Effects of substituting ytterbium for scandium on the microstructure and properties of Al-Sc and Al-Mg-Sc alloys
Nguyen Quoc Tuan

Effects of substituting ytterbium for scandium on the microstructure and properties of Al-Sc and Al-Mg-Sc alloys

Universidade do Minho
Escola de Engenharia
STATEMENT OF INTEGRITY

I hereby declare having conducted my thesis with integrity. I confirm that I have not used plagiarism or any form of falsification of results in the process of the thesis elaboration.

I further declare that I have fully acknowledged the Code of Ethical Conduct of the University of Minho.

University of Minho, Guimarães, 29th October 2014

Full name: Nguyen Quoc Tuan

Signature: _____________________________
Acknowledgments

This research have been carried out during my Ph.D program at Centre for Mechanical and Materials Technologies (CT2M), Department of Mechanical Engineering, University of Minho, Guimaraes, Portugal. There are many people who I would like to thank for their assistance in this thesis research. First and foremost, I would like to express my sincere gratitude and warm regards to my advisors Prof. Ana Maria Pinto and Prof. Luis Rocha for giving me opportunity to complete the Ph.D degree at their laboratory. Their important and helpful advice, support and guidance allowed me to learn a lot from their great scientific skills.

Special thanks to Prof. Joaquim Barbosa and Dr. Hélder Puga for their advices during my research and their support in casting experiment. I am grateful to Dr. Fatih Toptan and Alexandra Alves for their assistance during corrosion study. Many thanks to Dr. Edith Ariza for the assistance in SEM analysis and Miguel Abreu for the assistance in heat treatment experiment. I am also thankful to Prof. Augusto Lopes (University of Aveiro) for help me in TEM analysis. I would like to thank other colleagues, staff, and friend for their friendship, useful discussions and supports during the time I studying and living here.

I would like to express my warmly grateful to my family, my parents, and my girlfriend for their love, support, encouragement, and always standing by me during my Ph.D work.

Finally, this research would not have been performed without the support of the BRIDGING THE GAP Erasmus Mundus project funded by the European Commission program Erasmus Mundus External Cooperation Windows - Lot 12.

EMECW L12 MOBILITY GRANT AWARD CONTRACT BTG_575
Grant agreement n 2009/1661-001 001ECW
Abstract

Effects of substituting ytterbium for scandium on the microstructure and properties of Al-Sc and Al-Mg-Sc alloys

Aluminium alloys are widely applied in aircraft, automobile, marine and other engineering structures. The reason for this large application is due to a wide range of properties including low density, corrosion resistance and high strength to weight ratio.

Al(Sc) alloys represent a new class of potential alloys for high performance structural applications. The superior mechanical properties of these alloys are due to the formation of a high density of elastically-hard AlSc (L12, structure) precipitates which remain fully coherent with the α–Al matrix at elevated temperatures leading the Sc-containing Al alloys a good mechanical strength, hot cracking resistance and weld strength. The excellent properties obtained from the combination of solid-solution hardening and precipitation hardening in Al–Mg–Sc alloys make these alloys very attractive to automotive, aerospace, and structural applications. However, the Sc high cost limits the applications and the addition of cheaper alloying elements that substitutes partially Sc are not only desirable but crucial.

In order to reduce the cost of Sc–containing Al alloys and maintain their mechanical properties, the microstructure and mechanical properties of Al–Sc–Yb and Al–Mg–Sc–Yb alloys in comparison with Al–Sc and Al–Mg–Sc alloys were studied. The aging behaviour, precipitate morphologies, precipitate coarsening, precipitation hardening and corrosion behaviour of these alloys were investigated.

Transmission electron microscopy (TEM) and high-resolution TEM were used to understand the precipitation evolution. The results showed the similarity of microstructure, hardness and aging behaviour of Al–0.24Sc–0.07Yb alloy in comparison with Al–0.28Sc alloy and Al–4 wt% Mg–0.3 wt% Sc alloy with Al–4 wt% Mg–0.24 wt% Sc–0.06 wt% Yb alloy. The approximately spheroidal Al,Sc and Al,(Sc,Yb) precipitates were uniformly distributed throughout the α–Al matrix. The precipitates remain fully coherent with α–Al matrix even after aging at high temperature for long time.

In another aspect, the grain refinement in Al–Mg–Sc alloys with and without ultrasonic treatment at various pouring temperatures was investigated and understood. The average grain size of Al–Mg–Sc alloy remarkably decreases by increasing the content of Mg or by adding 0.3 wt% of Sc. The pouring temperature has a strong effect on the microstructure of Al–1Mg–0.3Sc alloy. Lower pouring temperature leads to smaller grain size and more homogeneous microstructure. Ultrasonic vibration proved to be a
potential grain refinement technique of Al–1Mg–0.3Sc. Significant grain refinement was obtained by applying ultrasonic treatment within the temperature range from 700 to 740 °C.

The corrosion behaviour of Al–Sc, Al–Sc–Yb, Al–Mg, Al–Mg–Sc and Al–Mg–Sc–Yb alloys in 3.5 wt% of NaCl solution was investigated by immersion and potentiodynamic polarisation analysis in order to understand the effect of Sc, Yb, and heat treatment on the localized corrosion and electrochemical behaviour. The presence of Fe–containing intermetallic phases promote the pitting corrosion. Yb has strong effect on the polarization behaviour of Al–Sc alloys. The addition of Yb decreases the corrosion tendency and improves the pitting corrosion resistance of Al–Sc alloy. The presence of a high density of fully coherent nano–sized Al3Sc or Al3(Sc,Yb) precipitates in heat treated alloy enhances the passivity of these alloys. The addition of Sc and Yb to Al–4Mg alloy decrease the susceptibility to corrosion of the heat treated alloys. More stable passive plateau and less susceptibility to pitting corrosion was observed in the polarization curves of Al–4Mg–0.3Sc and Al–4Mg–0.24Sc–0.06Yb alloys after heat treatment.
Resumo

Efeito da substituição parcial do escândio por itérbio na microestrutura e propriedades de ligas Al-Sc e Al-Mg-Sc

A baixa densidade, elevada resistência à corrosão e a elevada resistência específica são algumas das propriedades que suportam a utilização das ligas de alumínio em todas as áreas industriais, com particular destaque para a indústria dos transportes.

As ligas de alumínio com adição de escândio apresentam um elevado potencial para aplicações estruturais de elevados desempenho. As excelentes propriedades destas ligas resultam da precipitação de nanopartículas Al₃Sc finamente dispersas na matriz e que se mantêm coerentes com a matriz até temperaturas relativamente elevadas.

O efeito combinado do endurecimento por solução sólida e por precipitação, resultante da adição de Sc às ligas Al-Mg alarga o campo de aplicação destas ligas, nomeadamente à indústria dos transportes. No entanto o elevado custo do escândio tem limitado a aplicação destas ligas, pelo que a substituição parcial Sc por outros elementos de liga de menor custo é crucial para o desenvolvimento destes materiais.

Tendo em vista a redução do custo das ligas com Sc, mas mantendo o mesmo nível de propriedades, o presente trabalho incidiu no estudo do efeito da substituição parcial do Sc pelo Yb em ligas Al–Sc e Al–Mg–Sc.

Assim foi feito um estudo comparativo entre ligas Al–Sc e Al–Mg–Sc, com ligas Al–Sc–Yb e Al–Mg–Sc–Yb respetivamente, nomeadamente no que diz respeito à cinética de envelhecimento, tamanho, natureza e distribuição dos precipitados, cinética de coalescimento dos precipitados bem como no grau de endurecimento por precipitação e na resistência à corrosão das ligas.

