%Al] are in weight percentage.
Table 2-3 Chemical compositions of ASTM B93 and B94 standards for automotive Mg alloys AZ91D, AM60B and AM50A for ingots and die castings, respectively [16, 17].

<table>
<thead>
<tr>
<th>Alloy Designation</th>
<th>Alloy Composition (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>ASTM B93 standard for Mg alloys in ingot form</strong></td>
<td></td>
</tr>
<tr>
<td><strong>Alloy</strong></td>
<td><strong>Al</strong></td>
</tr>
<tr>
<td>AZ91D</td>
<td>8.5–9.5</td>
</tr>
<tr>
<td>AM60B</td>
<td>5.6–6.4</td>
</tr>
<tr>
<td>AM50A</td>
<td>4.5–5.3</td>
</tr>
</tbody>
</table>

| **ASTM B94 standard for Mg alloys in die casting form** | |
| **Alloy** | **Al** | **Zn** | **Mn** | **Si (max)** | **Fe (max)** | **Cu (max)** | **Ni (max)** | **Be** |
| AZ91D | 8.3–9.7 | 0.35–1.0 | 0.15–0.50 | 0.10 | 0.005 | 0.030 | 0.002 |
| AM60B | 5.5–6.5 | 0.22 | 0.24–0.6 | 0.10 | 0.005 | 0.010 | 0.002 |
| AM50A | 4.4–5.4 | 0.22 | 0.26–0.6 | 0.10 | 0.004 | 0.010 | 0.002 |

Also, it can be seen from Figure 2-9 that the specified maximum limit of Fe in the ingots could be fulfilled for different combination of casting temperatures and Mn additions. For instance, the normal casting temperature was 650 °C, and based on Figure 2-9, addition of slightly more than 0.3 wt.% Mn produced an alloy with approximately 0.2 wt% Mn and 0.003 wt% Fe. If the casting temperature of the ingots increased to 680 °C, and the Mn (0.2 wt%) and Fe (0.003 wt.%) contents in the ingots remained, the addition of Mn needed to be raised to 0.6 wt%, i.e., twice as much as that for ingot production at 650 °C.
Alloy AZ91

\[ \% \text{Fe} = 0.1772 - 5.95 \times 10^{-4} \times T(\text{C}) - 0.2924 \times \% \text{Mn} + 4.44 \times 10^{-4} \times T(\text{C}) \times \% \text{Mn} + 5.13 \times 10^{-7} \times T(\text{C})^{2} - 0.104 \times \% \text{Mn}^{2} \]

(a)

Alloy AM60

\[ \% \text{Fe} = \% \text{Al} \times 0.0218 \times \exp(0.91 - 10687 / T(\text{K})) - 0.00371 \times \% \text{Al} \times \% \text{Mn} \]

(b)
Figure 2-9 Temperature-dependent mutual solubilities of Fe and Mn in Mg alloys (a) AZ91, (b) AM60 and (c) AM50 [14].

The Mn solubility depended also on the aluminum content of the alloys (AZ91, AM60 and AM50) with Fe <0.0002% as illustrated in Figure 2-10. At a fixed casting temperature, the solubility of Mn increased with decreasing aluminum content. In the real casting operation, the high casting temperature was employed for the alloys (AM60 and AM50) low in Al content due to their high liquidus temperatures. The high Mn content was necessary to be used in these AM alloys.
Figure 2-10 Solubility of Mn in Mg-Al alloys, AZ91, AM60 and AM50 [15].

By combination the phase identification data of AZ91 and AM series obtained by the X-ray and electron microscopy techniques, Holta et al. [14] established the ternary Mg-Al-Mn phase diagram (Figure 2-11) with an assumption of negligence of Zn effect. Figure 2-11 shows the Mg-rich corners of Mg-Al-Mn phase diagrams at temperatures of (a) 660 and (b) 700 °C. The strong influence of 0.005 wt% Fe in the melt on phase development at the two temperatures was demonstrated.
Figure 2-11 Magnesium-rich corner of the Mg-Al-Mn phase diagram, (a) 660 and (b) 700 °C [14].
To minimize sludge formation and improve corrosion resistance, Holta et al. [14] provided the basic metallurgical principles for the production of the primary ingots and the die cast parts. The provided principles are listed below.

- The maximum iron content of the ingots should be lower than the limit for die casting (0.004 wt%) to allow for minor Fe pick-up during re-melting in the die casting operation;
- The maximum iron content of the finished die cast parts should not exceed 0.005 wt% to ensure acceptable corrosion performance of the parts;
- The minimum Mn content of the ingots should reflect the liquid solubility of the alloy at the anticipated minimum casting temperature. If high casting temperatures were used, the Mn content should be raised accordingly; and
- The minimum Mn content of the ingots should be low to ensure freedom in selection of low die casting temperatures.

After characterizing the die-casting Mg sludge from different companies, Corby et al. [18] indicated that it was necessary to have a residual quantity of Mn present in the primary ingot to protect the melt from iron pick-up upon re-melting in die casting shops. Ideally the melt should remain just under the Mn saturation point, so that any significant pick-up of iron would precipitate out of the melt as an intermetallic. In other words, the relationship between the primary producer’s ingot pouring temperature ($T_p$) and the die-casters furnace temperature ($T_d$) had an impact on the amount of sludge generated. If the ingots were re-melted at a lower furnace temperature ($T_d < T_p$), this would cause a solubility difference and force the precipitation of intermetallics, which formed as sludge. If the furnace temperature is higher, ($T_d > T_p$), then the metal was left susceptible to iron-pick up. The ideal situation
to protect the melt from iron pickup and minimize intermetallic sludge was to keep the melt
temperature consistently just below $T_p$ [18]. Practically, this was difficult to achieve when
there were constant temperature fluctuations caused by charging ingots. Temperature
cycling within the furnace during normal operation could cause both problems ($T_d < T_p$ and
$T_d > T_p$) to occur. As new ingots were added, the drop in temperature resulted in the melt
generating intermetallic particles. However, as the temperature returned to normal, the melt
was above the Mn saturation point and susceptible to iron pick-up. This might explain why
some particles in AZ91D handled at a high holding temperature, compared to those in
AM60 and AM50 holding at low temperatures, had high levels of iron, when the majority
were generally low. Alternatively, it could be due to iron variations within the melt [18].

2.3.2 Characterization of Mg Sludge

2.3.2.1 Chemical compositions of Mg die-casting alloys and sludge

Corby et al. [18] analyzed the sludge collected in two North American companies,
which was taken from the bottom of a 400 series stainless steel standard size crucible and
heated by gas. The process, Mg alloys and casting temperatures employed in the die-casting
process are listed in Table 2-4. The top shape of the furnace is approximately an oblong
area with a total length of 2300 mm, which has a 420mm radius at each end. The sidewalls
are tapered at approximately 5 degrees. The depth of the crucible is approximately 610 mm.
The sludge from Company A (A) had a residence time of 2-4 hours prior to cleaning and
Company B (B) had a residence time of 6-8 hours.
Table 2-4 Die casting process, Mg alloys and casting temperatures for sludge generation [18].

<table>
<thead>
<tr>
<th>Company (A)</th>
<th>Alloy</th>
<th>Die-casting Process</th>
<th>Casting Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>AZ91D</td>
<td>Hot Chamber</td>
<td>695</td>
</tr>
<tr>
<td></td>
<td>AM50A</td>
<td>Hot Chamber</td>
<td>652</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Company (B)</th>
<th>Alloy</th>
<th>Die-casting Process</th>
<th>Casting Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>AZ91D</td>
<td>Hot Chamber</td>
<td>665</td>
</tr>
<tr>
<td></td>
<td>AM60B</td>
<td>Hot Chamber</td>
<td>655</td>
</tr>
</tbody>
</table>

Tables 2-5 and 2-6 list the chemical compositions of the die casting alloys and the corresponding sludges, which were analyzed using Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES). The chemical analysis results indicate that all of the furnaces had the alloys within the ASTM specification except AM60B, which was high in Fe. Other than Mg, the main elements in the metallic portion of the sludge were Al and Mn. With the exception of AM60B, Fe made up a very low percentage of the melt composition. Mn made up a much larger proportion of the AM50A sludge compared to AZ91D and AM60, because of a higher Mn content in the melt or a lower furnace temperature, encouraging the precipitation of Mn rich particles.
Table 2-5 ICP results for melt compositions (wt%) taken from spectrometer discs [18].

<table>
<thead>
<tr>
<th>Element</th>
<th>AZ91D (A)</th>
<th>AZ91D (B)</th>
<th>AM60B</th>
<th>AM50A</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al %</td>
<td>8.48</td>
<td>8.75</td>
<td>6.05</td>
<td>4.91</td>
</tr>
<tr>
<td>Zn %</td>
<td>0.63</td>
<td>0.66</td>
<td>&lt;0.005</td>
<td>0.04</td>
</tr>
<tr>
<td>Mn %</td>
<td>0.20</td>
<td>0.16</td>
<td>0.27</td>
<td>0.28</td>
</tr>
<tr>
<td>Fe %</td>
<td>0.005</td>
<td>&lt;0.005</td>
<td>0.03</td>
<td>&lt;0.005</td>
</tr>
<tr>
<td>Cu %</td>
<td>0.002</td>
<td>&lt;0.002</td>
<td>&lt;0.002</td>
<td>&lt;0.002</td>
</tr>
<tr>
<td>Ni %</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;.001</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Be %</td>
<td>&lt;0.001</td>
<td>0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Cr %</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>0.001</td>
<td>&lt;0.001</td>
</tr>
</tbody>
</table>

Table 2-6 Metallic sludge composition [18].

<table>
<thead>
<tr>
<th>Element</th>
<th>AZ91D (A)</th>
<th>AZ91D (B)</th>
<th>AM60B</th>
<th>AM50A</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al %</td>
<td>10.6</td>
<td>10.7</td>
<td>8.10</td>
<td>9.72</td>
</tr>
<tr>
<td>Zn %</td>
<td>0.50</td>
<td>0.56</td>
<td>&lt;0.005</td>
<td>0.03</td>
</tr>
<tr>
<td>Mn %</td>
<td>1.95</td>
<td>2.69</td>
<td>3.81</td>
<td>7.95</td>
</tr>
<tr>
<td>Fe %</td>
<td>0.09</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>Cu %</td>
<td>&lt;0.002</td>
<td>&lt;0.002</td>
<td>&lt;0.002</td>
<td>&lt;0.002</td>
</tr>
<tr>
<td>Ni %</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;.001</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Be %</td>
<td>0.04</td>
<td>0.04</td>
<td>0.03</td>
<td>0.02</td>
</tr>
<tr>
<td>Cr %</td>
<td>0.009</td>
<td>0.005</td>
<td>0.002</td>
<td>0.005</td>
</tr>
</tbody>
</table>

2.3.2.2 Characterization of die-casting sludge

2.3.2.2.1 Morphology and sizes of intermetallics in die-casting sludge

The characteristics of the die-casting sludge were analyzed using a Scanning Electron Microscope (SEM) equipped with Electron Dispersive Spectroscopy (EDS) by Corby et al. [18].

Initial investigation through SEM, the majority of the sludge was entrapped magnesium, but also contained some magnesium oxide (black) and Al-Mn-Fe intermetallic (white) as
shown in Fig.2-12. The intermetallic particles tended to form in clusters, as demonstrated in Figure 2-12(a) and by the lack of them in Figure 2-12(b), but they were similar in appearance regardless of the melt composition as seen in Figure 2-12(c). Many of the particles display faceted edges, as illustrated in Figure 2-12(d). Particles ranged in size around 5-400 μm, however the majority of the particles were below 50μm. They also found other impurity in the AZ91D that were Al-Fe-Cr, Mg, O and Cl. Al-Fe-Cr phase was similar to that observed with interactions between the mild steel of the crucible and molten Mg-Al alloys. The Mg, O and Cl may leftover from MgCl₂ flux to extinguish the burning dross [18]. Figure 2-12(d) shows the largest particle appeared in the die cast AM50A alloy. The particle coarsening could result from the high Mn content in the alloy melt (Table 2-5), and/or the low furnace temperature (Table 2-4) promoting the precipitation of Mn-rich particles.
2.3.2.2 Chemical composition of intermetallics in die-casting sludge

The composition of the particles determined using a JOEL electron probe is shown in Figure 2-13. The results were generally within the atomic proportions for an Al₈(Mn, Fe)₅ phase, assuming that Fe does not greatly affect the stability of Al₈Mn₅ in the Al-Mn system, although the compositions of the particles [18] varied more than that previously reported by Holta et al. [14]. The possible compositions for β-Mn are marked, as is the composition for α-AlMnFe reportedly found in AM50 [14].
Figure 2-13 Probe results indicating that the majority of the particles could be $\text{Al}_8\text{(MnFe)}_5$ [14, 18].

The outlying particles with higher Mn from the AM50A alloy were all greater than 100 µm in size, although their morphology under SEM was indistinguishable from other particles, which could be a different type of Al-Mn-Fe phase.

The Fe compositions of the particles are given in Table 2-7. The Fe contents in the AM50A and AM60B alloys were generally lower than that found in the AZ91D samples. This was probably due to the lower furnace temperatures, which reduced the Fe pick-up from the steel of the crucible.
Table 2-7 Fe contents of intermetallic particles in sludge [18].

<table>
<thead>
<tr>
<th>At%</th>
<th>AZ91D (A)</th>
<th>AZ91D (B)</th>
<th>AM60B</th>
<th>AM50A</th>
</tr>
</thead>
<tbody>
<tr>
<td>Avg</td>
<td>2.01</td>
<td>1.98</td>
<td>0.70</td>
<td>0.55</td>
</tr>
<tr>
<td>Min</td>
<td>0.35</td>
<td>0.19</td>
<td>0.34</td>
<td>0.28</td>
</tr>
<tr>
<td>Max</td>
<td>4.36</td>
<td>10.50</td>
<td>1.77</td>
<td>0.74</td>
</tr>
<tr>
<td>σ (std)</td>
<td>1.16</td>
<td>2.34</td>
<td>0.34</td>
<td>0.13</td>
</tr>
</tbody>
</table>

EDS mapping of an AZ91D intermetallic particle in Figure 2-14 suggested that they were homogeneous in composition. It was difficult to distinguish between the α-Fe and β-Fe for low concentrations of Fe as the peak overlap took place.

Figure 2-14 EDS mapping of an AZ91D intermetallic. Elements appeared evenly distributed [18].
2.3.3 Al-Mn(-Fe) Intermetallic Formation and Thermodynamic Assessment

2.3.3.1 Al-Mn(-Fe) intermetallic formation and interaction with oxide

It was pointed out [13, 14, 18] that the composition of the sludge was roughly 60-80% metallic and 20-40% oxides, and intermetallics were estimated to be a low proportion, typically around 0.8 ± 0.8%. According to Holta [14], particles vary in Fe and Mn composition and are typically Al₈(Mn, Fe)₅ in AM60 and AZ91, and α-AlMnFe in AM50. To minimize the build-up of die-casting sludge and prevent large Al-Mn(-Fe) clusters from entering castings, Peng et al. [3] investigated mechanisms of Fe pick-up, and settling of Al-Mn(-Fe) particles in association with oxide films.

Two forms of casting experiments with alloy AZ91 were performed:

(1) to mimic Fe pick-up in industrial melts, 2 g of AZ91 was melted and held at 700 ºC for 4 h in uncoated Fe-0.2%C cylindrical crucibles with dimensions of inner diameter of 12 mm and inner height of 18 mm, within sealed quartz tubes backfilled with Ar;

(2) a similar procedure involving an Al₂O₃ crucible in quartz tubes was used to generate equivalent microstructures without Fe pick-up.

The casting samples were then solidified by placing the 700 ºC quartz tubes in the vertical cylindrical hole of a steel mold at room temperature with a cooling rate of 4 K/s in the range 700–650 ºC.

In real-time radiography experiments, the AZ91 specimen and cell were heated and melted at a constant rate of 0.5 K/s and subsequently cooled at a constant rate of either or 0.083 or 0.5 K/s. During heating and cooling, transmitted x-ray images were recorded at a rate of 2.5 frames per second.
They found that Fe pick-up from mild steel crucibles held at 700 °C caused the formation of a B2-Al(Mn,Fe) compound, resulting in two-phase Mn-bearing intermetallic particles consisting of a B2 core and a D8\textsubscript{10}-Al\textsubscript{8}Mn\textsubscript{5} shell. Zeng et al. [4] studied the nucleation and growth crystallography of Al\textsubscript{8}Mn\textsubscript{5} on B2-Al (Mn,Fe) in Mg alloy AZ91, and indicated that Al\textsubscript{8}Mn\textsubscript{5} nucleated on B2-Al(Mn,Fe) particles and an incomplete peritectic transformation resulted in a Fe-rich B2-Al(Mn,Fe) core enveloped by a low-Fe Al\textsubscript{8}Mn\textsubscript{5} shell.

At low Fe content (< 10 ppm), the particles were mostly D8\textsubscript{10}-Al\textsubscript{8}Mn\textsubscript{5} as shown in Figure 2-15. For both low-Fe and high-Fe AZ91, primary Al\textsubscript{8}Mn\textsubscript{5} particles were cyclic twinned and contained up to four Al\textsubscript{8}Mn\textsubscript{5} orientations similar to Ref. 4 (Figure 2-15). The particles had equiaxed polyhedral morphology with multiple facets and often contained internal liquid channels. In the sludge prepared in the Al\textsubscript{2}O\textsubscript{3} crucible containing entrained oxide, the attachment of Al\textsubscript{8}Mn\textsubscript{5} particles to the oxides was revealed by SEM. The direct observation on Al\textsubscript{8}Mn\textsubscript{5} particle settling and sludge formation by the real-time synchrotron x-ray radiography confirmed that Al\textsubscript{8}Mn\textsubscript{5} particles appeared to nucleate on entrained oxides (Figure 2-16). After numerous Al\textsubscript{8}Mn\textsubscript{5} particles became trapped and/or nucleated on entrained oxides, they continue to grow on cooling, leading to a large cluster of intermetallics. Also, the entrained oxides acted as filters to Al\textsubscript{8}Mn\textsubscript{5} particles, trapping them as they settle. The settling data were in reasonable agreement with Stokes’ law once correction factors for the thin sample geometry, the non-spherical particles, and the internal liquid channels are accounted for.
Figure 2-15 Typical cross-sections of primary Al-Mn(-Fe) particles in AZ91 after 4 h isothermal holding at 700 oC in (a) an Al2O3 crucible and (b) a mild steel crucible. In (a) and (b), the top are BSE-SEM images, the middle are corresponding EBSD phase maps and the bottom are IPF-X maps. (c) Pole figures for two families of planes from the sample in (a) showing cyclic twinning [3].
Typical 3D morphologies of primary Al₈Mn₅ particles nucleating on the oxide in AZ91 [3].

2.3.3.2 Thermodynamic assessment of Mg-Al-Mn system

To thermodynamically understand the formation of Al-Mn(-Fe) intermetallics in Mg Alloys AZ91, AM60 and AM50, the phase equilibria and solidification process for Mg-rich Mg–Al–Mn–Zn alloys were analyzed based on a combination of computational thermochemistry and thermal analysis with differential scanning calorimetry (DSC) measurements [19, 20]. They found that the primary precipitate was Al₈Mn₅ intermetallic phase at high Mn compositions (> 0.2 wt.%) in the Mg-rich Mg–Al–Mn–Zn alloys as shown in Figure 2-17. The computed results and DSC analysis indicated that, during the solidification of AZ91 alloy, the precipitation of the Al₈Mn₅ intermetallic phase took place at 642 °C. That was much higher than the temperature of 600 °C at which the initial formation of α-Mg solid solution occurred.
Figure 2-17 Calculated vertical sections of the Mg–Al–Mn–Zn phase diagram and the experimental data of Ref. [20] for the fixed 9.5 wt.% Al and 0.84 wt.% Zn alloy.

Shukla and Pelton [21] assessed thermodynamically the Mg-Al-Mn system with the FactSage thermochemical software. The solubility of Mn and the stability of Al$_8$Mn$_5$ precipitates in the Mg-Al alloys in the temperature range of 650-750 °C were predicted. With the Mn content of 0.4 wt.%, the precipitation of the Al$_8$Mn$_5$ intermetallic phase in the Mg-Al-Mn alloys containing 5.0 and 6.0 wt% would begin at 660 and 670 °C, respectively. Meanwhile, the Al$_8$Mn$_5$ intermetallic particles could precipitate at a high temperature of 700 °C in the Mg-9.0 wt.% Al-0.4 wt% Mn alloy, which was similar to AZ91 alloy. Ye and Liu [22] studied the in situ formation behaviors of Al$_8$Mn$_5$ particles in Mg–Al-Mn alloys by introducing 10 wt.% Al and 2.5 wt.% Mn into AM60 alloy in a vacuum furnace for 60 min at 750, 800, and 850 °C, respectively. It was that, with the absence of oxygen, Al$_8$Mn$_5$ was a stable phase in the Mg–Al–Mn system, and was formed in the liquid phase
(even at 850 °C) during the melt processing. Unlike many compounds formed in liquid phase, the Al₈Mn₅ particles resisted coarsening in the melt at high temperature even at a very high concentration. Increasing Mn content and/or melting temperature promoted the in situ formation of Al₈Mn₅ particles in the Mg–Al–Mn alloys. Figure 2-18 shows the massive presence of the Al₈Mn₅ particles in the Mg–10 wt.% Al–2.5 wt.%Mn alloy processed at 850 °C.

![Optical micrographs showing massive presence of Al₈Mn₅ particles in Mg–10 wt.% Al–2.5 wt.%Mn alloy processed at 850 °C, (a) low and (b) high magnifications](image)

**Figure 2-18** Optical micrographs showing massive presence of Al₈Mn₅ particles in Mg–10 wt.% Al–2.5 wt.%Mn alloy processed at 850 °C, (a) low and (b) high magnifications [22].

### 2.3.4 Rapid Assessment of Mg Oxide and Intermetallic in Mg Alloys

As the magnesium oxide served as the nucleation site for the Al-Mn(-Fe) intermetallics and played as major role (20-40%) in sludge, the techniques for the assessment of both the non-metallic inclusions (oxides) and metallic inclusions (intermetallics) were essential for controlling and minimizing sludge formation [23-31]. The common techniques could be classified into three main groups: spectroscopy, fracture test, infiltration, and hybrid. The
first three techniques were focused on the detection of non-metallic inclusions, while the last one was used to the simultaneous measurements of both the non-metallic inclusions (oxides) and metallic inclusions (intermetallics).

2.3.4.1 Spectroscopic technique

Fast neutron activation analysis (FNAA), glow discharge mass spectroscopy (GD-MS) and glow discharge atomic emission spectroscopy (GD-AES) were considered the methods of physical measurements for the determination of the chemical composition of Mg melts [23, 24]. The FNAA method employed the samples were irradiated with 14.8 MeV neutrons and the reaction product ($^{16}$N) was detected. The number of $^{16}$N atoms detected directly corresponded to the number of oxygen atoms in the sample [25]. In glow discharge source techniques, the sample was exposed to an argon plasma which uniformly eroded material from the sample surface. The sputtered atoms were ionized in this plasma and extracted into a mass spectrometer for separation and detection in GD-MS. In the case of GD-AES, a spectrometer was used to measure the wavelength and intensity of the light emitted by the sputtered atoms when they returned to the ground electronic state. FNAA, GD-MS and GD-AES had low detection limits (0.1–10 ppm) and high accuracy (5–20%). But, they all involved extensive sample preparation, and required sophisticated and expensive instrumentation. In particular, the FNAA method needed a neutron source such as a nuclear reactor, which resulted in the accessibility in question. Also, there was no industry specification for acceptable levels of oxygen in the samples and there was no exact correlation between the oxygen content within the sample and the oxide content. Furthermore, these methods provided little information on the oxide size and morphology [23, 24].
2.3.4.2 Fracture test

Fracture tests have long been recognized and are extensively employed as an inexpensive and rapid shop-floor means to evaluate the melt cleanness in foundries. It could be subdivided into two classes: K-Mold and light reflectance.

2.3.4.2.1 K-Mold

The K-Mold technique employed a flat plate with four notches cast into its cope surface (Figure 2-19) [23, 25]. These notches served as fracture points. The design of the knife edges in the mold enhanced the efficiency of capturing the oxides on the fracture faces through the effect of some eddy occurring during the mold filling. In one test, a number of sampling plates were cast in preheated molds using the molten metal to be evaluated. The cast plates were then fractured immediately by operators. The fracture surfaces were examined visually for oxides by naked eyes. The inclusion level was expressed as the number of defects seen per number of fracture surfaces examined.

![Figure 2-19 K-mould method](image)

**Figure 2-19** K-mould method [23, 25].

The main advantages of the K-mould were result quickness, very low cost, simple preparation of samples, and high sampling flexibility. But, the technique was less
quantitative and gave inaccurate results in comparison with the other techniques. Difficulties were encountered in detecting small oxide inclusions (<100 µm) and in assessing molten alloy in which the level of inclusions was somewhat lower [23, 25].

2.3.4.2.2 Light reflectance

In generally, the magnesium oxides were the most common inclusions present in magnesium alloys, and appeared darker than the relatively bright alloy metal as revealed by the optical microscope (Figure 2-20).

![Optical micrographs showing as-polished (a) a lacy oxide network in cast AM60, and (b) a snaky oxide film associated with a surface defect in cast AM60 [24].](image)

**Figure 2-20** Optical micrographs showing as-polished (a) a lacy oxide network in cast AM60, and (b) a snaky oxide film associated with a surface defect in cast AM60 [24].

Instead of using the unaided eye, an optical technique, i.e., a brightimeter, was developed based on the differences in optical characteristics between Mg and magnesium oxide for the evaluation of the fracture surface [26, 27]. In this optical technique, a conical cast sample was fractured and the fracture surface was placed in the aperture of a brightimeter. The sample was illuminated at a 45° angle and the intensity of the reflected light is measured (Figure 2-21). If oxide inclusions were present in the material, the
incident light was scattered at the surface of the specimen due to multiple reflections and refractions, which was called diffuse reflectance. In Mg alloys, the oxide inclusions absorbed lighter than the matrix, and consequently the reflectance of the specimen was reduced. As such, the content of the Mg oxide was correlated to light reflectance. However, this technique exhibited high detection limits (~2%). Its accuracy and consistency in detecting the oxide content of the melt and its capability of identifying other types of inclusions were questionable.

![Schematic diagram showing the principle of a brightimeter](image)

**Figure 2-21** Schematic diagram showing the principle of a brightimeter [26, 27].

### 2.3.4.3 Filtration

The hydro magnesium inclusion assessment method (HMIAM), an off-line inclusion assessment system that was developed by Norsk Hydro for molten magnesium in the early 1990s was a typical application of the vacuum filtration technique. The application of this technique to molten magnesium was well demonstrated. Figure 2-22 illustrates a HMIAM vacuum filtering system which consisted of a filter, a filter cup, a tapered plug and a vacuum container (steel tube) [28, 29]. In this technique, molten metal was drawn through
a sampling filter by vacuum behind the filter. Several procedures were involved in an entire test. First, a tapered plug was used to protect the filter from contamination before immersion. Next, the entire unit was immersed and kept in molten metal bath for a period of time, which allowed the unit to be preheated. Then, the tapered plug was pulled out and vacuum starts to suck the molten metal through the filter. After sampling a certain amount of melt, the unit was lifted out of the bath for cooling. Upon the solidification and cooling of the unit, the filter was removed from the filter cup and sectioned along the diameter perpendicular to the filter surface. The oxide inclusion concentration was determined by the volume of particles per unit weight of metal drawn through the filter.

**Figure 2-22** Norsk Hydro's magnesium inclusion assessment method (HMIAM) [23, 28, 29].

This technique had some advantages. Filtration could be carried out directly in the bulk molten metal at any designated location. A relatively large volume of the melt was filtered in a test, which improved the accuracy of inclusion assessment. However, the shortcomings
of this technique were acknowledged in practice. Upon completion of sucking, back flow of molten metal from the container to the filter cup might take place if the metal head was not appropriately balanced in the container by a corresponding vacuum. Also, after lifting the unit out of the molten metal bath, if the bottom of the filter cup was not chilled first, the inclusions in the filter cup would be drawn through the filter during the solidification of the melt. The leakage might occur during the sampling if any one of joints is not sealed tightly. In addition, the quantity and morphology of oxides in ingots or die cast components might be different from those observed on the filter due to different solidification conditions (e.g., melt temperature) [23].

2.3.4.4 Hybrid

Bronfin et al. [30, 31] developed a hybrid assessment method, named “MagOxide”, which combined the wet chemistry with Inductively Coupled Plasma Emission Spectrometry (ICP). The hybrid technique aimed at evaluating simultaneously the MgO and Al–Mn–Fe intermetallics in the primary and recycled Mg alloy ingot. The experimental procedures used in this technique included:

1. the α-Mg-matrix and eutectic phases such as β- Mg$_{17}$Al$_{12}$ phase of 2-3 g sample were dissolved in a mixture of organic solutions. But, the MgO particles and Al-Mn(-Fe) intermetallics remained in soluble in liquid solution. The dissolution process was conducted in Argon inert atmosphere at 30-40 °C to eliminate the reaction between organic solvents and water.

2. The solution was filtered and residues were rinsed with boric acid and distilled water.

3. The MgO and Al-Mn(-Fe) residues were dissolved in warm choric acid and filtered. The filtrate is then analyzed by ICP.
The Mg concentration obtained by ICP was converted to the concentration of MgO or oxygen assuming that the magnesium remained after dissolving in organic solution was only bound to oxygen. The technique also allowed to quantify a weight fraction of Al-Mn-Fe intermetallics and their phase composition.

Bronfin et al. [30] used this hybrid technique to analyze both the primary and recycled Mg ingots of AZ and AM series produced by different companies. The results showed the acceptable correlation in the MgO contents in the primary ingot detected by the FNAA and the MagOxide techniques (Table 2-8). The technique was capable of providing simultaneously the measurements of the MgO and Al-Mn intermetallic compounds in the AZ91 ingots recycled by the different companies, as given in Table 2-9.
Table 2-8 Oxygen and MgO contents in primary AZ and AM ingots [30].

<table>
<thead>
<tr>
<th>No.</th>
<th>Alloy</th>
<th>FNAA Oxygen [ppm]</th>
<th>FNAA MgO [ppm]</th>
<th>“MagOxide” – Wet Chemistry method MgO [ppm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>AZ91D</td>
<td>&lt;50</td>
<td>&lt;125</td>
<td>103</td>
</tr>
<tr>
<td>2.</td>
<td></td>
<td>&lt;50</td>
<td>&lt;125</td>
<td>133</td>
</tr>
<tr>
<td>3.</td>
<td></td>
<td>&lt;50</td>
<td>&lt;125</td>
<td>133</td>
</tr>
<tr>
<td>4.</td>
<td></td>
<td>&lt;50</td>
<td>&lt;125</td>
<td>90</td>
</tr>
<tr>
<td>5.</td>
<td>AM60B</td>
<td>&lt;50</td>
<td>&lt;125</td>
<td>61</td>
</tr>
<tr>
<td>6.</td>
<td></td>
<td>&lt;50</td>
<td>&lt;125</td>
<td>67</td>
</tr>
<tr>
<td>7.</td>
<td></td>
<td>&lt;50</td>
<td>&lt;125</td>
<td>59</td>
</tr>
<tr>
<td>8.</td>
<td>AM50A</td>
<td>&lt;50</td>
<td>&lt;125</td>
<td>66</td>
</tr>
<tr>
<td>9.</td>
<td></td>
<td>&lt;50</td>
<td>&lt;125</td>
<td>64</td>
</tr>
<tr>
<td>10.</td>
<td></td>
<td>&lt;50</td>
<td>&lt;125</td>
<td>83</td>
</tr>
</tbody>
</table>

The MagOxide method was considered as an inexpensive and reliable technique for cleanliness evaluation of primary and recycled Mg ingots. However, due to the fact that, in this method, the small samples (2-3 grams) were used in each test, the correct sampling and good statistics were needed. The technique required the tedious analytical procedure, and the massive sampling and analyses.
Table 2.9 Contents of MgO and Al-Mn intermetallic compounds in recycled AZ91 Ingots [30].

<table>
<thead>
<tr>
<th>Company</th>
<th>Weight fraction of MgO, ppm</th>
<th>Weight fraction of Al-Mn-Fe intermetallies, %</th>
<th>Typical composition of Al-Mn-Fe intermetallies, at %</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>42±12</td>
<td>0.419±0.018</td>
<td>Al_{62.1}Mn_{37.7}Fe_{0.2}</td>
</tr>
<tr>
<td>B</td>
<td>75±19</td>
<td>0.396±0.027</td>
<td>Al_{62.8}Mn_{36.9}Fe_{0.3}</td>
</tr>
<tr>
<td>C</td>
<td>125±64</td>
<td>0.426±0.025</td>
<td>Al_{62.5}Mn_{37.4}Fe_{0.1}</td>
</tr>
<tr>
<td>D</td>
<td>87±24</td>
<td>0.446±0.025</td>
<td>Al_{62.1}Mn_{37.7}Fe_{0.2}</td>
</tr>
<tr>
<td>E</td>
<td>93±24</td>
<td>0.494±0.023</td>
<td>Al_{60.8}Mn_{39.1}Fe_{0.1}</td>
</tr>
<tr>
<td>F</td>
<td>472±345</td>
<td>0.344±0.019</td>
<td>Al_{60.1}Mn_{38.8}Fe_{1.1}</td>
</tr>
<tr>
<td>Primary</td>
<td>35±6</td>
<td>0.417±0.011</td>
<td>Al_{60.5}Mn_{39.3}Fe_{0.2}</td>
</tr>
</tbody>
</table>

2.4 Summary

The establishment of the SF formula makes the control of sludge generation in casting of aluminum alloys easily achievable. Understanding of sludge formation in die casting of magnesium alloys is still immature, despite the fact that a number of studies have been reported on proper control of sludge generation in the primary ingot production. Information on the effects of melt holding and casting temperatures on sludge formation for die casting processes is inadequate, as the available relationships between the alloy chemistry, i.e., iron and manganese contents, and the casting temperatures are only applied to the primary Mg ingot production. There is a lack of general knowledge about the kinetics of Mg sludge formation during casting of Mg alloys. Therefore, it is essential to investigate systematically and methodically the simultaneous effects of casting and holding times and temperatures as well as the alloy chemistry on the sludge formation in die casting of magnesium alloy.
Characterization of Mg die casting sludge are focused only on the identification of phase constituents such as Al-Mn(-Fe) intermetallics and Mg oxides. Interaction between the intermetallic phase and oxide should be explored in practical die casting processes, because the previous investigated was performed only in a lab environment and on one alloy AZ91. Systematic work on nucleation, growth, and interaction of intermetallics with oxides in other automotive alloys such as AM60 and AM50 should be explored. Given the important role of oxides in the Mg sludge formation, the hybrid assessment techniques capable of simultaneously detecting different phase constituents in the Mg sludge need to be developed.
CHAPTER 3  
Experimental Procedure

3.1 Materials

3.1.1 Recycling Sludge and High Pressure Die Casting Sludge

To analyze the characteristics of commercial sludge generated in the Mg casting industry, sludge blocks were created from the recycling process of AZ91D Mg alloy and the high pressure die casting (HPDC) production process of AZ91D and AM60 Mg alloys, named the recycling sludge and HPDC sludge respectively. The sludge blocks provided by Meridian lightweight Technologies Inc (Meridian) are shown in Figure 3-1.

![Figure 3-1](image1.png)  
(a)  
![Figure 3-1](image2.png)  
(b)  
![Figure 3-1](image3.png)  
(c)  

**Figure 3-1** Photographs showing sludge blocks generated from (a) the recycling process of AZ91D Mg alloy, and (b) the HPDC production process of AZ91D and AM60 Mg alloys.
3.1.2 Aluminum and Magnesium Ingots, and Master Alloys

To understand the composition effect on the mechanism of sludge formation in the recycling and HPDC process, various experimental Mg alloys with different chemical compositions designed by the Taugchi method (Design of Experiment DOE) were prepared by using commercially pure Mg, Al, Mg-2wt.% Mn and Al-10wt.% Fe. The experimental raw metallic materials provided by Meridian were cut into cubes (20 mm x 20 mm x 10mm), so that they could be easily charged into a graphite crucible. All the raw material chemical compositions are listed in Table 3-1. Figures 3-2, 3-3, 3-4 and 3-5 display the original ingots and sectioned pieces of Pure Al, Mg, Mg-2wt.% Mn and Al-10wt.% Fe, respectively.