A evolução da microestrutura resultante de diferentes condições de envelhecimento foi avaliada através de Microscopia Eletrónica de Transmissão (TEM) e Microscopia Eletrónica de Transmissão de Alta Resolução e o grau de endurecimento foi avaliado através de ensaios de dureza Vickers. Os resultados mostram que a substituição parcial de Sc por Yb não induz alterações significativas no comportamento das ligas.

Comparando as ligas Al–0.28Sc e Al–0.24Sc–0.07Yb por um lado e as ligas Al–4Mg–0.3Sc e Al–4Mg–0.24Sc–0.06Yb por outro verifica-se uma grande semelhança tanto a nível de microestrutura como de dureza e cinética de envelhecimento. O endurecimento resulta formação de precipitados Al₃Sc e Al₃(Sc,Yb) coerentes, fina e uniformemente dispersos na matriz α–Al. Os precipitados mantêm a coerência com a matriz mesmo após envelhecimento prolongado a temperaturas elevadas.

Neste trabalho foi ainda estudado o efeito do tratamento por ultra-sons na estrutura de vazamento. Os
resultados mostram que os ultra-sons originam uma afinação significativa do grão. Verificou-se também que com o aumento do teor em Mg, a adição de Sc e a diminuição da temperatura de vazamento têm um efeito significativo na estrutura de vazamento.

O comportamento à corrosão das ligas Al–Sc, Al–Sc–Yb, Al–Mg, Al–Mg–Sc and Al–Mg–Sc–Yb numa solução de NaCl (3.5% wt.) foi estudado através de ensaios de imersão e de polarização potenciodinâmica, tendo sido avaliado o efeito da adição de Sc e Yb bem como do tratamento térmico no comportamento eletroquímico e corrosão localizada. A presença de fases intermetálicas ricas em Fe promove a corrosão por picada. A adição de Yb às ligas de Al–Sc diminui a tendência para a corrosão e melhora a resistência à corrosão por picada. A elevada presença de nano-precipitados coerentes de Al3Sc ou Al3(Sc,Yb) na liga tratada termicamente promove a passivação dessas ligas. A adição de Sc e Yb à liga Al–4Mg envelhecida diminui a susceptibilidade à corrosão nas ligas Al–4Mg–0.3Sc e Al–4Mg–0.24Sc–0.006Yb. Nas curvas de polarização potenciodinâmicas das ligas Al–4Mg–0.3Sc e Al–4Mg–0.24Sc–0.06Yb foi observado um patamar de passivação mais estável e uma menor susceptibilidade à corrosão por picada após o tratamento térmico das ligas.
# Table of Contents

Acknowledgments .................................................................................................................. iii
Abstract .................................................................................................................................. v
Resumo .................................................................................................................................... vii
Table of Contents .................................................................................................................... ix
List of Symbols and Acronyms ............................................................................................... xi
List of Figures .......................................................................................................................... xiii
List of Tables ........................................................................................................................... xvii

Chapter 1 – State of the art ....................................................................................................... 1
  1.1 Motivation for Research ................................................................................................. 3
  1.2 Literature Review ........................................................................................................... 5
    1.2.1 Al–Sc and Al–Mg–Sc alloys ....................................................................................... 5
    1.2.2 Precipitate coarsening kinetics ............................................................................... 11
    1.2.3 Precipitation strengthening ...................................................................................... 14
    1.2.4 The effect of Sc in aluminium alloys ........................................................................ 15
    1.2.5 Al–Sc–REMs alloys ................................................................................................. 23
    1.2.6 Grain refinement of Al alloys ................................................................................... 26
    1.2.7 Application of Sc-containing Al alloys .................................................................... 34
References ................................................................................................................................ 35

Chapter 2 – Experimental Procedures .................................................................................... 47
  2.1 Alloys processing ........................................................................................................... 48
    2.1.1 Al–Sc and Al–Sc–Yb alloys ....................................................................................... 48
    2.1.2 Al–Mg–Sc and Al–Mg–Sc–Yb alloys ......................................................................... 49
    2.1.3 Casting for grain refinement study .......................................................................... 49
  2.2 Heat treatments ............................................................................................................... 50
  2.3 Microstructural characterization of the alloys ................................................................. 51
    2.3.1 Optical microscopy and scanning electron microscopy .......................................... 51
    2.3.2 Transmission electron microscopy and high resolution electron microscopy ......... 51
  2.4 Electrochemical tests ....................................................................................................... 52

Chapter 3 – Effect of substituting Yb for Sc on the microstructure and age-hardening behaviour of Al-Sc alloys .... 55
  Introduction ............................................................................................................................ 55
  3.1 Results and discussion .................................................................................................... 56
    3.1.1 Age Hardening Behaviour of the as-cast Alloys ..................................................... 56
    3.1.2 Evolution of precipitates ......................................................................................... 58
List of Symbols and Acronyms

FCC  
Face-center cubic

REMs  
Rare-earth metals

TEM  
Transmission electron microscopy

HRTEM  
High resolution transmission electron microscopy

SEM  
Scanning electron microscopy

EDS  
Energy dispersive spectrometer

APT  
Atom-probe tomography

LSW theory  
Lifshitz-Slyozov-Wagner theory

APB  
Anti-phase-boundary energy

WR/A  
Warm rolled and aged

WR/CR/A  
Warm rolled/cold rolled and aged

ECAP  
Equal channel angular pressing

Ep  
Pitting potential

GRF  
Growth-restricting factor GRF

Epp  
Protection potential

SCE  
Saturated calomel electrode

OCP  
Open circuit potential

FFT  
Fast Fourier transform

PSDs  
Precipitates size distributions

$< R(t) >$  
Average precipitate radius at the onset of quasi-stationary coarsening at time $t$

$< R(t_0) >$  
Average precipitate radius at the onset of quasi-stationary coarsening at time $t_0$

$K_{KV}$  
Coarsening rate constants for $< R(t) >$

$\Delta C_i^\alpha(t)$  
Denotes supersaturation that is the difference between the concentration of $i^{th}$ component in the matrix

$< C_i^\alpha(t) >$  
Composition of the $i^{th}$ component in the matrix

$< C_i^\alpha(t \to \infty) >$  
Solid-solubility of the $i^{th}$ component in the matrix

$K_{i,KV}^{\alpha}$  
Coarsening rate constants for $\Delta C_i^\alpha(t)$

$N_v(t)$  
Precipitate density at the onset of quasi-stationary coarsening at time $t$

$N_v(t_0)$  
Precipitate density at the onset of quasi-stationary coarsening at time $t_0$

$V_v$  
Equilibrium volume fraction of precipitates

$\alpha$  
The matrix phases
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>The precipitate phases</td>
</tr>
<tr>
<td>$V_m$</td>
<td>Molar volume of the precipitate</td>
</tr>
<tr>
<td>$\Sigma$</td>
<td>Isotropic interfacial free energy</td>
</tr>
<tr>
<td>$R$</td>
<td>The ideal gas constant</td>
</tr>
<tr>
<td>$D_i$</td>
<td>The diffusion coefficient of the $i^{th}$ component</td>
</tr>
<tr>
<td>$C_i^\beta$</td>
<td>The composition of the $i^{th}$ component in the precipitate phase.</td>
</tr>
<tr>
<td>$k_i$</td>
<td>The distribution coefficient of the $i^{th}$ species between the matrix and precipitate phases that is defined by $C_i^\beta / C_i^\pi$</td>
</tr>
<tr>
<td>$k_{exp}$</td>
<td>The experimentally determined coarsening rate constant</td>
</tr>
<tr>
<td>$L$</td>
<td>The relative contribution of the elastic strain and interfacial energies</td>
</tr>
<tr>
<td>$E$</td>
<td>Precipitate–matrix lattice parameter mismatch</td>
</tr>
<tr>
<td>$C_{44}$</td>
<td>Elastic constant of the matrix</td>
</tr>
<tr>
<td>$L$</td>
<td>Precipitate size</td>
</tr>
</tbody>
</table>
List of Figures

Figure 1.1. Al–Sc phase diagram on the Al rich side [37] ................................................................. 5
Figure 1.2. The solvus line of Sc in Al [5, 39] .......................................................................................... 6
Figure 1.3. Atomic arrangement of the Al₃Sc phase .................................................................................. 7
Figure 1.4. The [001] diffraction pattern of Al₃Sc precipitates in Al–Sc alloy [7] ................................. 7
Figure 1.5. HRTEM image taken along the [100] zone axis of an Al₃Sc precipitate in Al–0.3 wt% Sc alloy aged at 300°C for 350 h [3] ........................................................................................................... 9
Figure 1.6. Great Rhombicuboctahedron morphology: (a) three dimensional precipitate; (b) [100] projection; and (c) [110] projection [3] .......................................................................................................................... 9
Figure 1.7. Isotherms of the solvus surface in the Al–Mg–Sc phase diagram: (a) [62] (b) [63] ............... 10
Figure 1.8. Isothermal section of the Al–Mg–Sc system at 430 °C [62] ................................................. 11
Figure 1.9. Liquidus surface of the Al rich corner in the Al–Mg–Sc system [63] ........................................ 11
Figure 1.10. Schematic of the interaction of dislocations and second phase particle .......................... 14
Figure 1.11. Schematic of a precipitate cutting....................................................................................... 15
Figure 1.12. Shear Strength vs. Particle Radius ...................................................................................... 15
Figure 1.13. Isothermal recrystallization kinetics of Al-Sc alloys........................................................... 18
Figure 1.14. The effect of annealing time and temperature on grain size of Al–0.2 wt% Sc alloy [92] ...... 19
Figure 1.15. SEM micrographs showing crystallographic pitting of: (a) Al–2.5Mg, (b) Al–2.5Mg–0.1Sc, (c) Al–2.5Mg–0.15Sc, and (d) SEM micrographs of Al–2.5Mg–0.15Sc showing covering of pits by gelatinous Al(OH)₃ [98] ......................................................................................................................... 21
Figure 1.16. Distribution of corrosion potentials of Al₃Sc, Al₃Ti, Al₃Zr and Al₃Mn .................................... 22
Figure 1.17. Magnitude of cathodic current sustained by Al₃Sc, Al (99.9999), Al₃Zr, Al₃Mn and Al₃Ti at a potential of −950 V_{sc} in 0.1 M NaCl [101,102] ............................................................................................................... 22
Figure 1.18. Grain refinement as a function of Sc addition in pure Al and Al–Zn–Mg–Zr [5] ............... 26
Figure 1.19. Comparison of grain refinement with Sc content from 0.05 wt% to 1.2 wt% [125] ............. 27
Figure 1.20. Detail of Al–Ti phase diagram showing the minimum Ti content for the peritectic reaction at 0.15% and 665°C [131] ................................................................................................................. 29
Figure 1.21. Constitutional undercooled zone in front of the interface. The size of the zone depends on the nucleant and the constitution of the melt [137] ................................................................................. 31
Figure 1.22. Graph from Spittle and Sadli’s grain size data plotted against the GRF [137] ................. 31
Figure 2.1. Outline of the research experimental procedure ................................................................. 47
Figure 2.2. Position of the analysed sections on the sample ........................................................................ 48
Figure 2.3. Schematic representation of the experimental setup used in the experiments ((1) SiC Crucible, (2) the melt and (3) Acoustic radiator) ........................................................................ 50
Figure 3.1. Vickers hardness curves of Al–0.28Sc, Al–0.24Sc–0.07Yb alloys at various aging temperatures with and without previous homogenization treatment .......................................................... 56
Figure 3.2. SEM micrographs of Al–0.24Sc–0.07Yb alloy: (a) as-cast and (b) homogenization treated..... 57
Figure 3.3. Isothermal ageing curves of Al–0.28Sc and Al–0.24Sc–0.07Yb alloys at: (a) 300 °C; (b) 325 °C; (c) 350 °C.......................................................................................................................... 58
Figure 3.4. TEM micrographs of Al–0.28Sc (a–b–c) and Al–0.24Sc–0.07Yb (d–e–f) alloys aged at 325 °C for 5 h, 325 °C for 7 days, and 350 °C for 7 days ................................................................. 59
Figure 3.5. TEM micrographs of Al–0.28Sc (a) and Al–0.24Sc–0.07Yb (b–c) alloys aged at 350 °C for 7 days: (a), (b) bright-field TEM image; and (c) dark-field TEM image ........................................... 60
Figure 3.6. Precipitates size distribution of Al–0.28Sc and Al–0.24Sc–0.07Yb alloys at different aging conditions: $d_{16}$, $d_{50}$, and $d_{84}$ are the precipitate diameters corresponding to 16, 50, and 84 % cumulative undersize particle size distribution ........................................................................................................... 62
Figure 3.7. High-resolution TEM images of Al–0.28Sc (a–c) and Al–0.24Sc–0.07Yb (b–d) alloys aged at 325 °C for 5 h and 350 °C for 7 days ................................................................. 63
Figure 3.8. Three-dimensional equilibrium morphology for $L = 1:2$ viewed along: (a) [100] direction and (b) [111] direction [23] ........................................................................................................... 64
Figure 4.1. Isochronal aging curves of Al–4Mg–0.3Sc and Al–4Mg–0.24Sc–0.06Yb alloys in comparison with Al–0.28Sc and Al–0.24Sc–0.07Yb alloys ................................................................. 72
Figure 4.2. Isothermal ageing curves of Al–4Mg–0.3Sc and Al–4Mg–0.24Sc–0.06Yb alloys in comparison with Al–0.28Sc and Al–0.24Sc–0.07Yb alloys aged at 300 °C, 325 °C, and 350 °C ................. 73
Figure 4.3. TEM micrographs of Al–4Mg–0.3Sc (a–b–c) and Al–4Mg–0.24Sc–0.06Yb (d–e–f) alloys aged at 325 °C for 5 h, 325 °C for 7 days, and 350 °C for 7 days ................................................................. 75
Figure 4.4. Precipitates size distribution of Al–4Mg–0.3Sc (a–b–c) and Al–4Mg–0.24Sc–0.06Yb (d–e–f) alloys aged at 325 °C for 5 h, 325 °C for 7 days, and 350 °C for 7 days: $d_{16}$, $d_{50}$, and $d_{84}$ are the precipitate diameters corresponding to 16, 50, and 84 % cumulative undersize particle size distribution .................. 76
Figure 4.5. SAD taken along the [100] or [110] crystallographic directions ....................................... 77
Figure 4.6. High-resolution TEM images, FFT and IFFT of precipitates in Al–4Mg–0.3Sc (a) and Al–4Mg–0.24Sc–0.06Yb (b) alloys aged at 325 °C for 5 h. .................................................................................. 78
Figure 4.7. High-resolution TEM images, FFT and IFFT of precipitates in Al–4Mg–0.3Sc (a–c) and Al–4Mg–0.24Sc–0.06Yb (b–d) alloys aged at 325 °C for 7 days (a–b) and 350 °C for 7 days (c–d). ............ 78
Figure 5.1. Optical micrographs of as-cast alloys cast at 700 °C: (a) Al–1Mg, (b) Al–0.3Sc, (c) Al–4Mg, (d) Al–1Mg–0.3Sc, (e) Al–4Mg–0.3Sc................................................................. 85
Figure 5.2. Average grain size and hardness of Al–1Mg, Al–0.3Sc, Al–4Mg, Al–1Mg–0.3Sc, Al–4Mg–0.3Sc as-cast alloys cast at 700 °C ............................................................................. 85
Figure 5.3. Optical micrographs of Al–1Mg–0.3Sc alloy cast at pouring temperatures: (a–b) 800 °C, (c–d) 770 °C: (a), (c) in the border of samples; (b), (d) in the centre of samples......................... 86
Figure 5.4. Optical micrographs of Al–1Mg–0.3Sc alloy cast at pouring temperatures: (a) 740 °C, (b) 720 °C, (c) 700 °C........................................................................................................... 87
Figure 5.5. Grain size distribution of Al–1Mg–0.3Sc cast samples for different pouring temperatures ...... 87
Figure 5.6. SEM micrograph and EDS spectra of intermetallic phase in Al–0.3Sc alloy cast at 700 °C ...... 89
Figure 5.7. SEM micrograph and EDS spectra of intermetallic phases in Al–1Mg–0.3Sc alloy cast at 700 °C .................................................................................................................. 89
Figure 5.8. SEM micrograph and EDS spectrum of oxide nucleus in Al–4Mg–0.3Sc alloy cast at 700 °C .. 90
Figure 5.9. SEM micrograph and EDS spectra of intermetallic phase (Z1) in Al–1Mg–0.3Sc alloy cast at 770 °C.................................................................................................................. 90
Figure 5.10. Schematic of α–Al nucleation on (a) oxides, (b) Al,Sc, and (c) Al,Sc nucleated on oxide particles .................................................................................................................. 91
Figure 5.11. Optical micrographs of Al–1Mg–0.3Sc alloy ultrasonic treated at different temperatures: (a) 800 °C, (b) 770 °C, (c) 740 °C, (d) 720 °C, (e) 700 °C ............................................................................ 92
Figure 5.12. Grain size distribution of Al–1Mg–0.3Sc samples ultrasonic treated at different temperatures .................................................................................................................. 92
Figure 5.13. Effect of ultrasonic treatment on the average grain size of Al–1Mg–0.3Sc alloys............. 93
Figure 5.14. Effect of ultrasonic treatment temperature on grain size distribution of Al–1Mg–0.3Sc cast samples ............................................................................................................. 94
Figure 6.1. SEM micrographs of Al–0.28Sc alloy (a–b–c) and Al–0.24Sc–0.07Yb alloy (d–e–f)............ 103
Figure 6.2. Evolution of OCP with time for Al–0.28Sc and Al–0.24Sc–0.07Yb alloys (as-cast and heat treated samples)........................................................................................................ 104
Figure 6.3. SEM micrographs of Al–0.28Sc alloy after immersion in 3.5 wt% NaCl solution for 4 days: (a–b–c) as-cast samples; (d–e–f) heat treated samples; (a–b–d–f) BSE images and (c–e) SE image.