Table 3-1 Chemical composition of raw metallic materials.

<table>
<thead>
<tr>
<th>Pure Al, Mg and Master-Alloys</th>
<th>Element (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Al</td>
</tr>
<tr>
<td>Mg-2% Mn</td>
<td>0.0042</td>
</tr>
<tr>
<td>Pure Mg</td>
<td>0</td>
</tr>
<tr>
<td>Pure Al</td>
<td>Bal.</td>
</tr>
<tr>
<td>Al-10% Fe</td>
<td>Bal</td>
</tr>
</tbody>
</table>
Figure 3-2 Pure aluminum, (a) original ingot, and (b) sectioned pieces.

Figure 3-3 Pure magnesium, (a) original ingot, and (b) sectioned pieces.

Figure 3-4 Mg-2 wt.% Mn master alloy, (a) original ingot, and (b) sectioned pieces.
3.2 Melt Preparation

When running a laboratory experiment, the list of safety procedures and sequence must be followed at all times:

1. Do not use water when running an experiment;
2. Ventilation System is ON;
3. Protection Gas is ON;
4. Safety hard hat with a full-face shield, safety shoes, lab coat and leather gloves should be worn all time;
5. Moulds and tools need to be preheated to approximately 150° Celsius;
6. Fire extinguisher can be quickly and easily accessed; and
7. There are at least two students in the lab when running an experiment.
3.2.1 Protective Gas and Melting Unit

Melting pure magnesium or magnesium alloys requires the use of a protective gas mixture in order to protect the melt from oxidation and burning. The gas mixture employed in this study was the Sulfur Hexafluoride SF$_6$ 0.5% plus carbon dioxide (CO$_2$) in balance. SF$_6$ is one of the most popular insulating gases. It has a number of nice properties: it's not flammable, it's non-toxic, it's moderately inexpensive and it's a good insulator (being an electronegative gas) with a breakdown strength of about 3 times that of air. Since SF$_6$ density is far higher than air and oxygen (see Table 3-2), it can cover on the top of the melt and separate it from air to prevent oxidizing. The flow rate of SF$_6$ mixed gas was controlled between 0.8 and 1.0 liter per minute with the outlet pressure of 20 to 25 psi during melting of magnesium alloys. To melt the raw ingot the electrical resistance furnace was employed for the experiment. Figure 3-6 shows the electrical furnace with a control unit and protective gas system.

Table 3-2 Densities of different gases.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Carbon monoxide</th>
<th>Air</th>
<th>Oxygen</th>
<th>Argon</th>
<th>Carbon dioxide</th>
<th>SF$_6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density of Gas (kg/m$^3$)</td>
<td>1.25</td>
<td>1.29</td>
<td>1.31</td>
<td>1.784</td>
<td>1.80</td>
<td>6.27</td>
</tr>
</tbody>
</table>
3.2.2 Tool Preheating

One very important point that needs to be addressed is always to preheat the tools, such as skimming rods, stirring rods, ingot pieces, permanent moulds and ingot moulds prior to immersing those tools into liquid magnesium or to cast ingots or any other type of test specimens. Tools and moulds need to be preheated and should always be free of moisture in order to avoid a violent reaction, which can be ignited by molten magnesium in contact with water. Tools were preheated around 150 °C on top of the furnace for at least 20 minutes prior to use.
3.2.3 Ingot Preheating

For safety considerations, sectioned raw materials were preheated before the melting process. The preheat raw ingot was loaded into a graphite crucible with a temperature of 500°C in a furnace. Fig.3-7 shows a graphite crucible with dimensions used during experiments. Table 3-3 shows the dimensions of the graphite crucible.

Figure 3-7 (a) a graphite crucible used for lab experiments, and (b) dimensions of the graphite crucible.
Table 3-3 The dimensions of the graphite crucible.

<table>
<thead>
<tr>
<th>Bottom Outside Diameter (BOD) (cm)</th>
<th>Top Outside Diameter (TOD) (cm)</th>
<th>Outside Height (OH) (cm)</th>
<th>Inside Diameter of Crucible (ID) (cm)</th>
<th>Inside Height (IH) (cm)</th>
<th>Crucible Volume (cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.2</td>
<td>8.5</td>
<td>12.0</td>
<td>5.7</td>
<td>10.5</td>
<td>267.9</td>
</tr>
</tbody>
</table>

3.2.4 Melting Process

Melting of magnesium alloys with desired chemical compositions established based on the design of experiment (DOE), was carried out in a 2.6 kw, 50/60 HZ electrical furnace with a maximum temperature of 1200 °C. The furnace temperature was set up at 750 °C. When running the experiment, the temperature of the inside crucible (melt) was kept around 630 ~690 °C. Both the control panel of the furnace and a handhold digital thermometer closely were employed to monitor the temperature of the melt. The set furnace temperature was decided by the DOE experimental alloys designed based on the common commercial magnesium alloy AZ91, AM60, and the fact that the heat loss resulted from skimming operation.

350 grams of cleaned raw materials for desired chemical compositions based on the DOE were loaded into a graphite crucible inside an electric resistance furnace. The crucible was heated to 500°C for 20 minutes of preheating to remove any entrapped moisture, and then the protective gas mixture was be fed into the furnace chamber at this stage to make sure that the magnesium and other alloy pieces were not oxidized as the metal temperature
increased. Meanwhile, the ventilation was turned on for adequate air circulation. After ingot were preheated, the temperature of the furnace was increased to a desired temperature. Once the raw materials were fully melted and reached the target temperature, the furnace cover was opened and the melt surface was skimmed by using the mild steel tool available for this operation. Then the melt was stirred thoroughly. After holding a fixed period at the desired temperature, the graphite crucible was removed from the furnace chamber, and air cooled with cover of protective gas until the completion of solidification. Figure 3-8 presents a flow chart showing the melting preparation procedure for the designed experimental alloys.
Figure 3-8 Flow chart showing the melt preparation procedure of lab experiments.
3.3 Microstructure Analysis

3.3.1 Specimen preparation

Figure 3-9 shows the procedure for sectioning specimens from sludge blocks for metallographic analysis. For the microstructure analysis of the DOE experimental alloys, specimens were chosen and sectioned from the bottom to the top of the air-cooled cast cylindrical sample as illustrated in Figure 3-10.

The procedure of specimen preparation included: sectioning, mounting, grinding, polishing

A. Sectioning

Specimens were cut from bottom, center and top of coupons in the form of cubes with the dimensions of 10x10x10 mm.

B. Mounting

Specimens were mounted by Buehler simplimet3 mount machine. The mount materials are one of the common plastic mounting materials, cold mounting material – epoxy. Then the mounted specimens were ground down on the 180 grit by using a belt grinder to smooth the edge of the specimens.

C. Grinding

The roughly ground mounted specimens went through a wet grinding process by using the series of SiC papers in the sequence procedures: 240, 320, 400, and 600 grit.

D. Polishing

Mechanical polishing was performed in two stages by using polishing machine and DP-PAN polishing cloth with 3 μm Al₂O₃ suspension, and 0.05 μm Al₂O₃ suspension. Rough
polishing (stage one) removed the major part of the disturbed metal remaining after the final grinding step. Finish polishing (stage two) removed the superficial scratches that remain after rough polishing. Then using cold water, liquid soap and ethyl alcohol cleaned the polished specimens, and dried with a hair dryer using cold air.

Figure 3-9 Photographs showing (a) the marking lines for sectioning of a sludge block, and (b) the sectioned specimens for metallographic analysis.

Figure 3-10 Photographs showing (a) an air-cooled cast cylindrical DOE Mg alloy sample prepared by the graphite crucible, and (b) the locations from which specimens were sectioned for metallographic analysis.
3.3.2 Optical Microscopy (OM) and Scanning Electron Microscopy (SEM)

An optical microscope (OM) was used to understand the distribution of sludge. Figure 3-11 shows the Buehler optical image analyzer 2002 system. Detailed features of the microstructure were obtained at high magnifications by a scanning electron microscope (SEM), Hitachi_ Tabletop Microscope TM3000 (Tokyo, Japan), with a maximum resolution of 30 nm in backscattered mode/1 lm in x-ray diffraction mapping mode, and magnifications of 10x to 10,000x to maximize the composition reading of the energy dispersive spectroscopy (EDS) data. Figure 2.12 shows scanning electron microscope (Hitachi Tabletop Microscope TM3000). A quantitative evaluation of specimen microstructures consisted of calculating area fractions of different phase constituents by using ImageJ, a public domain image processing system, to identify different microstructures through image contrast. The distribution of the intermetallic Al$_8$Mn$_5$ (sludge) phase and $\alpha$-Mg matrix structure were determined by the linear intercept method with the help of the ImageJ analysis software.
**Figure 3-11** Buehler Optical Image Analyzer Model 2002.

**Figure 3-12** Scanning electron microscope (Hitachi Tabletop Microscope TM3000).
CHAPTER 4
Design of Experiment by Taguchi Method

4.1 Design of Experiments Technique

The optimization of process parameters is usually performed to ensure done to have great control over quality, productivity and cost aspects of a manufacturing process. Offline quality control is considered to be an effective approach to improve product quality at a relatively low cost. Analysis of variance (ANOVA) is used to study the effect of process parameters on the technical process. The optimization approach is based on the Taguchi method, the signal to-noise (S/N) ratio and the analysis of variance (ANOVA) are employed to study the performance characteristics, and their contribution to the objective function.

The Taguchi methods with optimized processes is a statistical optimization approach for developed by Genichi Taguchi to improving the quality of manufactured goods. It has also been used widely in engineering design. The Taguchi method contains system design, parameter design, and tolerance design procedures to achieve a robust process and result for the best product quality [32]. As an engineering method for product or process design, the method focuses on determining the parameter (factor) settings producing the best levels of a quality characteristic with minimum variation. Taguchi designs provide a powerful and efficient method for optimizing processes that operate consistently and effectively over a variety of conditions. To determine the best design, it requires the use of a strategically designed experiment, which exposes the process to various levels of design parameters [33]. A typical procedure of the Taguchi method is shown in Figure 4-1.
Figure 4-1 Procedures for the Taguchi method [33].

Determine the Quality Characteristics

Identify Control Factors and Alternative levels

Design Matrix Experiment and Data Analysis Procedure

Conduct Experiments

Data Analysis and Optimum Level Determination

Performance Prediction
4.2 Design of Orthogonal Array and Signal-to-Noise Analysis

Based on the literature survey and industrial observation on Mg sludge formation, five factors of alloy chemical compositions and holding temperature and time along with four level were selected. The chosen five factors (Al, Mn, Fe and Holding Temperature and Time) with four levels were listed in Table 4-1. The detailed information of each factor and level employed in the orthogonal array of sixteen experiments are given in Table 4-2

Table 4-1 Design factors and levels.

<table>
<thead>
<tr>
<th>Level</th>
<th>Factor</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
<td>B</td>
<td>C</td>
<td>D</td>
<td>E</td>
</tr>
<tr>
<td></td>
<td>Al (wt%)</td>
<td>Mn (wt%)</td>
<td>Fe (wt%)</td>
<td>Holding Temperature (°C)</td>
<td>Holding Time (Mins)</td>
</tr>
<tr>
<td>1</td>
<td>6</td>
<td>0.15</td>
<td>0.001</td>
<td>630</td>
<td>30</td>
</tr>
<tr>
<td>2</td>
<td>7</td>
<td>0.25</td>
<td>0.004</td>
<td>650</td>
<td>60</td>
</tr>
<tr>
<td>3</td>
<td>8</td>
<td>0.35</td>
<td>0.007</td>
<td>670</td>
<td>90</td>
</tr>
<tr>
<td>4</td>
<td>9</td>
<td>0.45</td>
<td>0.01</td>
<td>690</td>
<td>120</td>
</tr>
</tbody>
</table>
Table 4-2 Designed experiment plans.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Al (%)</th>
<th>Mn (%)</th>
<th>Fe (%)</th>
<th>Holding Temperature (°C)</th>
<th>Holding Time (Mins)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6 (A1)</td>
<td>0.15 (B1)</td>
<td>0.001 (C1)</td>
<td>630 (D1)</td>
<td>30 (E1)</td>
</tr>
<tr>
<td>2</td>
<td>6 (A1)</td>
<td>0.25 (B2)</td>
<td>0.004 (C2)</td>
<td>650 (D2)</td>
<td>60 (E2)</td>
</tr>
<tr>
<td>3</td>
<td>6 (A1)</td>
<td>0.35 (B3)</td>
<td>0.007 (C3)</td>
<td>670 (D3)</td>
<td>90 (E3)</td>
</tr>
<tr>
<td>4</td>
<td>6 (A1)</td>
<td>0.45 (B4)</td>
<td>0.01 (C4)</td>
<td>690 (D4)</td>
<td>120 (E4)</td>
</tr>
<tr>
<td>5</td>
<td>7 (A2)</td>
<td>0.15 (B1)</td>
<td>0.004 (C2)</td>
<td>670 (D3)</td>
<td>120 (E4)</td>
</tr>
<tr>
<td>6</td>
<td>7 (A2)</td>
<td>0.25 (B2)</td>
<td>0.001 (C1)</td>
<td>690 (D4)</td>
<td>90 (E3)</td>
</tr>
<tr>
<td>7</td>
<td>7 (A2)</td>
<td>0.35 (B3)</td>
<td>0.01 (C4)</td>
<td>630 (D1)</td>
<td>60 (E2)</td>
</tr>
<tr>
<td>8</td>
<td>7 (A2)</td>
<td>0.45 (B4)</td>
<td>0.007 (C3)</td>
<td>650 (D2)</td>
<td>30 (E1)</td>
</tr>
<tr>
<td>9</td>
<td>8 (A3)</td>
<td>0.15 (B1)</td>
<td>0.007 (C3)</td>
<td>690 (D4)</td>
<td>60 (E2)</td>
</tr>
<tr>
<td>10</td>
<td>8 (A3)</td>
<td>0.25 (B2)</td>
<td>0.01 (C4)</td>
<td>670 (D3)</td>
<td>30 (E1)</td>
</tr>
<tr>
<td>11</td>
<td>8 (A3)</td>
<td>0.35 (B3)</td>
<td>0.001 (C1)</td>
<td>650 (D2)</td>
<td>120 (E4)</td>
</tr>
<tr>
<td>12</td>
<td>8 (A3)</td>
<td>0.45 (B4)</td>
<td>0.004 (C2)</td>
<td>630 (D1)</td>
<td>90 (E3)</td>
</tr>
<tr>
<td>13</td>
<td>9 (A4)</td>
<td>0.15 (B1)</td>
<td>0.01 (C4)</td>
<td>650 (D2)</td>
<td>90 (E3)</td>
</tr>
<tr>
<td>14</td>
<td>9 (A4)</td>
<td>0.25 (B2)</td>
<td>0.007 (C3)</td>
<td>630 (D1)</td>
<td>120 (E4)</td>
</tr>
<tr>
<td>15</td>
<td>9 (A4)</td>
<td>0.35 (B3)</td>
<td>0.004 (C2)</td>
<td>690 (D4)</td>
<td>30 (E1)</td>
</tr>
<tr>
<td>16</td>
<td>9 (A4)</td>
<td>0.45 (B4)</td>
<td>0.001 (C1)</td>
<td>670 (D3)</td>
<td>60 (E2)</td>
</tr>
</tbody>
</table>
In the optimization process, it is almost impossible to eliminate all errors caused by the variation of characteristics. An increase in the variance of multiple characteristics lowers the quality reliability of the process. The Taguchi method [34,35] uses the signal-to-noise (S/N) ratio instead of the average value to interpret the trial results data into a value for the characteristic evaluation in the optimum setting analysis. To minimize the influence of the error caused by the variation of characteristics, the signal-to-noise (S/N) ratio was employed, which converted the trail result data into a value for the response to evaluate the process in the optimum setting analysis. The S/N ratio consolidated several repetitions into one value which reflected the amount of variation present. This is because the S/N ratio can reflect both the average and the variation of the quality characteristics. There are several S/N ratios available depending on the types of characteristics: lower is best (LB), nominal is best (NB), and higher is best (HB). In the present study, sludge yield and size of sludge were treated as a characteristics value. Since the sludge yield and size of sludge were intended to be minimized, the S/N ratio for LB characteristics was selected, which was be calculated as follows:

\[
S/N_{LB} = -10 \log \left( \frac{1}{n} \sum_{i=1}^{n} \eta_{pi}^2 \right) \tag{5}
\]

where \( n \) is the repetition number of each experiment under the same condition for design parameters, and \( \eta_{pi} \) is the property of an individual measurement at the \( i_{th} \) test. After calculating and plotting the mean S/N ratios at each level for various factors, the optimal level, that was the largest S/N ratio among all levels of the factors, was determined.
The proposition for the minimize the sludge formation, the sludge yield (SY) and intermetallic size (IS) are multiple performance characteristics (two objectives) using a weighting method is defined as the Eqs. (6)–(8):

\[ Y_{SUM} = Y_P \times W \] (6)

Where

\[ Y_{SUM} = \begin{bmatrix} \eta_{1c} \\ \eta_{2c} \\ \vdots \\ \eta_{9c} \end{bmatrix}, \quad Y_P = \begin{bmatrix} \eta_{11} & \eta_{12} \\ \eta_{21} & \eta_{22} \\ \vdots & \vdots \\ \eta_{91} & \eta_{92} \end{bmatrix}, \quad w = \begin{bmatrix} w_1 \\ \vdots \\ w_3 \end{bmatrix} \] (7)

And

\[ \sum_{i=1}^{2} w_i = 1 \] (8)

where \( w_1 \) and \( w_2 \) are the weighting factor of sludge yield and intermetallic size, respectively. \( \eta_{jc} \) is the multi response, S/N ratio in the jth test, \( \eta_{ji} \) is the \( i \)th single response S/N ratio for the jth test; \( w_i \) is the weighting factor in the \( i \)th performance characteristics.