Figure 6.4. SEM micrographs of Al–0.24Sc–0.07Yb alloy after immersion in 3.5 wt% NaCl solution for 4 days: (a–b–c) as-cast samples; (d–e–f) heat treated samples.

Figure 6.5. Potentiodynamic polarization curves obtained in 3.5 wt% NaCl solution for Al–0.28Sc and Al–0.24Sc–0.07Yb alloys (as-cast and heat treated samples).

Figure 6.6. (a) Schematic view of the corrosion process: sample before immersion, corrosion reactions in the NaCl solution, and sample after exposure to the solution; (b) Schematic view of the cavity formation by localized alkaline corrosion.

Figure 6.7. SEM micrographs and EDS spectra of intermetallic phases in Al–4Mg alloy.

Figure 6.8. SEM micrographs and EDS spectra of intermetallic phases in Al–4Mg–0.3Sc alloy.

Figure 6.9. SEM micrographs and EDS spectra of intermetallic phases in Al–4Mg–0.24Sc–0.06Yb alloy.

Figure 6.10. Evolution of OCP values with time for Al–4Mg, Al–4Mg–0.3Sc and Al–4Mg–0.24Sc–0.06Yb alloys (as-cast and heat treated samples).

Figure 6.11. SEM micrographs of Al–4Mg alloy after immersion in 3.5 wt% NaCl solution for 4 days: (a–b) BSE images and (c) SE image.

Figure 6.12. SEM micrographs of Al–4Mg–0.3Sc alloy after immersion in 3.5 wt% NaCl solution for 4 days: (a–b–c) as-cast samples; (d–e–f) heat treated samples; (a–c–d–f) BSE images and (b–e) SE image.

Figure 6.13. SEM micrographs of Al–4Mg–0.24Sc–0.06Yb alloy after immersion in 3.5 wt% NaCl solution for 4 days: (a–b–c) as-cast samples; (d–e–f) heat treated samples; (a–c–d–f) BSE images and (b–e) SE image.

Figure 6.14. Potentiodynamic polarization curves obtained in 3.5 wt% NaCl solution for Al–4Mg, Al–4Mg–0.3Sc and Al–4Mg–0.24Sc–0.06Yb alloys (as-cast and heat treated samples).
List of Tables

Table 1.1. Solid solubility of Mg in Al [2] ........................................................................................................... 10
Table 1.2. Literature data on the effect of Sc on the strength of the various classes of wrought aluminium alloys .................................................................................................................................................................. 16
Table 1.3. Mechanical Properties of Al-Sc and Al-Mg-Sc Alloys [82] ................................................................. 17
Table 1.4. Corrosion rate of Al–Mg–Sc alloys in 3.5 wt% of NaCl (after 400 h) [98] ................................................. 20
Table 1.5. Corrosion rates of commercial aluminum alloys [98]............................................................................. 20
Table 1.6. Pitting potential (Ep) and protection potential (Epp) of Al–Mg–S alloy in 3.5 wt% NaCl [98] ....... 20
Table 1.7. Ep values of some selected aluminum alloys in 3.5 wt% NaCl [98] ......................................................... 21
Table 1.8. Radii and electronegativity for various metals [106] ............................................................................ 24
Table 1.9. Summary of the Important Grain Refinement Theories, in Terms of Their Understanding of Nucleation and the Effect of Solute ...................................................................................................................... 32
Table 2.1. Chemical composition of the Al–0.28Sc and Al–0.24Sc–0.07Yb as-cast alloys ........................................ 48
Table 2.2. Chemical composition of Al–4Mg, Al–4Mg–0.3Sc, and Al–4Mg–0.24Sc–0.06Yb as-cast alloys (wt%) .............................................................................................................................................................................. 49
Table 3.1. Average precipitate diameter and hardness of Al–0.28Sc and Al–0.24Sc–0.07Yb alloys ............... 61
Table 4.1. Average precipitate diameter and hardness of Al–4Mg–0.3Sc and Al–4Mg–0.24Sc–0.06Yb alloys ....................................................................................................................................................................................... 76
Table 6.1. Chemical compositions of intermetallic particles in Al–0.28Sc and Al–0.24Sc–0.07Yb alloys .................................................................................................................................................................................... 104
Table 6.2. Chemical compositions of intermetallic particles in Al–0.28Sc alloy after immersion in a 3.5 wt% NaCl solution for 4 days .................................................................................................................................................... 107
Table 6.3. Chemical compositions of intermetallic particles in Al–0.24Sc–0.07Yb alloy after immersion in a 3.5 wt% NaCl solution for 4 days ........................................................................................................................................... 109
Table 6.4. Summary of results of potentiodynamic polarization ........................................................................ 110
Table 6.5. Chemical compositions of intermetallic particles in Al–4Mg alloy after immersion in 3.5 wt% NaCl solution for 4 days ................................................................................................................................................. 116
Table 6.6. Chemical compositions of intermetallic particles in Al–4Mg–0.3Sc alloy after immersion in 3.5 wt% NaCl solution for 4 days ........................................................................................................................................... 119
Table 6.7. Chemical compositions of intermetallic particles in Al–4Mg–0.24Sc–0.06Yb alloy after immersion in 3.5 wt% NaCl solution for 4 days ........................................................................................................................................ 120
Table 6.8. Summary of results of potentiodynamic polarization ........................................................................ 121
Effects of substituting rare earth metals for scandium on the microstructure and properties of Al-Sc and Al-Mg-Sc alloys

CHAPTER 1 – STATE OF THE ART
Chapter 1 – State of the art

1.1 Motivation for Research

Aluminium alloys are widely applied in aircraft, automobile and other engineering structures. The reason for this large application is due to a wide range of excellent properties including low density, corrosion resistance and high strength to weight ratio. Some aluminium alloys are commonly used in aircraft and other aerospace structures: 7075, 6061, 6063, 2024, 5052 aluminium alloys. Al-Li alloys are used in space shuttle super lightweight external tank and Al-Cu alloys are used in the original space shuttle standard weight external tank as 2195, 2219 aluminium alloys. In Marine application, aluminium alloys are used for boat building and shipbuilding, and other marine and salt-water sensitive shore applications. They are 5052, 5059, 5083, 5086, 6061, 6063 aluminium alloys. In cycling frames and components, 2014, 6063, 7005, 7075 and scandium aluminium alloys were applied. 6111 aluminium alloy is extensively used for automotive body panels.

Al–Sc alloys have excellent mechanical properties at ambient and elevated temperatures due to the presence of a high density (as high as $10^{22} \text{ m}^{-3}$) of elastically-hard $\text{Al}_3\text{Sc}$ ($\text{L1}_2$ structure) precipitates [1-5], which remain coherent with the $\alpha$-Al matrix at elevated temperatures [1,3]. On a per-atom basis, Sc has the greatest strengthening effect of any existing alloying addition to Al [6]. The $\text{Al}_3\text{Sc}$ precipitates coarsen slowly up to $\sim 300^\circ\text{C}$, imparting good creep resistance in coarse-grained cast alloys [1-3,5,7-11]. The lattice parameter mismatch of Al and $\text{Al}_3\text{Sc}$ also contributes to the high creep resistance of Al–Sc alloys. The good interfacial strength between the $\text{Al}_3\text{Sc}$ precipitates and the aluminium matrix creates a significant lattice strain, which blocks dislocation motion and prevents grain growth [12]. Furthermore, the thermal stability of the $\text{Al}_3\text{Sc}$ precipitates suppresses recrystallization [13,14] and leads to a significant strengthening effect. In general, large aluminium alloy weldments are susceptible to hot cracking. However, the dispersion of thermally stable $\text{Al}_3\text{Sc}$ precipitates suppresses thermal cracking in the heat affected zone of the weldment [15-17]. Therefore Al-Sc alloys are widely used in the fabrication of sports equipment, aerospace components and in a range of structural applications.

Although Al–Sc alloys are very attractive field but they are limited by the cost and availability of Sc. The price of Al–2 wt% Sc master alloy is 512 $/\text{kg}$. A possible solution for this problem is solid solution strengthening to substitute alloying additions that are similar in nature to Sc to reduce the Sc content without decreasing of properties. Some previous researches showed that ternary additions to Al–Sc alloys
improve mechanical properties by solid solution strengthening as in the case of Mg [18-22], or by substituting for Sc in Al,Sc precipitates as in the cases of Ti and Zr [13-26]. Ti and Zr diffuse significantly more slowly than Sc in Al [27-29] and decrease the lattice parameter mismatch between the $\alpha$–Al matrix and the precipitates [30]. While both of these attributes increase coarsening resistance, the latter may decrease creep resistance by reducing elastic interactions with dislocations during climb bypass [23,24,31]. The ideal ternary additions for Al–Sc alloys should thus exhibit high solubility in Al,Sc and low diffusivity in $\alpha$–Al (like Ti and Zr), while moderately increasing the lattice parameter of Al,Sc (unlike Ti and Zr) [32]. The rare-earth metals (REMs) are attractive ternary additions to substitute Sc.

In this research, based on Al–0.28Sc and Al–4 wt% Mg–0.3 wt% Sc alloys, we studied dilution Al–Sc and Al–Mg–Sc alloys with microalloying additions of Yb. The effects of substituting Yb for Sc on the microstructure and the mechanical properties of Al–Sc alloy are investigated by using SEM, TEM, HRTEM and Vickers hardness. The precipitate evolution and precipitation hardening were understood.

In the aluminium casting industry grain refinement plays an important role to enhance mechanical properties as toughness, fracture resistance, fatigue strength and isotropic behaviour of the cast alloys. Grain refinement also reduces hot tearing, porosity and the pore size [33,34]. Several processes have been applied to achieve a fine, equiaxed and uniform grain microstructure. In this work, the role of Mg and Sc as well as the influence of pouring temperature on grain refinement of Al–1 wt% Mg–0.3 wt% Sc was studied. Moreover, the microstructures of Al–1 wt% Mg–0.3 wt% Sc alloy at various pouring temperatures without and with ultrasonic treatment were studied. The mechanism of grain refinement was proposed and understood. The age hardening behaviour of those alloys without and with ultrasonic treatment was investigated.

Almost researchers focused in microstructural and mechanical properties of these alloys. However, a limited work about corrosion behaviour has been studied. We have known that the chemical and mechanical characteristics have considerable influences on the passivity of Al alloys, resulting in the different corrosion behaviour. The existence of second phase in the alloy matrix also effects on the corrosion behaviour [35,36]. The corrosion resistant property of these alloys is very important property for application in shipbuilding and marine industry. In this research, the corrosion behaviour of these alloys will be studied to evaluation the capability for these alloys to apply in seawater environment.
1.2 Literature Review

1.2.1 Al–Sc and Al–Mg–Sc alloys

1.2.1.1 The binary Al–Sc system and Al,Sc phase

The binary Al–Sc phase diagram on the Al rich side is shown in Figure 1.1 which indicates the limited solubility of Sc in α–Al below the eutectic temperature [37,38]. The maximum solid solubility of Sc in α–Al is 0.38 wt% that occurs at the eutectic temperature of 660 °C as the following reaction:

\[
Liq. = \alpha(Al) + Al_3Sc \quad (1.1)
\]

Figure 1.1. Al–Sc phase diagram on the Al rich side [37].

The solid solubility of Sc in α–Al drops sharply below 0.1 wt% at 500 °C. The solid solubility of Sc in α–Al at various temperatures can be determined from Figure 1.2 [5,39]. However, the high supersaturated solid solution of Al–Sc alloy can be obtained by high cooling rate during solidification process. The supersaturated solid solutions of 0.6 wt% Sc in α–Al was achieved at the cooling rate of 100 °C [2], and the supersaturation in excess of 5 wt% Sc was obtained by quenching the melt with a rotating mill device [40]. The Al–Sc supersaturated solid solution decomposes into fine coherent Al,Sc precipitates with an ordered
L1₂ structure [41]. At ambient temperature the lattice parameters of α-Al and Al₃Sc are 0.40496 and 0.4105 nm, respectively [30, 42]. The lattice parameter mismatch is defined by following equation:

\[
\delta = 2 \frac{a_{Al_3Sc} - a_{Al}}{a_{Al} + a_{Al_3Sc}}
\]

(1.2)

where \(a_{Al_3Sc}\) and \(a_{Al}\) are lattice parameter at room temperature of Al₃Sc and α-Al.