The objective function was formulated according to the previous optimization criteria:

\[ \text{Minimize } f(X) = w_1 \cdot \eta_{SY} + w_2 \cdot \eta_{IS} \] (9)
4.3 Determination of Sludge Yield

Step One: Determination of density of the Al-Mn intermetallic-free alloy matrix

1. Acquire specimens from the Al-Mn intermetallic-free zone in the cylinder casting for the density measurement of the Al-Mn intermetallic-free Mg alloy matrix;

2. Measure the density of the Al-Mn intermetallic-free Mg alloy matrix with Archimedes principle;

\[ \rho_{alloy\ matrix} = \frac{w_a \times \rho_w}{W_a - w_w} \]  

where \( w_a \) and \( w_w \) are the weights of the Al-Mn intermetallic-free specimens in air and water, respectively, \( \rho_w \) is the density of water.

Step Two: Determination of the volume fraction of the Al-Mn intermetallic in the Al-Mn intermetallic-concentrated layer

3. Acquire specimens from the Al-Mn intermetallic-concentrated layer at the bottom of the cylinder casting for the determination of the volume fraction of the Al-Mn intermetallic;

4. Determine the volume fraction of the Al-Mn intermetallic in the Al-Mn intermetallic-concentrated layer (\( V_{Al-Mn\ in\ layer} \)) by image analysis (ImageJ) with the help of an optical microscope (OM) and a scanning electron microscope (SEM);
Step Three: Determination of Density of the Al-Mn intermetallic-concentrated layer

5. Determine the volume fraction of the Mg alloy matrix ($V_{\text{Matrix in layer}}$) in the Al-Mn intermetallic-concentrated layer

$$V_{\text{Matrix in layer}} = 1 - V_{\text{Al-Mn in layer}} \quad (11)$$

6. Calculate the density of the Al-Mn intermetallic-concentrated layer, which consists of (a) Al-Mn intermetallic and (b) alloy matrix, based on the Rule of Mixtures;

$$\rho_{\text{layer}} = \rho_{\text{matrix alloy}} \times V_{\text{Matrix in layer}} + \rho_{\text{Al-Mn}} \times V_{\text{Al-Mn in layer}} \quad (12)$$

where $\rho_{\text{Al-Mn}}$ is the density of the Al-Mn intermetallic (4.43 g/cm$^3$) [3]

Step Four: Determination of the Volume of the Al-Mn intermetallic-concentrated layer

7. Measure the thickness of the Al-Mn intermetallic-concentrated layer ($t_{\text{layer}}$) at the bottom of the cylinder casting with an optical microscope or SEM;

8. Calculate the volume of the Al-Mn intermetallic-concentrated layer ($V_{\text{layer}}$) with the known diameter of the cylinder casting ($d_{cs}$);

$$V_{\text{layer}} = \frac{1}{4} \pi d_{cs}^2 \times t_{\text{layer}} \quad (13)$$

Step Five: Determination of the weight of the Al-Mn intermetallic in the cylinder casting

9. Calculate the total weight of the Al-Mn intermetallic in the Al-Mn intermetallic-concentrated layer ($W_{\text{Al-Mn in layer}}$);

$$W_{\text{Al-Mn in layer}} = \rho_{\text{Al-Mn}} \times V_{\text{Al-Mn in layer}} \times v_{\text{layer}} \quad (14)$$
10. Determine the weight of the Al-Mn intermetallic in the entire cylinder casting ($W_{\text{Al-Mn in cs}}$), which should be equivalent to the weight of the Al-Mn intermetallic in the Al-Mn intermetallic-concentrated layer ($W_{\text{Al-Mn in layer}}$)

$$W_{\text{Al-Mn in cs}} = W_{\text{Al-Mn in layer}} \quad (15)$$

Step Six: Calculation of Sludge Yield

11. Calculate the sludge (Al-Mn intermetallic) yield ($SY$) with the following equation:

$$SY = \frac{W_{\text{Al-Mn in cs}}}{W_{\text{cs}}} \quad (16)$$

where $SY$ is the sludge yield (%), $W_{\text{Al-Mn}}$ is the weight of the Al-Mn intermetallic (g), and $W_{\text{cs}}$ is the weight of the cylinder casting.
Figure 4-2 Schematical illustration showing a Mg cylinder casting with an Al-Mn intermetallic-free area and an Al-Mn intermetallic-concentrated layer.

4.4 Analysis of variance (ANOVA)

The purpose of the analysis of variance is to investigate the contribution of each factor (chemical element) with multiple characteristics that significantly affect the sludge yield and intermetallic size. Following the analysis, it is relatively easy to identify the effect order of factors on the sludge yield and intermetallic size, and the contribution of factors to sludge yield and intermetallic size. In this study, variation due to both the four factors and the possible error was taken into consideration. The ANOVA was established based on the sum of the square (SS), the degree of freedom (D), the variance (V), and the percentage of the contribution to the total variation (P). The five parameters symbol typically used in ANOVA are described below:
1. Sum of squares (SS). \( SS_P \) denotes the sum of squares of factors A, B, C, and D; \( SS_e \) denotes the error sum of squares; \( SS_T \) denotes the total sum of squares.

The total sum of square SST from S/N ratio was calculated as:

\[
SS_T = \sum_{i=1}^{m} \eta_i^2 - \frac{1}{m} \left[ \sum_{i=1}^{m} \eta_i \right]^2
\]

where \( m \) is the total number of the experiments, and \( \eta_i \) is the factor response at the \( i \)th test.

The sum of squares from the tested factors, \( SS_P \), was calculated as:

\[
SS_P = \sum_{i=1}^{m} \frac{\left( S_{\eta_{ij}} \right)^2}{t} - \frac{1}{m} \left[ \sum_{i=1}^{m} \eta_i \right]^2
\]

where \( m \) is the number of the tests (\( m = 16 \)), \( j \) the level number of this specific factor \( p \), \( t \) is the repetition of each level of the factor \( p \), and \( S_{\eta_{ij}} \) the sum of the multi-response S/N ratio involving this factor \( p \) and level \( j \).

2. Degree of freedom (D). \( D \) denotes the number of independent variables. The degree of freedom for each factor (\( D_P \)) is the number of its levels minus one. The total degrees of freedom (\( D_T \)) are the number of total numbers of the result data points minus one, i.e., the total number of trials times the number of repetitions minus one. The degree of freedom for the error (\( D_e \)) is the number of the total degrees of freedom minus the total of degree of freedom for each factor.

3. Variance (V). Variance is defined as the sum of squares of each trial sum result involved the factor, divided by the degrees of freedom of the factor:

\[
V_p \,(\%) = \frac{SS_p}{D_p} \times 100
\]
4. The corrected sum of squares (SS_p). SS_p is defined as the sum of squares of factors minus the error variance times the degree of freedom of each factor:

\[ SS_p' = SS_p - D_p V_e \]  \hspace{1cm} (20)

5. Percentage of the contribution to the total variation (P). P_p denotes the percentage of the total variance of each individual factor:

\[ P_p (\%) = \frac{SS_p'}{SS_p} \times 100 \]  \hspace{1cm} (21)
CHAPTER 5

Characterization of Mn and/or RE containing Intermetallics in AZ91D Recycling Ingot Sludge, and AZ91D, AM60 and AE44 Die Casting Sludges

5.1 Characterization of Mn-containing Intermetallics in AZ91D Recycling Ingot Sludge

Figure 5-1 presents SEM micrographs showing a microstructure panoramic view at low magnification of the sludge generated in the AZ91D recycling process. The panoramic micrograph showed that the sludge contained some secondary particles, but in low quantities, in the Mg matrix. To identify Mn-containing intermetallic phases and determine their volume fraction and morphology, seven regions, named Spots 1-7 in the panoramic view, were randomly selected for SEM and EDS analyses in detail. Spots 5 and 7 were selected as representatives of all seven spots for the presentation of phase identification and determination of volume fractions of Mn-containing intermetallic phases. Given below are the detailed SEM and EDS results of Spots 5 and 7. The SEM image in BSE mode and EDS elemental maps for Spot 5 in the AZ91D recycling ingot sludge are given in Figure 5-2. It can be seen from the EDS elemental maps in Figure 5-2 that spot 5 primarily contained Mg metal in majority and Al-Mn-concentrated regions with little iron and oxygen. The results of the EDS analysis as shown in Figure 5-3 and the element analysis in atomic percentages listed in Table 5-1 indicated that the microstructure of Spot 5 consisted of α-Mg matrix (dark), and Mn-containing intermetallic phases (gray), and MgO inclusion (black) as shown in Figure 5-2 (a). There were elements Al, Mn and Fe in the Mn-containing intermetallic phase. For Spot 7, the SEM and EDS results are presented in Figures 5-5. The α-Mg matrix (dark) and Mn-containing intermetallic (gray) phases were
present in the microstructure of Spot 7, which were similar to those in Spot 5. Also, oxygen was detected. Table 5-2 lists the elements in analyzed $\alpha$-Mg matrix, Mn-containing intermetallic and MgO of Spot 7 shown in Figures 5-6. Based on the atomic percentages listed in Tables 5-1 and 5-2 for point 3 in Spot 5 and points 5 and 6 in Spot 7, the ratios between the Al and Mn were calculated to be approximately 1.6. These ratios around 1.6 suggested that the Mn-containing intermetallic particles could be considered as $\text{Al}_8\text{Mn}_5$ phase.

To determine the volume fraction of the Al-Mn intermetallic phase in the AZ91D recycling ingot sludge, the micrographs of Figures 5-2(a) and 5-4(a) were converted to binary black and white images by using the ImageJ pixel analysis software, as shown in Figures 5-7(a) and (b) respectively. During conversion, the SEM micrographs in Figures 5-2(a) and Figure 5-4(a) were imported into the ImageJ, and the type of 32-bit image was selected to maximize the resolution. The adjustment of threshold was made by increasing the brightness of the primary $\alpha$-Mg area fraction, until the entire $\alpha$-Mg territory turned white, and the $\text{Al}_8\text{Mn}_5$ intermetallic region of interest in black was revealed. In Figure 5-7, the black area represented Al-Mn intermetallics, while the white area was illustrated by the $\alpha$-Mg phase. As shown in Figures 5-7 (a) and (b), the volume fractions of the $\text{Al}_8\text{Mn}_5$ intermetallic phase for spots 5 and 7 were 3.15% and 2.75%, respectively. Based on the measured volume fractions, the weight percentages of the $\text{Al}_8\text{Mn}_5$ intermetallic phase in Mg alloys AZ91D and AM60B were calculated by the following equation:

$$W_{\text{Al-Mn}}^{\text{AZ91 or AM60}} = \frac{\rho_{\text{Al-Mn}} \times V_{\text{Al-Mn}}}{\rho_{\text{Al-Mn}} \times V_{\text{Al-Mn}} + \rho_{\text{Mg}} \times V_{\text{Mg}}}$$

(22)
where $W_{Al-Mn}^{AZ91 \ or \ AM60}$ is the weight percentage of the Al$_8$Mn$_5$ intermetallic phase for Mg alloys AZ91D and AM60B, $\rho_{Al-Mn}$ is the density of the Al$_8$Mn$_5$ intermetallic (4.43 g/cm$^3$), $V_{Al-Mn}$ is the measured volume fraction of Al$_8$Mn$_5$ intermetallic, $\rho_{Mg}$ is the density of Mg (1.74 g/cm$^3$), and $V_{Mg}$ is the volume fraction of Mg. It is worthwhile mentioning that Equation 22 excluded the MgO content, since the MgO phase was hard to be distinguished from the intermetallic particles in the black and white image. The overestimation of the weight percentage of the Al$_8$Mn$_5$ intermetallic phase resulting from the exclusion of the MgO content might be mitigated by the minor difference in densities between the Al$_8$Mn$_5$ (4.43 g/cm$^3$) and MgO (3.58 g/cm$^3$) phases, compared to the Mg density (1.74 g/cm$^3$).

The calculated weight percentages of the Al$_8$Mn$_5$ intermetallic phase for spots 5 and 7 were 7.65 and 6.71 wt.%, respectively. The volume fractions and weight percentages of the Al$_8$Mn$_5$ intermetallic phase in the AZ91D recycling ingot sludge for the selected seven spots illustrated in Figure 5-1 are summarized in Table 5-3. Overall, the average volume fraction and weight percentage of the Al$_8$Mn$_5$ intermetallic phase in the AZ91D recycling ingot sludge were 0.92% and 2.77%, respectively. The high values of the standard deviation indicated that the distribution of the Al$_8$Mn$_5$ intermetallic phases in the sludge was non-uniform in a large extent.
**Figure 5-1** SEM micrographs at low magnification showing a microstructure panoramic view of the AZ91D recycling ingot sludge with seven spots selected for EDS analyses.
Figure 5-2 EDS results for Spot 5 in the AZ91D recycling ingot sludge: (a) SEM micrograph in BSE mode, and elemental maps for (b) all detected elements, (c) Mg, (d) Al, (e) Mn, (f) Fe and (g) O.
Figure 5-3 EDS spectra (a), (b) and (c) for the areas containing $\alpha$-Mg matrix (dark), and Mn-containing intermetallic phases (gray), and MgO inclusion (black) for points 1-3 as shown in Figure 5-2 (a), respectively.

Table 5-1 Elements in analyzed $\alpha$-Mg matrix, Mn-containing intermetallic phase and MgO of Spot 5 shown in Figure 5-2.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Element</th>
<th>Atomic (at. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Point 1</td>
</tr>
<tr>
<td>$\alpha$-Mg matrix</td>
<td>Mg</td>
<td>92.13</td>
</tr>
<tr>
<td></td>
<td>Al</td>
<td>7.87</td>
</tr>
<tr>
<td>Mn-containing intermetallic</td>
<td>Mg</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Al</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Mn</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Fe</td>
<td>-</td>
</tr>
<tr>
<td>MgO</td>
<td>Mg</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Al</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>-</td>
</tr>
</tbody>
</table>
Figure 5-4 SEM micrograph showing microstructure of Spot 7.

(a)
Figure 5-5 EDS results for Spot 7 in the AZ91D recycling ingot sludge: (a) SEM micrograph in BSE mode, and elemental maps for (b) overall detected elements, (c) Mg, (d) Al, (e) Mn, (f) Fe and (g) O.
Figure 5-6 EDS spectra (a), (b) and (c) for the areas containing α-Mg matrix (dark), and Mn-containing intermetallic phases (gray), and MgO inclusion (black) for Point 4, 5 and 7 as shown in Figure 5-4, respectively.

Table 5-2 Elements in analyzed α-Mg matrix, Mn-containing intermetallic phase and MgO of Spot 7 shown in Figures 5-4

<table>
<thead>
<tr>
<th>Phase</th>
<th>Element</th>
<th>Atomic (at. %)</th>
<th>Point 4</th>
<th>Point 5</th>
<th>Point 6</th>
<th>Point 7</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-Mg matrix</td>
<td>Mg</td>
<td>93.21</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Al</td>
<td>6.79</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Mn-containing intermetallic</td>
<td>Mg</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>41.91</td>
<td>41.58</td>
</tr>
<tr>
<td></td>
<td>Al</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>35.78</td>
<td>33.58</td>
</tr>
<tr>
<td></td>
<td>Mn</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>20.36</td>
<td>22.76</td>
</tr>
<tr>
<td></td>
<td>Fe</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.95</td>
<td>2.08</td>
</tr>
<tr>
<td>MgO</td>
<td>Mg</td>
<td>-</td>
<td>78.53</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Al</td>
<td>-</td>
<td>5.21</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>-</td>
<td>16.26</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Figure 5-7 Binary black and white images showing the volume fraction of Al\_8Mn\_5 intermetallic phases in (a) Spot 5 and (b) Spot 7 of the AZ91D recycling ingot sludge.
Table 5-3 Volume Fractions and weight Percentages of Al$_8$Mn$_3$ intermetallic phases in AZ91D recycling ingot sludge

<table>
<thead>
<tr>
<th>Number of Spots</th>
<th>Volume Fraction of Intermetallic (%)</th>
<th>Weight Percentage of Intermetallic (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.27</td>
<td>0.68</td>
</tr>
<tr>
<td>2</td>
<td>0.21</td>
<td>0.53</td>
</tr>
<tr>
<td>3</td>
<td>0.17</td>
<td>0.43</td>
</tr>
<tr>
<td>4</td>
<td>1.15</td>
<td>2.88</td>
</tr>
<tr>
<td>5</td>
<td>3.15</td>
<td>7.65</td>
</tr>
<tr>
<td>6</td>
<td>0.21</td>
<td>0.53</td>
</tr>
<tr>
<td>7</td>
<td>2.75</td>
<td>6.72</td>
</tr>
<tr>
<td>Average</td>
<td>0.92</td>
<td>2.77</td>
</tr>
<tr>
<td>Standard Deviation</td>
<td>1.10</td>
<td>3.27</td>
</tr>
</tbody>
</table>
5.2 Characterization of Mn-containing Intermetallics in AZ91D Die Casting Sludge

Figure 5-8 presents SEM micrographs showing a microstructure panoramic view at low magnification of the sludge generated in the AZ91D die casting process. The panoramic micrograph showed that the sludge contained some secondary particles, but in low quantities, in the Mg matrix. To identify Mn-containing intermetallic phases and determine their volume fraction and morphology, seven regions, named Spots 8-13 in the panoramic view, were randomly selected for SEM and EDS analyses in detail. Spots 8 and 12 were selected as representatives of all six spots for the presentation of phase identification and determination of volume fractions of Mn-containing intermetallic phases. Given below are the detailed SEM and EDS results of Spots 8 and 12. The SEM image in BSE mode and EDS elemental maps for Spot 12 in the AZ91D die casting sludge are given in Figure 5-9.

It can be seen from the EDS elemental maps in Figure 5-9 (b) that spot 12 primarily contained Mg metal in majority and Al-Mn-concentrated regions with little iron and oxygen. The results of the EDS analysis as shown in Figure 5-10 and the element analysis in atomic percentages listed in Table 5-4 indicated that the microstructure of Spot 12 consisted of $\alpha$-Mg matrix (dark), and Mn-containing intermetallic phases (gray), and MgO inclusion (black) as shown in Figure 5-9 (a). There were elements Al, Mn and Fe in the Mn-containing intermetallic phase. For Spot 8, the SEM and EDS results are presented in Figures 5-11. The $\alpha$-Mg matrix (dark) and Mn-containing intermetallic (gray) phases were present in the microstructure of Spot 8, which were similar to those in Spot 12. Always, oxygen was detected. Table 5-5 lists the elements in analyzed $\alpha$-Mg matrix, Mn-containing intermetallic and MgO of Spot 8 shown in Figures 5-12. Based on the atomic percentages listed in Tables 5-4 and 5-5 for point 12 in Spot 8 and points 9 in Spot 12, the ratios between
the Al and Mn were calculated to be approximately 1.6. These ratios around 1.6 suggested that the Mn-containing intermetallic particles could be considered as $\text{Al}_8\text{Mn}_5$ phase.