The lattice parameter mismatch of α-Al matrix phase and Al₃Sc precipitate phase at room temperature are calculated and shows the value of 1.35 %. While at 300°C, this mismatch decreases to about 1.1% due to thermal expansion [43]. The crystallography of Al₃Sc was reported in similarity with Cu₃Au, Ni₃Al and Ni₃Fe lattice structure. This lattice structure is ordered L1₂ structure and space group Pm3m [41]. The atomic arrangement in Al₃Sc is shown in Figure 1.3. This structure is ordered face-center cubic (FCC), but in fact the Al₃Sc lattice structure is simple cubic lattice that contains one Sc and three Al atoms.

\[\text{Figure 1.2. The solvus line of Sc in Al [5,39].}\]

The diffraction patterns of Al₃Sc precipitates are almost similar to that of FCC materials. But one characteristic for diffraction patterns of Al₃Sc precipitates was noted. The reflections such as \(\{100\}\), \(\{010\}\), and \(\{110\}\) reflections which are invisible in an FCC material will be appeared in a diffraction pattern of Al₃Sc precipitate. The diffraction pattern taken along the [001] axis of Al₃Sc precipitates in Al–Sc alloy is shown in Figure 1.4 [7]. The \(\{100\}\) and \(\{010\}\) reflections of Al₃Sc precipitates and the \(\{200\}\) and \(\{020\}\) reflections of the α–Al matrix were observed.
The Al₃Sc phase can be formed in Al–Sc alloys through possible four ways:

1) Al₃Sc is the first phase forming in the hypereutectic Al–Sc alloys during solidification. According to the Al–Sc binary phase diagram in Figure 1.1, with the Al–Sc alloys contain Sc higher than the eutectic composition (0.55 wt%), the Al₃Sc phase will be formed in the melt and exists as second phase particles in the α–Al matrix during solidification [44,45]. The morphology and the nucleation mechanism of Al₃Sc in the Al–0.7 wt% Sc alloy casted at various cooling rate was studied by Hyde et al. [45,46]. This result showed that the Al₃Sc particles were heterogeneously nucleated on oxides within the melt. The morphology of Al₃Sc particles exhibit the faceted cubic shape at slow cooling rate (~1 K s⁻¹), and become unstable along the
cube edges and corners, forming growth perturbations. The overall shape is cubic morphology with cellular-dendritic sub-structures.

2) According to reaction (1.1), Al₃Sc phase can be formed by the eutectic formation in hypo- and hypereutectic Al–Sc alloys. Hyde et al. [45,46] suggested that the eutectic Al₃Sc could be formed in the Al–0.7 wt% Sc alloy during solidification.

3) Al₃Sc phase can be formed by discontinuously precipitation from supersaturated solid solution. In this way, the supersaturated solid solution of Sc in α-Al decomposes into α-Al and Al₃Sc at a moving grain boundary. The driving force for the grain boundary migration is the volume free energy that is released during the precipitation. According to Norman et al. [44] and Blake et al. [7], the grain boundaries migrated during cooling, and left a fan shaped array of precipitates behind the moving grain boundaries. The morphology of coherent rod-like precipitates was observed.

4) Al₃Sc phase can be formed by continuously precipitation (nucleation and growth) from supersaturated solid solution. Continuous precipitation of Al₃Sc occurs during the isothermal treatment of as-cast alloy with supersaturated solid solution of Sc in α-Al. This process includes three stages: nucleation, growth and coarsening stage of Al₃Sc precipitates. The homogeneous nucleation and diffusion controlled growth is main mechanism of continuous precipitation [10,11,47]. Some investigations reported the heterogeneous nucleation of Al₃Sc precipitates on dislocation [3,11,13] and grain boundaries [4,11,13,48]. In the continuous precipitation, the morphology of Al₃Sc precipitates is almost spherical [41,49-52]. There are some investigations showed the different morphology. The Al₃Sc precipitates with spherical, cuboidal, and/or cauliflower shape were indicated in Riddle et al. [53] and Novotny et al. [11]. The Al₃Sc precipitate with large oblong morphology was observed in Al–0.06 at. % Sc aged at 400 °C for 24 h. According to Marquis et al. [3] the morphology of Al₃Sc consists of 6 {100} (cube), 12 {110} (rhombic dodecahedron), and 8 {111} (octahedron) facets, that corresponds to a Great Rhombicuboctahedron. The Figure 1.5 and 1.6 show the HRTEM image taken along the [100] zone axis of an Al₃Sc precipitate obtained by aging Al–0.3 wt% Sc at 300°C for 350 h and the Great Rhombicuboctahedron morphology with various projections.
1.2.1.2 The Al–Mg–Sc system

Aluminum alloys with magnesium as a main alloying element are widely used in industry as non-aging, ductile, medium-strength, weldable, and corrosion-resistant materials [54]. However, their relatively low strength characteristics hinder their use as structural materials in ship building and the aerospace industry. Alloying with scandium is the excellent way to solve these problems [2]. Some previous researches indicated that the strength of Al–Mg alloys can be substantially improved by the addition of small amount of scandium due to the presence of elastically hard, coherent and nano–sized Al₃Sc (L1₂) particles, which strongly inhibit the dynamic recrystallization and dislocation movement [55-61].
In the Al-Mg-Sc ternary system, the mutual solid solubilities of Mg and Sc are decreased with the decrease of temperature. The solid solubility of Mg in Al at various temperatures is shown in Table 1.1.

<table>
<thead>
<tr>
<th>t, °C</th>
<th>450</th>
<th>427</th>
<th>400</th>
<th>377</th>
<th>350</th>
<th>327</th>
<th>300</th>
<th>277</th>
<th>177</th>
<th>127</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td>wt%</td>
<td>17.4</td>
<td>15.3</td>
<td>13.5</td>
<td>11.5</td>
<td>9.9</td>
<td>8.1</td>
<td>6.7</td>
<td>5.5</td>
<td>2.6</td>
<td>2.0</td>
<td>1.9</td>
</tr>
<tr>
<td>at%</td>
<td>18.5</td>
<td>16.4</td>
<td>-</td>
<td>12.5</td>
<td>-</td>
<td>9.0</td>
<td>-</td>
<td>6.4</td>
<td>3.3</td>
<td>2.7</td>
<td>2.3</td>
</tr>
</tbody>
</table>

The maximum solid solubility of Mg in Al is 17.4 wt% (18.5 at%) at 450 °C in a binary Al-Mg alloy and it decreases to 10.5 wt% (11.6 at%) with 0.007 at% Sc at 447 °C [2]. The mutual solubility of Mg and Sc in Al at 430 °C is 10.5 wt% (11.6 at%) and 0.01 wt% (0.006 at%) respectively. Turkina and Kuzmina [62] and Pisch et al. [63] calculated the solid-solubility of Sc and Mg that is shown in Figure 1.7.

![Figure 1.7. Isotherms of the solvus surface in the Al–Mg–Sc phase diagram: (a) [62] (b) [63].](image)

The Al–Mg–Sc phase diagram was studied by Turkina and Kuzmina [62] up to 26 wt% Mg and 3 wt%. Isothermal section of the Al–Mg–Sc system at 430 °C was constructed and shown in Figure 1.8. The given portion of the phase diagram includes a single-phase field of the aluminium based solid solution, two two-phase fields (Al) + MgAl, and (Al) + AlSc, and a three-phase field (Al) + MgAl + AlSc.
Figure 1.8. Isothermal section of the Al–Mg–Sc system at 430 °C [62].

Alexander Pisch *et al.* [63] indicated that the eutectic composition of Sc decreases with increasing Mg content in the Al–Mg–Sc alloy. The eutectic composition of Sc reduces down to 0.3 wt% Sc for 7 wt% Mg at 625°C (Figure 1.9).

Figure 1.9. Liquidus surface of the Al rich corner in the Al–Mg–Sc system [63].

### 1.2.2 Precipitate coarsening kinetics

Some previous studies about Al–(0.2–0.5) wt% Sc indicated that very fine, coherent, and homogeneously distributed Al,Sc precipitates are formed during heat treatment process at various temperature from 300–400 °C [37,41]. The evolution of precipitate follows the sequence of an initial incubation stage and nucleation, the precipitates nucleate from a supersaturated solid solution and grow, and then a gradual coarsening by Ostwald ripening [41,49]. No GP zones or metastable precipitates are observed [41]. The coarsening kinetics of the coherent precipitates obey the diffusion limited coarsening theory proposed by
Lifshitz and Slyozov [64] and Wagner [65] (LSW theory). The LSW theory is applied for binary alloys that are assumed as follow [66,67]:

- No elastic interactions occur among precipitates, thereby limiting the precipitate volume fraction to zero;
- The linearized version of the Gibbs-Thomson equation is valid;
- Coarsening occurs in a stress-free matrix;
- Dilute solution theory obtains;
- Diffusion fields of precipitates do not overlap;
- Precipitates have a spherical morphology;
- Precipitates form with the correct composition as given by the equilibrium phase diagram;
- Coarsening is a self-similar process.

The LSW theory was developed for concentrated multicomponent systems by Umantsev and Olson [68] and then studied more detail for ternary alloys which included capillary effects by Kuehmann and Voorhees [69]. The time exponent for the evolution of average precipitate radius \( <R(t)> \) of the ternary alloys was predicted to be 1/3, the same as for the binary alloys, but a different rate constant, \( K_{i,KV} \), with the LSW model. Three following equations derived from the Kuehmann and Voorhees model for coarsening in ternary alloys [69] assume that quasi-stationary coarsening is occurring:

\[
< R(t) >^3 - < R(t_0) >^3 = K_{KV}(t - t_0) \tag{1.3}
\]

\[
N_v(t)^{-1} - N_v(t_0)^{-1} = 4.74 \frac{K_{KV}}{V_v}(t - t_0) \tag{1.4}
\]

\[
\Delta C_i^α(t) = < C_i^α(t) > - < C_i^α(t \to \infty) > = K_{i,KV}^{α}(t)^{-1/3} \tag{1.4}
\]

where \( K_{KV} \) and \( K_{i,KV}^α \) are the coarsening rate constants for \( < R(t) > \) and \( \Delta C_i^α(t) \), respectively; \( < R(t) > \) and \( < R(t_0) > \) are the average precipitate radius at the onset of quasi-stationary coarsening at time \( t \) and \( t_0 \), respectively; \( N_v(t) \) and \( N_v(t_0) \) is the precipitate density at the onset of quasi-stationary coarsening at time \( t \) and \( t_0 \), respectively; \( V_v \) is equilibrium volume fraction of precipitates; the superscript \( α \) refers to the matrix phases; \( \Delta C_i^α(t) \) denotes supersaturation that is the difference between the concentration of \( i^α \) component in the matrix, \( < C_i^α(t) > \) is the composition of the \( i^α \) component in the matrix, and \( < C_i^α(t \to \infty) > \) is the solid-solubility of the \( i^α \) component in the matrix.

The theoretical expression of \( K_{KV} \) for the evolution of the precipitate radius is given by:
\[ K_{KV} = \frac{8\sigma V_m}{9RT \sum_i (\frac{C_i^\alpha (1 - k_i)^2}{D_i})} \]

where \(V_m\) is the molar volume of the precipitate; \(\sigma\) is an isotropic interfacial free energy; \(R\) is the ideal gas constant; \(T\) is the absolute temperature; \(C_i^\alpha\) is the composition of the \(i^{th}\) component in the matrix; \(D_i\) is the diffusion coefficient of the \(i^{th}\) component; \(k_i\) is the distribution coefficient of the \(i^{th}\) species between the matrix (\(\alpha\)) and precipitate (\(\beta\)) phases that is defined by \(C_i^\beta / C_i^\alpha\).

In Al–Sc–Yb alloys, the \(i^{th}\) component is Sc and Yb.

The theoretical expression of \(K_{i,KV}^\alpha\) is given by:

\[ K_{i,KV}^\alpha = \frac{2\sigma V_m k_{exp}^{-1/3} (C_i^\beta - C_i^\alpha)}{RT \sum_i (C_i^\alpha (1 - k_i)^2)} \]

where \(k_{exp}\) is the experimentally determined coarsening rate constant, \(C_i^\beta\) is the composition of the \(i^{th}\) component in the precipitate phase.

In the Al–Sc alloys, Al_{3}Sc precipitates have slow coarsening rate due to the very low solid solubility of Sc in Al. As coherent precipitates coarsen, they eventually lose their coherency with the matrix, resulting in a decrease in the overall mechanical properties of the alloy and a rapid increase in coarsening rate. In Al–Sc alloys, a rapid coarsening of the precipitates was reported above 400 °C. Below this temperature, particles remain stable and coherent for long periods of time. The research of Iwamura and Miura [1] about the coarsening behaviour of the Al_{3}Sc particles in Al–0.2 wt% Sc alloy at 400–490 °C indicated that the coherent stage exists when the precipitate radius below 15 nm, semi-coherent stage exists when the precipitate radius over 40 nm, and the radius for coherent/semi-coherent transition where coherent and semi-coherent precipitates coexist is 15–40 nm.

Mg present in solid solution with \(\alpha\)-Al that leads to reduce the lattice parameter mismatch between the matrix and Al_{3}Sc precipitates. As a consequence, Al_{3}Sc precipitates still remain coherent with \(\alpha\)-Al matrix even in the large size. The lattice parameter mismatch is reduced from 1.35 to 0.54%, and the coherency loss occurs when precipitates coarse up to 116 nm in Al–6.3Mg–0.21Sc (wt%) alloy [52] and 80 nm in Al–3 wt% Mg–0.2 wt% Sc alloy.
1.2.3 Precipitation strengthening

Adding Sc leads to significantly increase strength of Al due to the formation of Al,Sc precipitates. In the binary Al-Sc alloy, the most effective strengthening was reported when the alloys were perform the aging in the temperature range 250–350 °C. Yield strength of Al increases from 15 to 159 and 199 Mpa by adding 0.23 and 0.38 wt% Sc, respectively [5]. Adding 0.3 wt% of Sc increases the yield stress of Al-1 wt% Mg from 43 to 288 MPa and the ultimate tensile stress from 111 to 303 MPa [5]. Sc is the most effective precipitation hardening element per atomic fraction than any existing alloying addition [50, 70] (Only Au has a stronger strengthening effect than Sc [49]). However, the amount of Sc that can be precipitated from supersaturated solid solution is rather limited.

In the precipitation strengthening mechanisms, the dislocations in a material can interact with the precipitate particles through two ways: cutting or Orowan-bypassing mechanisms (Figure 1.10). Cutting or shearing occurs for small and coherent precipitates. As a result, new surfaces (b in Figure 1.10) of precipitate would get exposed to the matrix and the precipitate/matrix interfacial energy would increase. In the cutting mechanism, the strengthening effect of the precipitates is approximately proportional to the precipitate size (Figure 1.12). Four mechanisms can contribute to strengthen alloys when the dislocations shear through precipitates. They are: coherency strain, anti-phase-boundary energy (APB), interfaces, and modulus effect (Figure 1.11). There is a few researches studying about the strengthening mechanisms of binary Al–Sc alloys. The strengthening in Al–Sc alloys from coherency strain and APB energy was proposed by Parker et al. [71] and from shear modulus mismatch between the matrix and the precipitates was confirmed by Marquis et al. [4,48].