To determine the volume fraction of the Al-Mn intermetallic phase in the AZ91D die casting sludge, the micrographs of Figures 5-9(a) and 5-11(a) were converted to binary black and white images by using the ImageJ pixel analysis software, as shown in Figures 5-13(a) and (b) respectively. During conversion, the SEM micrographs in Figures 5-9(a) and Figure 5-11(a) were imported into the ImageJ, and the type of 32-bit image was selected to maximize the resolution. The adjustment of threshold was made by increasing the brightness of the primary $\alpha$-Mg area fraction, until the entire $\alpha$-Mg territory turned white, and the $\text{Al}_8\text{Mn}_5$ intermetallic region of interest in black was revealed. In Figure 5-13, the black area represented Al-Mn intermetallics, while the white area was illustrated by the $\alpha$-Mg phase. As shown in Figures 5-13 (a) and (b), the volume fractions of the $\text{Al}_8\text{Mn}_5$ intermetallic phase for spots 12 and 8 were 10.13% and 7.42%, respectively. Based on the measured volume fractions, the weight percentages for spot 12 and 8 were calculated, which were 22.30 and 16.95 wt.%, respectively. The volume fractions and weight percentages of the $\text{Al}_8\text{Mn}_5$ intermetallic phase in the AZ91D die casting sludge for the selected six spots illustrated in Figure 8 are summarized in Table 6. Overall, the average volume fraction and weight percentage of the $\text{Al}_8\text{Mn}_5$ intermetallic phase in the AZ91D die casting sludge were 4.54% and 10.33%, respectively. The high values of the standard deviation indicated that the distribution of the $\text{Al}_8\text{Mn}_5$ intermetallic phases in the sludge was non-uniform in a large extent.
Figure 5-8 SEM micrographs at low magnification showing a microstructure panoramic view of the AZ91D die casting sludge with six spots selected for EDS analyses.
Figure 5-9 EDS results for Spot 12 in the AZ91D die casting sludge: (a) SEM micrograph in BSE mode, and elemental maps for (b) all detected elements, (c) Mg, (d) Al, (e) Mn, (f) Fe and (g) O.
Figure 5-10 EDS spectra (a), (b) and (c) for the areas containing α-Mg matrix (dark), and Mn-containing intermetallic phases (gray), and MgO inclusion (black) for points 8-10 as shown in Figure 5-9 (a), respectively.
Table 5-4 Elements in analyzed α-Mg matrix, Mn-containing intermetallic phase and MgO of Spot 4 shown in Figure 5-9.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Element</th>
<th>Atomic (at. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Point 8</td>
</tr>
<tr>
<td>α-Mg matrix</td>
<td>Mg</td>
<td>90.03</td>
</tr>
<tr>
<td></td>
<td>Al</td>
<td>9.97</td>
</tr>
<tr>
<td>Mn-containing intermetallic</td>
<td>Mg</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Al</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Mn</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Fe</td>
<td>-</td>
</tr>
<tr>
<td>MgO</td>
<td>Mg</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Al</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>-</td>
</tr>
</tbody>
</table>
(d)

(e)
Figure 5-11 EDS results for Spot 8 in the AZ91D die casting sludge: (a) SEM micrograph in BSE mode, and elemental maps for (b) all detected elements, (c) Mg, (d) Al, (e) Mn, (f) Fe and (g) O.
Figure 5-12 EDS spectra (a), (b) and (c) for the areas containing α-Mg matrix (dark), and Mn-containing intermetallic phases (gray), and MgO inclusion (black) for points 11-13 as shown in Figure 5-11 (a), respectively.

Table 5-5 Elements in analyzed α-Mg matrix, Mn-containing intermetallic phase and MgO of Spot 8 shown in Figures 5-11(a).

<table>
<thead>
<tr>
<th>Phase</th>
<th>Element</th>
<th>Atomic (at. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Point 11</td>
</tr>
<tr>
<td>α-Mg matrix</td>
<td>Mg</td>
<td>91.98</td>
</tr>
<tr>
<td></td>
<td>Al</td>
<td>8.02</td>
</tr>
<tr>
<td>Mn-containing intermetallic</td>
<td>Mg</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Al</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mn</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fe</td>
<td></td>
</tr>
<tr>
<td>MgO</td>
<td>Mg</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Al</td>
<td></td>
</tr>
<tr>
<td></td>
<td>O</td>
<td></td>
</tr>
</tbody>
</table>
**Figure 5.13** Binary black and white images showing the volume fraction of Al₈Mn₅ intermetallic phases in (a) Spot 12 and (b) Spot 8 of the AZ91D die casting sludge.
Table 5-6 Volume Fractions and weight Percentages of Al$_8$Mn$_5$ intermetallic phases in AZ91D die casting sludge.

<table>
<thead>
<tr>
<th>Number of Spots</th>
<th>Volume Fraction of Intermetallic (%)</th>
<th>Weight Percentage of Intermetallic (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>1.76</td>
<td>16.95</td>
</tr>
<tr>
<td>9</td>
<td>6.93</td>
<td>15.94</td>
</tr>
<tr>
<td>10</td>
<td>0.12</td>
<td>0.30</td>
</tr>
<tr>
<td>11</td>
<td>0.85</td>
<td>2.15</td>
</tr>
<tr>
<td>12</td>
<td>10.13</td>
<td>22.30</td>
</tr>
<tr>
<td>13</td>
<td>1.76</td>
<td>4.36</td>
</tr>
<tr>
<td>Average</td>
<td>4.54</td>
<td>10.33</td>
</tr>
<tr>
<td>Standard Deviation</td>
<td>4.15</td>
<td>9.19</td>
</tr>
</tbody>
</table>
5.3 Characterization of Mn-containing Intermetallics in AM60B Die Casting Sludge

Figure 5-14 presents SEM micrographs showing a microstructure panoramic view at low magnification of the sludge generated in the AM60B die casting process. The panoramic micrograph showed that the sludge contained a large number of secondary particles, but in low quantities, in the Mg matrix. To identify Mn-containing intermetallic phases and determine their volume fraction and morphology, seven regions, named Spots 14-19 in the panoramic view, were randomly selected for SEM and EDS analyses in detail. Spots 16 and 18 were selected as representatives of all six spots for the presentation of phase identification and determination of volume fractions of Mn-containing intermetallic phases. Given below are the detailed SEM and EDS results of Spots 16 and 18. The SEM image in BSE mode and EDS elemental maps for Spot 16 in the AM60B die casting sludge are given in Figure 5-15. It can be seen from the EDS elemental maps in Figure 5-15 (b) that spot 16 primarily contained Mg metal in majority and Al-Mn-concentrated regions with little iron and oxygen. The results of the EDS analysis as shown in Figure 5-16 and the element analysis in atomic percentages listed in Table 5-7 indicated that the microstructure of Spot 16 consisted of $\alpha$-Mg matrix (dark), and Mn-containing intermetallic phases (gray), and MgO inclusion (black) as shown in Figure 5-15 (a). There were elements Al, Mn and Fe in the Mn-containing intermetallic phase. For Spot 4, the SEM and EDS results are presented in Figures 5-17. The $\alpha$-Mg matrix (dark) and Mn-containing intermetallic (gray) phases were present in the microstructure of Spot 18, which were similar to those in Spot 16. Also, a certain amount of oxygen was detected. Table 5-8 lists the elements in analyzed $\alpha$-Mg matrix, Mn-containing intermetallic and MgO of Spot 18 shown in Figures 5-18. Based on the atomic percentages listed in Tables 5-7 and 5-8 for
point 15 in Spot 16 and point 18 in Spot 18, the ratios between the Al and Mn were calculated to be approximately 1.6. These ratios around 1.6 suggested that the Mn-containing intermetallic particles could be considered as Al$_8$Mn$_5$ phase.

To determine the volume fraction of the Al-Mn intermetallic phase in the AM60B die casting sludge, the micrographs of Figures 5-15(a) and 5-17(a) were converted to binary black and white images by using the ImageJ pixel analysis software, as shown in Figures 5-19(a) and (b) respectively. During conversion, the SEM micrographs in Figures 5-15(a) and Figure 5-17(a) were imported into the ImageJ, and the type of 32-bit image was selected to maximize the resolution. The adjustment of threshold was made by increasing the brightness of the primary $\alpha$-Mg area fraction, until the entire $\alpha$-Mg territory turned white, and the Al$_8$Mn$_5$ intermetallic region of interest in black was revealed. In Figure 5-19, the black area represented Al-Mn intermetallics, while the white area was illustrated by the $\alpha$-Mg phase. As shown in Figures 5-19 (a) and (b), the volume fractions of the Al$_8$Mn$_5$ intermetallic phase for spots 16 and 18 were 15.99% and 21.89%, respectively. Based on the measured volume fractions, the weight percentages for spot 2 and 4 were calculated, which were 32.64 and 41.64wt.%, respectively. The volume fractions and weight percentages of the Al$_8$Mn$_5$ intermetallic phase in the AM60B die casting sludge for the selected six spots illustrated in Figure 5-14 are summarized in Table 5-9. Overall, the average volume fraction and weight percentage of the Al$_8$Mn$_5$ intermetallic phase in the AM60B die casting sludge were 17.03% and 34.07%, respectively. The low values of the standard deviation indicated that the distribution of the Al$_8$Mn$_5$ intermetallic phases in the sludge was very uniform.
Figure 5-14 SEM micrographs at low magnification showing a microstructure panoramic view of the AM60B die casting sludge with six spots selected for EDS analyses.
(a) MgO

16

α-Mg

14

Al₆Mn₅

15

(111)
Figure 5-15 results for Spot 16 in the AM60B die casting sludge: (a) SEM micrograph in BSE mode, and elemental maps for (b) all detected elements, (c) Mg, (d) Al, (e) Mn, (f) Fe and (g) O.
Figure 5-16 EDS spectra (a), (b) and (c) for the areas containing $\alpha$-Mg matrix (dark), and Mn-containing intermetallic phases (gray), and MgO inclusion (black) for points 14-16 as shown in Figure 5-15 (a), respectively.
Table 5-7 Elements in analyzed $\alpha$-Mg matrix, Mn-containing intermetallic phase and MgO of Spot 2 shown in Figure 5-15.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Element</th>
<th>Atomic (at. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Point 14</td>
</tr>
<tr>
<td>$\alpha$-Mg matrix</td>
<td>Mg</td>
<td>93.26</td>
</tr>
<tr>
<td></td>
<td>Al</td>
<td>6.74</td>
</tr>
<tr>
<td>Mn-containing intermetallic</td>
<td>Mg</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Al</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Mn</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Fe</td>
<td>-</td>
</tr>
<tr>
<td>MgO</td>
<td>Mg</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Al</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>-</td>
</tr>
</tbody>
</table>
Figure 5-17 EDS results for Spot 18 in the AM60B die casting sludge: (a) SEM micrograph in BSE mode, and elemental maps for (b) all detected elements, (c) Mg, (d) Al, (e) Mn, (f) Fe and (g) O.
Figure 5-18 EDS spectra (a), (b) and (c) for the areas containing α-Mg matrix (dark), and Mn-containing intermetallic phases (gray), and MgO inclusion (black) for points 17-19 as shown in Figure 5-17 (a), respectively.

Table 5-8 Elements in analyzed α-Mg matrix, Mn-containing intermetallic phase and MgO of Spot 4 shown in Figures 5-17 (a).

<table>
<thead>
<tr>
<th>Phase</th>
<th>Element</th>
<th>Atomic (at. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Point 17</td>
</tr>
<tr>
<td>α-Mg matrix</td>
<td>Mg</td>
<td>91.65</td>
</tr>
<tr>
<td></td>
<td>Al</td>
<td>8.35</td>
</tr>
<tr>
<td>Mn-containing</td>
<td>Mg</td>
<td>-</td>
</tr>
<tr>
<td>intermetallic</td>
<td>Al</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Mn</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Fe</td>
<td>-</td>
</tr>
<tr>
<td>MgO</td>
<td>Mg</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Al</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>-</td>
</tr>
</tbody>
</table>
Figure 5-19 Binary black and white images showing the volume fraction of Al₈Mn₅ intermetallic phases in (a) Spot 16 and (b) Spot 18 of the AM60B die casting sludge.
**Table 5-9** Volume Fractions and weight Percentages of Al₈Mn₅ intermetallic phases in AM60B die casting sludge.

<table>
<thead>
<tr>
<th>Number of Samples</th>
<th>Volume Fraction of Intermetallic (%)</th>
<th>Weight Percentage of Intermetallic (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>14</td>
<td>21.70</td>
<td>41.37</td>
</tr>
<tr>
<td>15</td>
<td>15.80</td>
<td>32.33</td>
</tr>
<tr>
<td>16</td>
<td>15.99</td>
<td>32.64</td>
</tr>
<tr>
<td>17</td>
<td>14.41</td>
<td>30.00</td>
</tr>
<tr>
<td>18</td>
<td>21.89</td>
<td>41.64</td>
</tr>
<tr>
<td>19</td>
<td>12.36</td>
<td>26.42</td>
</tr>
<tr>
<td><strong>Average</strong></td>
<td><strong>17.03</strong></td>
<td><strong>34.07</strong></td>
</tr>
<tr>
<td><strong>Standard Deviation</strong></td>
<td><strong>3.92</strong></td>
<td><strong>6.18</strong></td>
</tr>
</tbody>
</table>
5.4 Characterization of Mn-containing Intermetallics in AE44 Die Casting Sludge

Figure 5-20 presents SEM micrographs showing a microstructure panoramic view at low magnification of the sludge generated in the AE44 die casting process. The panoramic micrograph showed that the sludge contained a number of relatively large secondary particles in the Mg matrix. To identify Mn and RE (rare earth element) containing intermetallic phases and determine their volume fraction and morphology, seven regions, named Spots 20-24 in the panoramic view, were randomly selected for SEM and EDS analyses in detail. Spots 21 and 22 were selected as representatives of all five spots for the presentation of phase identification and determination of volume fractions of Mn-containing intermetallic phases. Given below are the detailed SEM and EDS results of Spots 21 and 22. The SEM image in BSE mode and EDS elemental maps for Spot 22 in the AE44 die casting sludge are given in Figure 5-21. It can be seen from the EDS elemental maps in Figure 5-21 (b) that spot 22 primarily contained Mg metal in majority and Al-Mn-RE concentrated regions with little iron and oxygen. The results of the EDS analysis as shown in Figure 5-22 and the element analysis in atomic percentages listed in Table 5-10 indicated that the microstructure of Spot 22 consisted of α-Mg matrix (dark), and Al-Mn-Re intermetallic phases (dark gray), and Al-RE containing intermetallic phase (light phase), and MgO inclusion (black) as shown in Figure 5-21 (a). The detected intermetallic phase contained RE. For Spot 21, the SEM and EDS results are presented in Figures 5-23. The α-Mg matrix (dark), Al-Mn-RE containing intermetallic (dark gray) and Al-RE containing intermetallic (light grey) phases were present in the microstructure of Spot 2, which were similar to those in Spot 22. Also, oxygen was detected. Table 5-11 lists the elements in analyzed α-Mg matrix, Al-Mn-RE containing intermetallic, Al-RE containing intermetallic...
phase and MgO of Spot 22 shown in Figures 5-24. Based on the atomic percentages listed in Tables 5-10 and 5-11 for Spot 21 and Spot 22. There were two kinds of intermetallics phase represent in the AE44 die casting sludge, one with Al, Mn and RE, and the other one containing only Al and RE which were Al-Mn-RE and Al-RE intermetallics respectively.

To determine the volume fraction of the Al-Mn-RE and Al-RE intermetallic phase in the AE44 die casting sludge, the micrographs of Figures 5-21(a) and 5-23(a) were converted to binary black and white images by using the ImageJ pixel analysis software, as shown in Figure 5-25(a) and (b) respectively. During conversion, the SEM micrographs in Figure 5-21(a) and Figure 5-23(a) were imported into the ImageJ, and the type of 32-bit image was selected to maximize the resolution. The adjustment of threshold was made by increasing the brightness of the primary $\alpha$-Mg area fraction, until the entire $\alpha$-Mg territory turned white, and the Al-Mn-RE and Al-RE intermetallic region of interest in black was revealed. In Figure 5-25, the black area represented Al-Mn-RE and Al-RE intermetallics, while the white area was illustrated by the $\alpha$-Mg phase. As shown in Figures 5-25 (a) and (b), the volume fractions of the Mn and RE-containing intermetallic phase for spots 22 and 21 were 29.67% and 23.39%, respectively. Based on the measured volume fractions, the weight percentages of the Al-Mn-Re and Al-RE intermetallics in Mg alloy AE44 were calculated by the following equation:

$$W_{\text{AE44}}^{\text{Al-RE-(Mn)}} = \frac{\rho_{\text{Al-RE-(Mn)}} \times V_{\text{Al-RE-(Mn)}}}{\rho_{\text{Al-RE-(Mn)}} \times V_{\text{Al-RE-(Mn)}} + \rho_{\text{Mg}} \times V_{\text{Mg}}}$$

(23)

where $W_{\text{AE44}}^{\text{Al-RE-(Mn)}}$ is the weight percentage of the Al-Mn-RE and Al-RE intermetallics for Mg alloy AE44, $\rho_{\text{Al-RE-(Mn)}}$ is the density of the Al-Mn-RE and Al-RE intermetallics (4.58 g/cm³), $V_{\text{Al-RE-(Mn)}}$ is the measured volume fraction of the Al-Mn-RE and Al-RE
intermetallics, \( \rho_{Mg} \) is the density of Mg (1.74 g/cm\(^3\)), and \( V_{Mg} \) is the volume fraction of Mg. The density (4.58 g/cm\(^3\)) of the Al-Mn-RE and Al-RE intermetallics was calculated from the stoichiometric ratios of the Al-Mn-RE and Al-Re intermetallic phases, which were detected by the SEM and EDS analyses. The weight percentages of the Al-Mn-RE and Al-RE intermetallics for spot 22 and 21 were 52.59 and 44.53 wt.%, respectively. The volume fractions and weight percentages of the Al-Mn-RE and Al-RE intermetallic phase in the AE44 die casting sludge for the selected five spots illustrated in Figure 5-20 are summarized in Table 5-12. Overall, the average volume fraction and weight percentage of the Al-Mn-RE and Al-RE intermetallic phase in the AE44 die casting sludge were 23.83\% and 44.81\%, respectively. The low values of the standard deviation indicated that the distribution of the Al-Mn-RE and Al-RE intermetallic phases in the sludge was homogeneous in the Mg matrix.
Figure 5-20 SEM micrographs at low magnification showing a microstructure panoramic view of the AE44 die casting sludge with five spots selected for EDS analyses.
(f)

(g)
Figure 5-21 EDS results for Spot 22 in the AE44 die casting sludge: (a) SEM micrograph in BSE mode, and elemental maps for (b) all detected elements, (c) Mg, (d) Al, (e) Mn, (f) O, (g) Ce, (h) Pr, (i) La and (j) Nd.
Figure 5-22 EDS spectra (a), (b), (c) and (d) for the areas containing α-Mg matrix (dark), and intermetallic phases contain RE and Mn (dark gray), and RE-containing intermetallic phases (bright gray), and MgO inclusion (black) for points 20-23 as shown in Figure 5-21 (a), respectively.
Table 5-10 Elements in analyzed α-Mg matrix, Mn and RE containing intermetallic phase and MgO of Spot 1 shown in Figure 5-22.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Element</th>
<th>Atomic (at. %)</th>
<th>Point 20</th>
<th>Point 21</th>
<th>Point 22</th>
<th>Point 23</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>α-Mg matrix</td>
<td>Mg</td>
<td>92.26</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Al</td>
<td>7.74</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>RE and Mn-containing intermetallic</td>
<td>Mg</td>
<td>-</td>
<td>52.66</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Al</td>
<td>-</td>
<td>23.26</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Mn</td>
<td>-</td>
<td>15.53</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>RE</td>
<td>-</td>
<td>8.55</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Re- containing intermetallic</td>
<td>Mg</td>
<td>-</td>
<td>-</td>
<td>64.87</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Al</td>
<td>-</td>
<td>-</td>
<td>20.81</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Mn</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>RE</td>
<td>-</td>
<td>-</td>
<td>14.32</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>MgO</td>
<td>Mg</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>67.56</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Al</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>3.24</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>29.2</td>
<td>-</td>
</tr>
</tbody>
</table>
MgO

Al-RE

α-Mg

Al-Mn-RE

24

25

26

27
Figure 5-23 EDS results for Spot 21 in the AE44 die casting sludge: (a) SEM micrograph in BSE mode, and elemental maps for (b) all detected elements, (c) Mg, (d) Al, (e) Mn, (f) O, (g) Ce, (h) Pr, (i) La and (j) Nd.
Figure 5-24 EDS spectra (a), (b), (c) and (d) for the areas containing α-Mg matrix (dark), and intermetallic phases contain RE and Mn (dark gray), and RE-containing intermetallic phases (light grey), and MgO inclusion (black) for points 24-27 as shown in Figure 5-23(a), respectively.
Table 5-11 Elements in analyzed $\alpha$-Mg matrix, Mn and RE containing intermetallic phase and MgO of Spot 2 shown in Figure 5-23.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Element</th>
<th>Atomic (at. %)</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Point 24</td>
<td>Point 25</td>
<td>Point 26</td>
<td>Point 27</td>
<td></td>
</tr>
<tr>
<td>$\alpha$-Mg matrix</td>
<td>Mg</td>
<td>91.07</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Al</td>
<td>8.93</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>RE and Mn-containing intermetallic</td>
<td>Mg</td>
<td>-</td>
<td>60.61</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Al</td>
<td>-</td>
<td>22.35</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mn</td>
<td>-</td>
<td>10.45</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>RE</td>
<td>-</td>
<td>6.59</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Re-containing intermetallic</td>
<td>Mg</td>
<td>-</td>
<td>-</td>
<td>60.27</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Al</td>
<td>-</td>
<td>-</td>
<td>22.81</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mn</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>RE</td>
<td>-</td>
<td>-</td>
<td>16.92</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>MgO</td>
<td>Mg</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>81.34</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Al</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>3.22</td>
<td></td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>15.44</td>
<td></td>
</tr>
</tbody>
</table>
Figure 5-25 Binary black and white images showing the volume fraction of AlMnRE and AlRE intermetallic phases in (a) Point 22 and (b) Point 21 of the AE44 die casting sludge.
Table 5-12 Volume Fractions and weight Percentages of intermetallic phases in AE44 die casting sludge.

<table>
<thead>
<tr>
<th>Number of Samples</th>
<th>Volume Fraction of Intermetallic (%)</th>
<th>Weight Percentage of Intermetallic (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>19.45</td>
<td>38.84</td>
</tr>
<tr>
<td>21</td>
<td>23.39</td>
<td>44.53</td>
</tr>
<tr>
<td>22</td>
<td>29.67</td>
<td>52.59</td>
</tr>
<tr>
<td>23</td>
<td>18.32</td>
<td>37.10</td>
</tr>
<tr>
<td>24</td>
<td>28.33</td>
<td>50.97</td>
</tr>
<tr>
<td>Average</td>
<td>23.83</td>
<td>44.81</td>
</tr>
<tr>
<td>Standard Deviation</td>
<td>5.10</td>
<td>6.96</td>
</tr>
</tbody>
</table>
5.5 Factors influencing intermetallic formation in sludge

As given in the proceeding sections, the weight percentages of the Mn-containing intermetallics in the AZ91D recycling ingot sludge, AZ91D, AM60B and AE44 die casting sludges were 2.77, 10.33, 34.07 and 44.81 wt.%, respectively. The content of the Mn-containing intermetallic varied considerably in the sludges generated by various types of Mg alloys, e.g., AZ91D, AM60B and AE44, as well as different processes such as ingot recycling and die casting production. Table 5-13 lists the chemical compositions of the analyzed Mg alloys, AZ91D, AM60B and AE44. Compared to that (0.29 wt.%) of the AZ91D in ingot form, the AZ91D die casting alloy had relatively high Mn content (0.33 wt.%), which could generate more Mn-containing intermetallics in the die casting sludge than that in the recycling sludge. The comparison of the AZ91D and AM60B alloy revealed that the considerably high Mn content of 0.42 wt.% in the AM60B led to the formation of the Mn-containing intermetallics of 34.07 wt.% in the AM60B die casting sludge, which was the second highest amount among the four analyzed sludges. In the AE44 alloy, the presence of 0.37 wt.% Mn and about 4 wt.% RE produced two types of the intermetallic phases, i.e., Al-Mn-RE and Al-RE. As a result, both the Mn-containing and Mn-free phases contributed 44.81 wt.% intermetallics in the AE44 die casting sludge, which was the highest in the analyzed sludges. It appeared that the Mn contents with or without additional RE considerably affected the formation of Mn and/or RE-containing intermetallics in the Mg sludge. Certainly, the RE addition made the case further worse.
Table 5.13 Chemical compositions of the analyzed Mg alloys, AZ91, AM60 and AE44 alloys in ingot and die casting forms.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Composition (wt.%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Al</td>
<td>Zn</td>
</tr>
<tr>
<td>AZ91 (Recycling ingot)</td>
<td>9.00</td>
<td>0.68</td>
</tr>
<tr>
<td>AZ91D (Die casting)</td>
<td>9.00</td>
<td>0.68</td>
</tr>
<tr>
<td>AM60B (Die casting)</td>
<td>6.00</td>
<td>0.22</td>
</tr>
<tr>
<td>AE44 (Die casting)</td>
<td>4.00</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Thorvaldsen et al. [13] assessed sludge and dross during the melting and handling of Mg alloys, AZ91D, AM60 and AS41, in Mg die casting operations. They found that there were three major constituents in the Mg sludge, of which average composition was 29% ± 14% in oxides, 0.8% ± 0.8% in intermetallic and 70% ± 14% in entrapped Mg metal. The intermetallic percentage was estimated from the Mn analyses. The sludge content was affected by process parameters and operation procedure, e.g., the agitation of melt surface, the melt holding temperature, the charging and discharging operations, and the gas protection system. The discrepancy in the intermetallic percentage between the present work and the results of Thorvaldsen et al. [13] might arise from the variation of process parameters, operation condition and assessment method. However, the SEM study on intermetallics in the AZ91D, AM60B and AM50A die casting sludges by Corby et al. [18] indicated that the high amount of Al₈(Mn, Fe)₅ intermetallics present in the die casting sludge was similar to the findings in the present study, despite the difference in melt holding.
temperatures as illustrated in Table 5-14. No intermetallic percentage data were given by Corby et al. [18]. Their results showed that a decrease in the melt holding temperature and an increase in the holding time increased the size of the intermetallic particles. Nevertheless, the reported results of influencing factors such as chemical compositions and processing parameters on the intermetallic contents in the die casting sludges appeared somewhat inconsistent in the literature.

**Table 5-14** Comparison of melt holding temperatures for sludge generation.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Melt Holding Temperature [18] (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AZ91D</td>
<td>665-695</td>
</tr>
<tr>
<td>(Die casting)</td>
<td></td>
</tr>
<tr>
<td>AM60B</td>
<td>655</td>
</tr>
<tr>
<td>(Die casting)</td>
<td></td>
</tr>
<tr>
<td>AM50A</td>
<td>652</td>
</tr>
<tr>
<td>(Die casting)</td>
<td></td>
</tr>
</tbody>
</table>
CHAPTER 6

Control of Intermetallic Formation in Sludge of Mg Alloys by Taguchi Method

6.1 Determination of optimal levels for sludge yield

To according Eqs. (17) – (21), two sludge yield measurements for each experiment were converted into a S/N ratio. Table 6-1 compares the calculated mean S/N ratios with the sludge yield data and level numbers. In the following discussion, the S/N ratios were employed as a response index to compare the sludge yields of the different designed alloys and casting parameters instead of directly using the values of the sludge yield.

The response of each factor to its individual level was calculated by averaging the S/N ratios of all experiments at each level for each factor. The determined factor responses are summarized in Table 6-2. Figures 6.1-6.4 show the effect of the five factors, Al, Mn, Fe, Holding Temperature and Holding Time on the mean S/N ratios, respectively.

Figure 6-1 shows the response of the S/N ratio to Al content. It can be seen from Figure 6-1 that the mean S/N ratio dropped to the bottom of the curve as the Al content increase to 7% (level 2) from 6% (level 1). When the Al content kept increasing to 8% (level 3), the mean S/N ratio bounced back upward. The upward tendency was kept further rising to 9% (level 4), which gave the highest value of mean S/N ratio. The observation on the response of the S/N ratio to the Al content might be mainly due to the variation of Mn content. Since both Mn and Fe were almost insoluble in liquid magnesium and instead reacted with Al solute to form Al-Mn-Fe intermetallic. It was observed that an increase in Al content resulted in the generation of more Al-Mn-Fe intermetallics due to the Mn demand. However, further extending the Al content, if the Al content over the Mn saturation point, the additional Al could react with Mg to form Mg$_{17}$Al$_{12}$ intermetallic phase during
solidification.

The response of the S/N ratio to Mn content is shown in Figure 6-2. The mean S/N ratio demonstrated an almost linearly decrease tendency from 0.15% (level 1) to 0.45% (level 4). This might result from the high affecting of the Mn with Al and impurity Fe, to form Al-(Mn,Fe) intermetallics for Fe eliminate at high temperature over 700°C in liquid Mg. In the production of Mg alloys, sufficient Mn is usually added to ensure that the Fe:Mn ratio is less than 0.032, which substantially improves the corrosion resistance [37,38]. As a result, the rich Mn content in Mg alloy promoted the formation of the intermetallic in the sludge.

Figure 6-3 shows response of the S/N ratio to the Fe content. The mean S/N ratio decreased at first as the Fe content increased from 10 ppm (level 1) to 40 ppm (level 2). Then, the S/N ratio rose, while the Fe content became to 70 ppm (level 3). Lastly, the S/N ratio decreased to the lowest value as the Fe content increased to 100 ppm (level 4). The purpose of introducing additional iron up to 100 ppm to the alloys was to simulate the iron picking process in the steel crucible used in the industry, since the Fe-free high-quality graphite crucible was employed in this study. At high temperatures, with inappropriate manganese content, magnesium and the alloying elements could react with the steel crucible. The variation of S/N ratio with the Fe content could be caused by the different Fe/Mn ratio. It was reported that the proper control of the manganese and iron ratio was the essential role for sludge formation [38].

Figure 6-4 shows the response of the S/N ratio to the holding temperature parameter similar to that for the Al content. The mean S/N ratio decreased at first as the holding temperature increased from 630°C (level 1) to 650°C (level 2). The S/N ratio then increased
to its highest value as the holding temperature parameter increased to 690°C (level 4). At 650°C (level 2), the lowest S/N ratio was produced. It was might be due to the precipitation of the Al$_8$Mn$_5$ intermetallic phase took place at 642°C by thermal analysis with differential scanning calorimetry (DSC) measurements which was report by Thorvaldsen et al [13]. The high S/N ratio at 690°C suggested that there might be a low tendency of intermetallic precipitation at a high temperature. At a relatively low temperature of 630°C, the high viscosity and poor fluidity could result in low precipitation of intermetallic in Mg sludge.

Figure 6-5 presents the response of the S/N ratio to the holding time parameter, which was similar to that for the iron content. The mean S/N ratio decreased at first as the holding time increased from 30 min (level 1) to 60 mins (level 2). Then, the S/N ratio increased when the holding time increased to 90 mins (level 3). Lastly, the S/N ratio decreased to the lowest value as the holding time rose to 120 mins (level 4). Although there were no specific holding times used in the foundry report, the adoption of the holding times in this study was based on down time experienced in the Mg casting operation. The result of the S/N ratio indicated the long holding time encouraged the intermetallic formation in the Mg sludge.

By selecting the highest value of mean S/N ratio for each factor, the optimal level was determined. On this basis, the optimum combination of the levels in terms of minimizing the intermetallic formation of the designed alloy was A4B1C1D4E1 as shown in Figure 6-6. They were 9wt.% Al, 0.15wt.%Mn, 0.001wt.% (10 ppm) Fe, 690°C for holding temperature and holding at 30 mins respectively. In contrast, the most sludge yield combination of designed alloy was A2B4C4D2E4, which were 7wt.% Al, 0.45wt.%Mn, 0.01wt.% (100 ppm) Fe, 650°C for holding temperature and 120mins for holding time.
Table 6-1 The S/N ratios calculated from the determined sludge yield relevant to the experiments designed by the Taguchi method.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Al (wt.%)</th>
<th>Mn (wt.%)</th>
<th>Fe (wt.%)</th>
<th>Holding Temperature (°C)</th>
<th>Holding Time (Mins)</th>
<th>Sludge Yield (%)</th>
<th>S/N Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6 (A1)</td>
<td>0.15 (B1)</td>
<td>0.001 (C1)</td>
<td>630 (D1)</td>
<td>30 (E1)</td>
<td>0.33</td>
<td>0.28</td>
</tr>
<tr>
<td>2</td>
<td>6 (A1)</td>
<td>0.25 (B2)</td>
<td>0.004 (C2)</td>
<td>650 (D2)</td>
<td>60 (E2)</td>
<td>0.45</td>
<td>0.46</td>
</tr>
<tr>
<td>3</td>
<td>6 (A1)</td>
<td>0.35 (B3)</td>
<td>0.007 (C3)</td>
<td>670 (D3)</td>
<td>90 (E3)</td>
<td>0.52</td>
<td>0.52</td>
</tr>
<tr>
<td>4</td>
<td>6 (A1)</td>
<td>0.45 (B4)</td>
<td>0.01 (C4)</td>
<td>690 (D4)</td>
<td>120 (E4)</td>
<td>0.59</td>
<td>0.62</td>
</tr>
<tr>
<td>5</td>
<td>7 (A2)</td>
<td>0.15 (B1)</td>
<td>0.004 (C2)</td>
<td>670 (D3)</td>
<td>120 (E4)</td>
<td>0.41</td>
<td>0.42</td>
</tr>
<tr>
<td>6</td>
<td>7 (A2)</td>
<td>0.25 (B2)</td>
<td>0.001 (C1)</td>
<td>690 (D4)</td>
<td>90 (E3)</td>
<td>0.43</td>
<td>0.45</td>
</tr>
<tr>
<td>7</td>
<td>7 (A2)</td>
<td>0.35 (B3)</td>
<td>0.01 (C4)</td>
<td>630 (D1)</td>
<td>60 (E2)</td>
<td>0.57</td>
<td>0.58</td>
</tr>
<tr>
<td>8</td>
<td>7 (A2)</td>
<td>0.45 (B4)</td>
<td>0.007 (C3)</td>
<td>650 (D2)</td>
<td>30 (E1)</td>
<td>0.63</td>
<td>0.62</td>
</tr>
<tr>
<td>9</td>
<td>8 (A3)</td>
<td>0.15 (B1)</td>
<td>0.007 (C3)</td>
<td>690 (D4)</td>
<td>60 (E2)</td>
<td>0.31</td>
<td>0.34</td>
</tr>
<tr>
<td>10</td>
<td>8 (A3)</td>
<td>0.25 (B2)</td>
<td>0.01 (C4)</td>
<td>670 (D3)</td>
<td>30 (E1)</td>
<td>0.46</td>
<td>0.46</td>
</tr>
<tr>
<td>11</td>
<td>8 (A3)</td>
<td>0.35 (B3)</td>
<td>0.001 (C1)</td>
<td>650 (D2)</td>
<td>120 (E4)</td>
<td>0.53</td>
<td>0.51</td>
</tr>
<tr>
<td>12</td>
<td>8 (A3)</td>
<td>0.45 (B4)</td>
<td>0.004 (C2)</td>
<td>630 (D1)</td>
<td>90 (E3)</td>
<td>0.63</td>
<td>0.61</td>
</tr>
<tr>
<td>13</td>
<td>9 (A4)</td>
<td>0.15 (B1)</td>
<td>0.01 (C4)</td>
<td>650 (D2)</td>
<td>90 (E3)</td>
<td>0.32</td>
<td>0.33</td>
</tr>
<tr>
<td>14</td>
<td>9 (A4)</td>
<td>0.25 (B2)</td>
<td>0.007 (C3)</td>
<td>630 (D1)</td>
<td>120 (E4)</td>
<td>0.42</td>
<td>0.41</td>
</tr>
<tr>
<td>15</td>
<td>9 (A4)</td>
<td>0.35 (B3)</td>
<td>0.004 (C2)</td>
<td>690 (D4)</td>
<td>30 (E1)</td>
<td>0.51</td>
<td>0.53</td>
</tr>
<tr>
<td>16</td>
<td>9 (A4)</td>
<td>0.45 (B4)</td>
<td>0.001 (C1)</td>
<td>670 (D3)</td>
<td>60 (E2)</td>
<td>0.61</td>
<td>0.62</td>
</tr>
</tbody>
</table>
Table 6-2 The mean factor response of sludge yield.

<table>
<thead>
<tr>
<th>Levels</th>
<th>Al (%)</th>
<th>Mn (%)</th>
<th>Fe (%)</th>
<th>Holding Temperature (°C)</th>
<th>Holding Time (Mins)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6.79</td>
<td>9.36</td>
<td>6.83</td>
<td>6.72</td>
<td>6.70</td>
</tr>
<tr>
<td>2</td>
<td>5.91</td>
<td>7.09</td>
<td>6.42</td>
<td>6.07</td>
<td>6.41</td>
</tr>
<tr>
<td>3</td>
<td>6.58</td>
<td>5.46</td>
<td>6.79</td>
<td>6.59</td>
<td>6.68</td>
</tr>
<tr>
<td>4</td>
<td>6.83</td>
<td>4.20</td>
<td>6.08</td>
<td>6.73</td>
<td>6.33</td>
</tr>
</tbody>
</table>

Figure 6-1 Effect of Al content on the mean S/N ratio.
Figure 6-2 Effect of Mn content on the mean S/N ratio.

Figure 6-3 Effect of Fe content on the mean S/N ratio.
Figure 6-4 Effect of Holding Temperature on the mean S/N ratio.

Figure 6-5 Effect of Holding Temperature on the mean S/N ratio.
6.1.1 Factor Contributions

The contribution of each factor to the sludge yield was determined by performing the analysis of variance based on Eqs. (17) – (21). The results of the analysis of variance (ANOVA) and contribution of the five factors are summarized in Table 6-3. The contribution of the five factors, the Al content, Fe content, holding temperature and holding time was 3.32%, 2.22%, 1.88% and 0.66%, respectively. The contribution of Mn content (91.91%) was significantly higher than the sum (8.08%) of the contributions of all the other four factors. It was evident that, among the selected factors, the Mn content had the major influence on the intermetallic formation. Furthermore, it could be assumed that the Al, Fe, holding temperature and holding time have almost the same effect on intermetallic formation in the sludge because of the minor difference in the contribution percentages among these four factors.

Figure 6-6 Single response signal-to-noise graph for case the only considering only the sludge yield.
It was evident from Table 6-3 that the ANOVA analysis not only specified how important a factor was to the intermetallic formation by numbers but also showed their relative effect. By ranking their relative contributions, the sequence of the five factors affecting the intermetallic formation was the Mn, Al, Fe contents and the holding temperature and holding time. It is also worthwhile mentioning that, in the ANOVA analysis, if the percentage error ($P_e$) contribution to the total variance is lower than 15%, no important factor is missing in the experimental design. In contrast, if the percent contribution of the error exceeds 50%, certain significant factors are overlooked and the experiments must be re-designed. As shown in Table 6-3, the percentage error ($P_e$) was 0%. This indicated that no significant factors were missing in the experimental design.
Table 6-3 Results of the ANOVA for sludge yield.

<table>
<thead>
<tr>
<th>Factors</th>
<th>Degree of freedom (D)</th>
<th>Sum of squares (SS_p)</th>
<th>Variance (V)</th>
<th>Corrected sums of squares (SS_p')</th>
<th>Contribution</th>
<th>Rank</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al (%)</td>
<td>3</td>
<td>2.15</td>
<td>0.72</td>
<td>2.15</td>
<td>3.32%</td>
<td>2</td>
</tr>
<tr>
<td>Mn (%)</td>
<td>3</td>
<td>59.47</td>
<td>19.82</td>
<td>59.47</td>
<td>91.91%</td>
<td>1</td>
</tr>
<tr>
<td>Fe (%)</td>
<td>3</td>
<td>1.43</td>
<td>0.48</td>
<td>1.43</td>
<td>2.22%</td>
<td>3</td>
</tr>
<tr>
<td>Holding Temperature (°C)</td>
<td>3</td>
<td>1.22</td>
<td>0.41</td>
<td>1.22</td>
<td>1.88%</td>
<td>4</td>
</tr>
<tr>
<td>Holding Time (Mins)</td>
<td>3</td>
<td>0.43</td>
<td>0.14</td>
<td>0.43</td>
<td>0.66%</td>
<td>5</td>
</tr>
<tr>
<td>error</td>
<td>0.00</td>
<td>0.00</td>
<td></td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>6.286</td>
<td></td>
<td></td>
<td>100%</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

6.1.2 Confirmation Experiment

The confirmation experiment was the final step in verifying the conclusions from the previous round of experimentation. If the results of the confirmation runs are not consistent with the expected conclusions, a new Taguchi method design is required. The least sludge yield confirmation experiment was performed by setting the experimental condition of the five factors as: 9%Al, 0.15%Mn, 0.001%Fe and 690°C for the holding temperature and 30
min for the holding time. The levels of the corresponding factors for the most sludge yield confirmation was 7wt.%Al, 0.45wt.%Mn, 0.01wt.%Fe, 650°C for holding temperature and 120mins for holding time. Figure 6-7 presents the SEM micrographs showing the Al-Mn intermetallic-free zone and the Al-Mn intermetallic-concentrated layer of the confirmation alloy with the least sludge. The thickness of the sludge concentrated layer for least sludge yield confirmation was 0.5 mm, which was the least of thin thickness in this study. Based on the measured layer thickness, the sludge yield of 0.26 was calculated by Eq. (10) – (16), which was the lowest yield obtained in the present study. The Al-Mn intermetallic zone and the Al-Mn intermetallic-concentrate layer of the confirmation alloy with the most sludge yield was revealed in Figure 6-8, the measured thickness of the Al-Mn intermetallic-concentrated layer for the most sludge yield confirmation was 1mm, the subsequently calculated sludge yield was 0.65, which was the highest value of the sludge yield in this study.
Figure 6-7 SEM micrographs showing the Al-Mn intermetallic-free zone and the Al-Mn intermetallic-concentrated layer of the alloys with least sludge yield from the confirmation experiment.
Figure 6-8 SEM micrographs showing the Al-Mn intermetallic-free zone and the Al-Mn intermetallic-concentrated layer of the alloy with most sludge yield from the confirmation experiment.
6.1.3 Summary for sludge Yield

The Taguchi method for the design of experiment was used for minimizing the Al-Mn intermetallic formation in the sludge during the Mg alloy die casting process. The Mn content was found to be the major factor affecting the sludge formation, while Al content, Fe content, holding temperature and holding time have a similar contribution, but smaller effect on the sludge production. The contribution Al content, Mn content, Fe content, holding temperature and holding time were 3.32%, 91.91%, 2.22%, 1.88% and 0.66%, respectively. The least sludge yield combination were 9%Al, 0.15%Mn, 0.001%Fe and 690°C for holding temperature and 30 min holding time and the most sludge yield combination were 7%Al, 0.45%Mn, 0.01%Fe, 650°C for holding temperature and 120mins for holding time.

6.2 Determination of optimal levels for intermetallic size

Base on the Eq. (17) - (21), two measurements of the intermetallic size (IS) for each experiment were converted into a S/N ratio. Table 6-4 compares the calculated mean S/N ratios with the IS data and level numbers. In the following discussion, the S/N ratios were employed as a response index to compare the intermetallic size for different designed alloys and casting parameters instead of directly using the values of the intermetallic size.

The response of each factor to its individual level was calculated by averaging the S/N ratios of all experiments at each level for each factor. The determined factor responses are summarized in Table 6-5. Figures 6.9-6.13 show the effect of the five factors, Al, Mn, Fe, holding Temperature and holding time on the mean S/N ratios, respectively.

Figure 6-9 shows the response of the S/N ratio to Al content. It can be seen from Figure 6-9 that the mean S/N ratio dropped to the bottom of the curve as the Al content increased.
to 7% (level 2) from 6% (level 1). When the Al content keeps increasing to 8% (level 3), the mean S/N ratio bounced back upward. The upward tendency kept further rising to 9% (level 4), which showed the highest value of mean S/N ratio. The observation on the response of the S/N ratio to Al content might be mainly due to the variation of Mn content and the holding temperature. Since both Mn and Fe were almost insoluble in liquid Mg, and instead reacted with Al solute to form Al-Mn-Fe intermetallic. It was observed that the increase in Al content results in the generation large size intermetallic due to the Mn demand and holding temperature. However, further extending the Al content, if the Al content over the Mn saturation point, the additional Al reacted with $\alpha$-Mg to form Mg$_{17}$Al$_{12}$ intermetallic phase during solidification.

The response of the S/N ratio to Mn content is shown in Fig 6-10. The mean S/N ratio demonstrated a decrease tendency from 0.15% (level 1) to 0.25% (level 2), the mean response S/N ratio of the IS decreased from -22.13 to -23.22. The ratio showed almost no increase to -23.03 (+0.8%) when Mn rose to 0.35% (level 3). Then S/N ratio decreased to lowest as the Mn increased to 0.45% (level 4). This might result from the variation of the Mn amount reacting with Al and impurity Fe for elimination Fe. In the Mg alloy production, sufficient Mn is usually added to ensure that the Fe:Mn ratio is less than 0.032 which substantially improves the corrosion resistance [37,38]. The variation of S/N ratio with the Fe content could be caused by the different Fe/Mn ratio. It was reported that the proper control of the manganese and iron ratio was the essential role for intermetallic size [38].

Figure 6-11 shows response of the S/N ratio to the Fe content. The mean S/N ratio showed almost no difference from 10 ppm (level 1) to 70 ppm (level 3), since the ratio
from level 1 to level 2 only decreased 0.70%, and from level 2 to level 3, only increased 0.56%. As the Fe increased to 100 ppm (level 4), the S/N ratio decreased to the lowest value. The purpose to add additional iron content to the alloy was to simulate the iron picking process in the steel crucible, as the Fe-free high-quality graphite crucible was employed in this study. At high temperatures, could with inappropriate manganese content, magnesium and the alloying elements can react with the steel crucible. Changes in the melt temperature led to intermetallic cluster. Therefore, the manganese and iron ratio were the essential role for intermetallic cluster and it was also proof the fluctuation S/N ratio with the iron content increase.

Figure 6-12 shows the response of the S/N ratio to the holding temperature parameter similar to that for the Al content. The mean S/N ratio continuously decreased from -21.96 to -23.81 since the holding temperature increased from 630°C (level 1) to 670°C (level 3). However, after level 3 the S/N bounced up to -23.20 with the holding temperature up to 690°C (level 4). Since 630°C (level 1) was the highest S/N ratio that intend intermetallic may not cluster easily. it was might be due to the 630°C just over the commercial Mg alloy liquids temperature and molten had poor fluidity. But the intermetallic was not well-precipitation at 690°C (level 4).

Fig 6-13 presents the response of the S/N ratio to the holding time parameter. The mean S/N ratio increased to peak at first as the holding time increased from 30mins (level 1) to 60mins (level 2). Then the S/N ratio decreased through the holding time increased to 90mins (level 3). Lastly, the S/N ratio decreased to the lowest value as the holding time increased to 120 (level 4). Although there were no specific holding times used in the foundry report, the adoption of the holding time in this study was based on down time
experienced in the Mg casting operation. The result of the S/N ratios indicated the long holding time encouraged the intermetallic cluster.

By selecting the highest value of mean S/N ratio for each factor, the optimal level was determined. On this basis, the optimum combination of the levels in terms of minimizing the IS of the designed alloy the smallest IS was A4B1C1D1E2 as shown in Figure 6-14, which were 9wt.% Al, 0.15wt.%Mn, 0.001wt.% (10 ppm) Fe, 630°C for holding temperature and holding at 60 mins. In contrast, the largest intermetallic size combination of designed alloy was A2B4C4D3E4 which were 7wt.%Al, 0.45wt.%Mn, 0.01wt.% (100 ppm) Fe, 670°C for holding temperature and 120mins for holding time.
Table 6-4 The S/N ratios calculated from the determined intermetallic size relevant to the experiments designed by the Taguchi method.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Al (wt.%)</th>
<th>Mn (wt.%)</th>
<th>Fe (wt.%)</th>
<th>Holding Temperature (°C)</th>
<th>Holding Time (Mins)</th>
<th>Intermetallic Size (μm)</th>
<th>Test 1</th>
<th>Test 2</th>
<th>S/N Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6 (A1)</td>
<td>0.15 (B1)</td>
<td>0.001 (C1)</td>
<td>630 (D1)</td>
<td>30 (E1)</td>
<td></td>
<td>11.54</td>
<td>9.5</td>
<td>-20.48</td>
</tr>
<tr>
<td>2</td>
<td>6 (A1)</td>
<td>0.25 (B2)</td>
<td>0.004 (C2)</td>
<td>650 (D2)</td>
<td>60 (E2)</td>
<td></td>
<td>13.09</td>
<td>13.23</td>
<td>-22.39</td>
</tr>
<tr>
<td>3</td>
<td>6 (A1)</td>
<td>0.35 (B3)</td>
<td>0.007 (C3)</td>
<td>670 (D3)</td>
<td>90 (E3)</td>
<td></td>
<td>14.81</td>
<td>14.64</td>
<td>-23.36</td>
</tr>
<tr>
<td>4</td>
<td>6 (A1)</td>
<td>0.45 (B4)</td>
<td>0.01 (C4)</td>
<td>690 (D4)</td>
<td>120 (E4)</td>
<td></td>
<td>16.43</td>
<td>15.9</td>
<td>-24.17</td>
</tr>
<tr>
<td>5</td>
<td>7 (A2)</td>
<td>0.15 (B1)</td>
<td>0.004 (C2)</td>
<td>670 (D3)</td>
<td>120 (E4)</td>
<td></td>
<td>19.02</td>
<td>12.2</td>
<td>-24.07</td>
</tr>
<tr>
<td>6</td>
<td>7 (A2)</td>
<td>0.25 (B2)</td>
<td>0.001 (C1)</td>
<td>690 (D4)</td>
<td>90 (E3)</td>
<td></td>
<td>17.4</td>
<td>14.91</td>
<td>-24.19</td>
</tr>
<tr>
<td>7</td>
<td>7 (A2)</td>
<td>0.35 (B3)</td>
<td>0.01 (C4)</td>
<td>630 (D1)</td>
<td>60 (E2)</td>
<td></td>
<td>11.03</td>
<td>15.06</td>
<td>-22.41</td>
</tr>
<tr>
<td>8</td>
<td>7 (A2)</td>
<td>0.45 (B4)</td>
<td>0.007 (C3)</td>
<td>650 (D2)</td>
<td>30 (E1)</td>
<td></td>
<td>17.58</td>
<td>17.28</td>
<td>-24.83</td>
</tr>
<tr>
<td>9</td>
<td>8 (A3)</td>
<td>0.15 (B1)</td>
<td>0.007 (C3)</td>
<td>690 (D4)</td>
<td>60 (E2)</td>
<td></td>
<td>12.43</td>
<td>12.49</td>
<td>-21.91</td>
</tr>
<tr>
<td>10</td>
<td>8 (A3)</td>
<td>0.25 (B2)</td>
<td>0.01 (C4)</td>
<td>670 (D3)</td>
<td>30 (E1)</td>
<td></td>
<td>17.2</td>
<td>17.01</td>
<td>-24.66</td>
</tr>
<tr>
<td>11</td>
<td>8 (A3)</td>
<td>0.35 (B3)</td>
<td>0.001 (C1)</td>
<td>650 (D2)</td>
<td>120 (E4)</td>
<td></td>
<td>15.01</td>
<td>16.05</td>
<td>-23.83</td>
</tr>
<tr>
<td>12</td>
<td>8 (A3)</td>
<td>0.45 (B4)</td>
<td>0.004 (C2)</td>
<td>630 (D1)</td>
<td>90 (E3)</td>
<td></td>
<td>15.58</td>
<td>13.55</td>
<td>-23.29</td>
</tr>
<tr>
<td>13</td>
<td>9 (A4)</td>
<td>0.15 (B1)</td>
<td>0.01 (C4)</td>
<td>650 (D2)</td>
<td>90 (E3)</td>
<td></td>
<td>13.04</td>
<td>12.33</td>
<td>-22.07</td>
</tr>
<tr>
<td>14</td>
<td>9 (A4)</td>
<td>0.25 (B2)</td>
<td>0.007 (C3)</td>
<td>630 (D1)</td>
<td>120 (E4)</td>
<td></td>
<td>12.04</td>
<td>12.13</td>
<td>-21.64</td>
</tr>
<tr>
<td>15</td>
<td>9 (A4)</td>
<td>0.35 (B3)</td>
<td>0.004 (C2)</td>
<td>690 (D4)</td>
<td>30 (E1)</td>
<td></td>
<td>14.78</td>
<td>11.79</td>
<td>-22.52</td>
</tr>
<tr>
<td>16</td>
<td>9 (A4)</td>
<td>0.45 (B4)</td>
<td>0.001 (C1)</td>
<td>670 (D3)</td>
<td>60 (E2)</td>
<td></td>
<td>14.56</td>
<td>14.2</td>
<td>-23.16</td>
</tr>
</tbody>
</table>
Table 6-5 The factor response of intermetallic size.

<table>
<thead>
<tr>
<th>Levels</th>
<th>Al (%)</th>
<th>Mn (%)</th>
<th>Fe (%)</th>
<th>Holding Temperature (°C)</th>
<th>Holding Time (Mins)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>-23.87</td>
<td>-23.22</td>
<td>-23.07</td>
<td>-23.28</td>
<td>-22.47</td>
</tr>
<tr>
<td>3</td>
<td>-23.42</td>
<td>-23.03</td>
<td>-22.94</td>
<td>-23.81</td>
<td>-23.23</td>
</tr>
<tr>
<td>4</td>
<td>-22.35</td>
<td>-23.86</td>
<td>-23.33</td>
<td>-23.20</td>
<td>-23.43</td>
</tr>
</tbody>
</table>

Figure 6-9 Effect of Al content on the mean S/N ratio.
Figure 6-10 Effect of Mn content on the mean S/N ratio.

Figure 6-11 Effect of Fe content on the mean S/N ratio.
Figure 6-12 Effect of Holding Temperature content on the mean S/N ratio.

Figure 6-13 Effect of Holding Time content on the mean S/N ratio.
6.2.1 Factor Contribution

The results of the analysis of variance (ANOVA) and contribution of the five factors are summarized in Table 6-6. The contribution of five factor Al content, Mn content, Fe content, holding temperature and holding time was 27.41%, 27.65%, 1.97%, 33.52% and 9.44% respectively. It was evident that, among the selected factors, the holding temperature parameter had the highest contribution of 33.52% on the IS. Mn (27.65%) and Al (27.41%) were ranked as the second and third highest contributors which were a very close contribution to each other. The holding time and Fe content were the lowest two least contributors which were 9.44% and 1.97%, respectively.

It was evident from Table 6-6 that the ANOVA analysis not only specified how important a factor was to the IS by numbers but also showed their relative effect. By
ranking their relative contributions, the sequence of the five factors affecting the IS was holding time, the Mn and Al contents, the holding time, and the Fe content. It is also worthwhile mentioning that, in the ANOVA analysis, if the percentage error \( (P_e) \) contribution to the total variance is lower than 15%, no important factor is missing in the experimental design. In contrast, if the percent contribution of the error exceeds 50%, certain significant factors are overlooked and the experiments must be re-designed. As shown in Table 6-6, the percentage error \( (P_e) \) was 0%. This indicates that no significant factors were missing in the experimental design.

6.2.2 Summary for Intermetallic Size

The Taguchi method for the design of experiment was used for minimizing the IS during the Mg alloy die casting process. The contribution Al content, Mn content, Fe content, holding temperature and holding time are 27.41%, 27.65%, 1.97%, 33.52% and 9.44%, respectively. The holding temperature was found to be the most significant factor affecting the IS, while Mn content, Al content, holding time and Fe content were ranked the second to fifth. For the smallest IS combination of the optimum levels and factor was 9wt.%Al, 0.15wt.%Mn, 0.001wt.%Fe and 630°C for the holding temperature and 30 min for the holding time. For the largest IS combination was 7wt.%Al, 0.45wt.%Mn, 0.01wt.%Fe, 670°C for the holding temperature and 120 mins for the holding time. However, the confirmation experiment for the size of the intermetallic still needs be performed.
Table 6-6 Results of the ANOVA for intermetallic size.

<table>
<thead>
<tr>
<th>Factors</th>
<th>Degree of freedom (D)</th>
<th>Sum of squares (SS_p)</th>
<th>Variance (V)</th>
<th>Corrected sums of squares (SS_p’)</th>
<th>Contribution</th>
<th>Rank</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al (%)</td>
<td>3</td>
<td>6.06</td>
<td>2.02</td>
<td>6.06</td>
<td>27.41%</td>
<td>3</td>
</tr>
<tr>
<td>Mn (%)</td>
<td>3</td>
<td>6.11</td>
<td>2.04</td>
<td>6.11</td>
<td>27.65%</td>
<td>2</td>
</tr>
<tr>
<td>Fe (%)</td>
<td>3</td>
<td>0.44</td>
<td>0.15</td>
<td>0.44</td>
<td>1.97%</td>
<td>5</td>
</tr>
<tr>
<td>Holding Temperature (°C)</td>
<td>3</td>
<td>7.41</td>
<td>2.47</td>
<td>7.41</td>
<td>33.52%</td>
<td>1</td>
</tr>
<tr>
<td>Holding Time (Mins)</td>
<td>3</td>
<td>2.09</td>
<td>0.70</td>
<td>2.09</td>
<td>9.44%</td>
<td>4</td>
</tr>
<tr>
<td>error</td>
<td>0</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>6.286</td>
<td></td>
<td></td>
<td>100%</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
6.3 Chemical, Process and Comprehensive Sludge Factors for Al-containing Mg Alloys

For casting Al alloys, the formulae, named Sludge Factor (SF), as a function of the chemical composition and/or melt holding temperature were established, which enabled the control of sludge formation [5,6,39]. To develop a Sludge Factor for Mg alloys, multivariate linear regression analyses were carried out with the DOE results. Since either chemical compositions or processing parameters played an important role in sludge formation in terms of their yield intermetallic sizes. Three groups of the SFs were categorized. The first group contained the Chemical Sludge Factors (CSF) only dependent on the chemical compositions, i.e., Al, Mn and Fe contents, while the Sludge Factors in group two were influenced by the processing parameters of the melt holding temperature and time, named Process Sludge Factor (PSF). Group three possessed the SFs determined by both the chemical compositions and the processing parameters, called Comprehensive Sludge Factor (CPSF). In each group, two types of the SFs, were defined based on the output results of the DOE, i.e., sludge yield and intermetallic size.

In Group One, the regression analyses gave the CSFs as follows:

\[
CSF_{\text{SY}}(\text{wt.\%}) = 2.11 \times 10^{-2} \times (\text{wt.\% Al}) + 1.01 \times (\text{wt.\% Mn}) + 3.13 \times (\text{wt.\% Fe})
\]

where CSF_{\text{SY}} was Chemical Sludge Factor for the sludge yield, and the regression coefficient \( R^2 \) was 0.9932 with standard error \( S = 0.0451 \);

\[
CSF_{\text{IS}}(\mu m) = 1.12 \times (\text{wt.\% Al}) + 13.66 \times (\text{wt.\% Mn}) + 177.07 \times (\text{wt.\% Fe})
\]

where CSF_{\text{IS}} was Chemical Sludge Factor for the intermetallic size, the regression coefficient \( R^2 \) was 0.9720 with standard error \( S = 2.6769 \).

In Group Two, the regression analyses provided the PSFs below:
PSF\textsuperscript{SY} (wt.%) = \(7.21 \times 10^{-4} \times T + 9.41 \times 10^{-5} \times t\) \hspace{1cm} (26)

where PSF\textsuperscript{SY} was Process Sludge Factor for the sludge yield, T was the temperature (°C), t was the time (minute), and the regression coefficient R\textsuperscript{2} was 0.9536 with standard error S = 0.1140;

\[
PSF\textsuperscript{IS} (\mu m) = 2.10 \times 10^{-2} \times T + 6.24 \times 10^{-3} \times t
\] \hspace{1cm} (27)

where PSF\textsuperscript{IS} was Process Sludge Factor for the intermetallic size, T was the temperature (°C), t was the time (minute), and the regression coefficient R\textsuperscript{2} was 0.9854 with standard error S = 1.8651.

In Group Three, the regression analyses showed the CPSFs as follows:

\[
CPSF\textsuperscript{SY} (wt.%) = -2.57 \times 10^{-3} \times (wt. \% Al) + 9.18 \times 10^{-1} \times (wt. \% Mn) + 1.20 \times (wt. \% Fe) + 3.26 \times 10^{-4} \times T + 7.42 \times 10^{-5} \times t
\] \hspace{1cm} (28)

where CPSF\textsuperscript{SY} was Comprehensive Sludge Factor for the sludge yield, and the regression coefficient R\textsuperscript{2} was 0.9971 with standard error S = 0.0324;

\[
CPSF\textsuperscript{IS} (\mu m) = -2.83 \times 10^{-1} \times (wt. \% Al) + 7.73 \times (wt. \% Mn) + 56.23 \times (wt. \% Fe) + 2.02 \times 10^{-2} \times T + 6.21 \times 10^{-3} \times t
\] \hspace{1cm} (29)

where CPSF\textsuperscript{IS} was Comprehensive Sludge Factor for the intermetallic size, the regression coefficient R\textsuperscript{2} was 0.9896 with standard error S = 1.7724.

In statistics, the value of the regression coefficients R\textsuperscript{2} is an indicator of how well the equation (model) resulting from the regression analysis explains the relationship among the variables. As a statistical measure of fit, it indicates how much variation of a dependent variable is explained by the independent variable(s) in a regression model [40]. Although high R-squared values are good, they do not show how far the data points are from the regression line. High R-squared values are needed for models to produce precise
predictions. It is impossible to use R-squared to evaluate the precision of the predictions. But, the standard error of the regression provides the absolute measure of the typical distance that the data points fall from the regression line, which measures the precision of the model’s predictions [41]. Figure 6-15 presents the regression coefficients $R^2$ with the standard errors for six developed SFs, i.e., $\text{CSF}^{\text{SY}}$, $\text{PSF}^{\text{SY}}$, $\text{CPSF}^{\text{SY}}$, $\text{CSF}^{\text{IS}}$, $\text{PSF}^{\text{IS}}$, and $\text{CPSF}^{\text{IS}}$. All the regression coefficients $R^2$ for six developed SFs had a relatively high value above 0.95, indicating that the measured data points were closer to the fitted values. Examination of the standard errors revealed that the SFs for the sludge yield, i.e., 0.0451 for $\text{CSF}^{\text{SY}}$, 0.1140 for $\text{PSF}^{\text{SY}}$, and 0.0324 for $\text{CPSF}^{\text{SY}}$, had lower S values than those for the intermetallic size, i.e., 2.6769 for $\text{CSF}^{\text{IS}}$, 1.8651 for $\text{PSF}^{\text{IS}}$, 1.7724 for $\text{CPSF}^{\text{IS}}$, respectively. The standard error analyses indicated that the SFs for the sludge yield could generate more precise predications than those for the intermetallic size. Also, among the six SFs, the $\text{CPSF}^{\text{SY}}$ had the lowest S value of 0.0324 with the highest $R^2$ of 0.9971, which should give the most accuracy in prediction of sludge yield in Mg alloys.
Figure 6-15 Regression coefficients $R^2$ with standard errors for six developed SFs.

CSFSY, PSFSY, CPSFSY, CSFIS, PSFIS, and CPSFIS stand for the sludge factors of CSF$^{SY}$, PSF$^{SY}$, CPSF$^{SY}$, CSF$^{IS}$, PSF$^{IS}$, and CPSF$^{IS}$, respectively.

Figure 6-16 illustrates the comparison of predicted sludge yields and intermetallic sizes with the experimental measurements for the confirmation experiment with the least sludge formation. For the confirmation experiment with the most sludge formation, the predicted sludge yields and intermetallic sizes were compared with the experimental measurements in Figure 6-17. In both Figure 6-16 and 6-17, CSFSY, PSFSY, CPSFSY, CSFIS, PSFIS, and CPSFIS stand for the sludge factors of CSF$^{SY}$, PSF$^{SY}$, CPSF$^{SY}$, CSF$^{IS}$, PSF$^{IS}$, and CPSF$^{IS}$, while Exp. SY and Exp. IS representing the experimental measurements of the sludge yield and intermetallic size, respectively. In the least sludge cases, the predicted sludge yield of 0.50 wt.% and intermetallic size of 14.66 µm by PSF$^{SY}$ and PSF$^{IS}$ were deviated significantly from the experimental counterparts of 0.26 wt.% and 12.22 µm.
Meanwhile, the CSF$^{SY}$, CPSF$^{SY}$, CSF$^{IS}$, and CPSF$^{IS}$ computed the sludge yields of 0.35 and 0.34 wt.% and intermetallic sizes of 13.02 and 12.81, which were very close to the measured data of 0.26 wt.% and 12.22 µm. For the most sludge case, the measured sludge yield and intermetallic size were of 0.65 wt.% and 16.02 µm, respectively. The predicted sludge yields and intermetallic sizes by CSF$^{SY}$, PSF$^{SY}$, CPSF$^{SY}$, CSF$^{IS}$, PSF$^{IS}$, and CPSF$^{IS}$ were 0.64, 0.48 and 0.63 wt.%, and 16.32, 14.39 and 15.95 µm, respectively. The comparison of predicted sludge yields and intermetallic sizes with the experimental measurements indicated that the CPSF$^{SY}$ and CPSF$^{IS}$ gave high accuracy in prediction, as the prediction of the PSF$^{SY}$ and PSF$^{IS}$ had a relatively large deviation from the experimental data. Based on the comparisons made for both the cases, the sludge yields and intermetallic sizes predicted by the CSF$^{SY}$ and CSF$^{IS}$ showed a good fit to the experimental data. Furthermore, the prediction by the CPSF$^{SY}$ and CPSF$^{IS}$ was improved over those of the CSF$^{SY}$ and CSF$^{IS}$. Their predicted results were in excellent agreement with the experimentally measured sludge yield and intermetallic size, although the CPSF$^{SY}$ and CPSF$^{IS}$ models with five independent variables including both chemical elements and process parameters were more complicated than those of the CSF$^{SY}$ and CSF$^{IS}$ with only three chemistry-related independent variables.
Figure 6-16 Comparison of predicted sludge yields and intermetallic sizes with the experimental measurements for the confirmation experiment with the least sludge formation.

Figure 6-17 Comparison of predicted sludge yields and intermetallic sizes with the experimental measurements for the confirmation experiment with the most sludge formation.
CHAPTER 7

Conclusions

1. The weight percentages of the Mn and RE containing intermetallics in the AZ91D recycling ingot sludge, AZ91D, AM60B and AE44 die casting sludges were 2.77, 10.33, 34.07 and 44.81 wt.%, respectively.

2. Mn-containing intermetallic particles in the AZ91D recycling ingot sludge, AZ91D, and AM60B die casting sludges were identified to be Al$_8$Mn$_5$ phase, as the ratios between the Al and Mn were calculated to be approximately 1.6 based on the SEM and EDS analyses.

3. The weight percentages of the Mn-containing intermetallic in the AZ91D recycling ingot sludge, AZ91D, and AM60B die casting sludges, which were generated by the Al-containing Mg alloys, depended on not only the Mn content in the alloys but also the processing conditions.

4. There were two types of intermetallic phases in the AE44 die casting sludge, which were generated by the Al and RE-containing Mg alloy. The two types of the intermetallics were Al-Mn phase and Al-Mn-RE phase. The contents of both Mn and RE additions in the AE44 die casting sludge should be responsible for the sludge formation in the Al and RE-containing alloy.

5. To understand the intermetallic formation in the sludge of magnesium alloys, the Design of Experiment based on the Taguchi method was employed to systematically study the effects of chemical compositions and process parameters on the yield and the intermetallic size particles in the sludge of magnesium alloys.
6. The results showed that, among the selected five factors, Al, Mn and Fe contents as well as holding temperatures and times, Mn was found to be the most influencing factor (91.91%) for the sludge yield, as the other factors had a similar, but much smaller effect on the yield with the Al, Fe, holding temperatures and time contributions of 3.32%, 2.22%, 1.88% and 0.66%, respectively.

7. On the intermetallic size, the holding temperature made the major effect of 33.52% and both the Al and Mn contents had the moderate influences of 27.41% and 27.65%, while the Fe content and holding time contributed only 1.97% and 9.44%, respectively.

8. To achieve the least sludge yield, i.e., the best performance characteristic, the optimum combination (A4B1C1D4E1) with the maximum S/N ratios was 9 wt.% Al, 0.15 wt.% Mn, 0.001 wt.% Fe, 690 °C as the holding temperature, and 30 minutes as the holding time.

9. The combination (A2B4C4D2E4) for the worst performance characteristics, i.e., the most sludge yield, was 7 wt.% Al, 0.45 wt.%, 0.01 wt.%, 650 °C as the holding temperature, and 120 minutes as the holding time.

10. For the intermetallic sizes, the combination (A4 B1C1D1E2, i.e., 9 wt.% Al, 0.15 wt.% Mn, 0.001 wt.%, 630 °C as the holding temperature, and 60 minutes as the holding time, resulted in the smallest intermetallic size. However, the largest intermetallic size was produced by the combination (A2B4C4D3E4) of 7 wt.% Al, 0.45 wt.% Mn, 0.01 wt.% Fe, and 670 °C as the holding temperature, and 120 minutes as the holding time.
11. To build a Sludge Factor for Mg alloys, multivariate linear regression analyses were carried out with the DOE results. Six Sludge Factor equations for the sludge yield and intermetallic size were established as a function of the chemical compositions and/or the processing parameters.

12. The comparison of the sludge yields and intermetallic sizes predicted by the SFs with the experimental measurements indicated that the Comprehensive Sludge Factor (CPSF) with five independent variables including both chemical elements and process parameters gave high accuracy in prediction, as the prediction of the Process Sludge Factor (PSF) with only the two processing parameters of the melt holding temperature and time showed a relatively large deviation from the experimental data.

13. The established Sludge Factors enable engineers to predict the sludge yield and intermetallic size in Mg alloys during die casting, and to cost-effectively design process parameters with known chemical compositions. To minimize the sludge formation, the SFs can be used as a control measure for the avoidance of sludge buildup in holding crucibles, hard spots in cast components, reduced fluidity of liquid metal to flow into a die.
CHAPTER 8

Future Work

The study carried out in this thesis provides the groundwork to pursue further investigation of cost-effective Mg die casting processes in the future. The following aspects are worth exploring.

1. To characterize the morphology of intermetallics in Mg sludge in relation to chemical compositions and process parameters;
2. To evaluate the corrosion resistance of Mg alloys with intermetallic precipitation;
3. To determine the effect of intermetallic formation on corrosion resistance of Mg alloys;
4. To evaluate the mechanical properties of Mg alloys with intermetallic precipitation; and
5. To determine the effect of intermetallic formation on mechanical properties and corrosion resistance of Mg alloys.
REFERENCES


[36] Bolin Fu, Characterization of The Mechanical Performance of The AE44-2And AE44-4 High Pr and AE44-4 High Pressure Die Cast Mg-Rare Die Cast Mg-Rare Earth Alloys, Master Thesis, University of Western Ontario, 2020, 12.


NAME: Yintian Fu

PLACE OF BIRTH: Shiyan, Hubei, China

YEAR OF BIRTH: 1995

EDUCATION:
Wuhan Maple Leaf International School, Wuhan, Hubei, China, 2012

University of Windsor, B.Sc., Windsor, ON, 2015

University of Windsor, M.Sc., Windsor, ON, 2019