![Figure 1.10. Schematic of the interaction of dislocations and second phase particle.](image-url)
The Orowan-bypassing mechanism happens for larger precipitate particles. In this case, dislocation bowing between the precipitates and loop forming occurs when either the precipitates exceed a critical size or after they lose coherency (Figure 1.10). The strengthening effect of the precipitates is approximately proportional inversely to the precipitate size and the mean particle spacing (Figure 1.12). Torma et al. [72] study showed that the Orowan dislocation mechanism control the strengthening of Al–0.18 and 0.31 wt% Sc alloys at room temperature with coherent precipitates larger than 4.3 nm in radius. In Al–0.3 wt% Sc alloy, Marquis et al. [4] predicted a transition from cutting mechanism to Orowan bypass mechanism at a precipitate radius of 2.1 nm.

![Figure 1.11. Schematic of a precipitate cutting.](image)

![Figure 1.12. Shear Strength vs. Particle Radius.](image)

**1.2.4 The effect of Sc in aluminium alloys**

**1.2.4.1 Mechanical properties**

The overview of yield strength and ultimate tensile strength of Al alloys containing Sc with deferent series is shown in Table 1.2. It can be seen that the yield strength of pure Al increases dramatically from 15 to 198 and 240 MPa by adding 0.23 wt% and 0.38 wt% of Sc, respectively [73]. With all series of Al alloys, the strength of alloy increase significantly when adding Sc.
Table 1.2. Literature data on the effect of Sc on the strength of the various classes of wrought aluminium alloys

<table>
<thead>
<tr>
<th>Alloy system</th>
<th>Ref.</th>
<th>Alloy</th>
<th>Yield Strength (MPa)</th>
<th>Ultimate Tensile Strength (MPa)</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>1xxx</td>
<td>[73]</td>
<td>Al</td>
<td>15</td>
<td>48</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Al–0.23Sc</td>
<td>198</td>
<td>208</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Al–0.38Sc</td>
<td>240</td>
<td>264</td>
<td>Cold rolled material (89%), aged 288 °C/8h</td>
</tr>
<tr>
<td>2xxx</td>
<td>[74]</td>
<td>2618</td>
<td>~260</td>
<td>~330</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>2618 + Sc,Zr</td>
<td>~340</td>
<td>~390</td>
<td>Rolled sheet, solution heat treated, aged to peak hardness at 200 °C (16-20h)</td>
</tr>
<tr>
<td>5xxx</td>
<td>[57]</td>
<td>Al–1Mg</td>
<td>50</td>
<td>120</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Al–1Mg–Sc (1515)</td>
<td>160</td>
<td>250</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Al–2Mg–Mn</td>
<td>90</td>
<td>190</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Al–2Mg–Sc (1523)</td>
<td>200</td>
<td>270</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Al–4Mg–Mn</td>
<td>140</td>
<td>270</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Al–4Mg–Sc (1535)</td>
<td>280</td>
<td>360</td>
<td>As hot worked or annealed condition</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Al–5Mg–Mn</td>
<td>170</td>
<td>300</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Al–5Mg–Sc (1545)</td>
<td>290</td>
<td>380</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Al–6Mg–Mn</td>
<td>180</td>
<td>340</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Al–6Mg–Sc (1570)</td>
<td>300</td>
<td>400</td>
<td></td>
</tr>
<tr>
<td>6xxx</td>
<td>[76]</td>
<td>6082</td>
<td>333/338</td>
<td>351/357</td>
<td>Extruded rods, T5 age hardening at 185°C/4h (1st value) and 165°C/24h</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6082 + Sc,Zr</td>
<td>329/333</td>
<td>362/366</td>
<td></td>
</tr>
<tr>
<td></td>
<td>[77]</td>
<td>6060</td>
<td>81</td>
<td>163</td>
<td>Extruded rods, T1 condition</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6060 + Sc,Zr</td>
<td>182</td>
<td>247</td>
<td></td>
</tr>
<tr>
<td></td>
<td>[78]</td>
<td>1370</td>
<td>380</td>
<td>430</td>
<td>Rolled sheet, T6 condition</td>
</tr>
<tr>
<td>7xxx</td>
<td>[79]</td>
<td>7017</td>
<td>400</td>
<td>475</td>
<td>Hot rolled plate, solution heat treated + aged to max. hardness at 120°C</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7017 + 0.25Sc</td>
<td>415</td>
<td>490</td>
<td></td>
</tr>
<tr>
<td></td>
<td>[80]</td>
<td>Al–8.6Zn–2.6Mg–2.4Cu–0.1Zr</td>
<td>649</td>
<td>672</td>
<td>Extruded rod, T6 condition</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Al–8.6Zn–2.6Mg–2.4Cu–0.1Zr–0.2Sc</td>
<td>689</td>
<td>715</td>
<td></td>
</tr>
<tr>
<td>Al-Li</td>
<td>[81]</td>
<td>1420 (=1421 without Sc)</td>
<td>270/280</td>
<td>440/450</td>
<td>Rolled sheet. Strength in longitudinal direction (1st value) and transverse direction (2nd value)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1421</td>
<td>320/340</td>
<td>460/480</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1423</td>
<td>350/330</td>
<td>460/460</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1424</td>
<td>320/320</td>
<td>475/425</td>
<td></td>
</tr>
</tbody>
</table>
Tables 1.3 shows the mechanical properties of Al–Mg–0.5 wt% Sc alloy with various compositions of Mg [82]. The yield strength and ultimate tensile strength of Al–0.5 wt% Sc alloy slightly increase and the elongation decreases when the content of Mg increase from 2 to 6 wt%.

<table>
<thead>
<tr>
<th>Alloys</th>
<th>Yield Strength (MPa)</th>
<th>Ultimate Tensile Strength (MPa)</th>
<th>Elongation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al–0.5Sc</td>
<td>158.63</td>
<td>213.80</td>
<td>14</td>
</tr>
<tr>
<td>Al–2Mg–0.5Sc</td>
<td>202.08</td>
<td>265.35</td>
<td>10</td>
</tr>
<tr>
<td>Al–4Mg–0.5Sc</td>
<td>215.87</td>
<td>272.43</td>
<td>9.5</td>
</tr>
<tr>
<td>Al–6Mg–0.5Sc</td>
<td>255.19</td>
<td>286.22</td>
<td>9</td>
</tr>
</tbody>
</table>

**1.2.4.2 Recrystallization resistance**

Recrystallization in deformed materials is the formation of new grains free of dislocations by the formation and migration of high angle grain boundaries with misorientation angles larger than 10–15° under the stored energy of deformation [83,84]. Recrystallization involves the growth of subgrains by mechanisms such as migration of low angle boundaries in an orientation gradient or strain induced boundary migration. Recrystallization is an important way to be considered for designing microstructures with required mechanical properties in aluminium alloys [84]. Previous studies about aluminium alloys have shown that through recrystallization controlling, fine grained microstructures with grain sizes of 1–2 μm can improve the yield strength in comparison with coarse grained materials [85,86].

Precipitates can act as a factor to retard recrystallization. Two different conditions are required to form Al,Sc precipitates for recrystallization resistance: (i) Sc is in solid solution before the deformation to ensure during annealing, the Al,Sc precipitates nucleate and grow before recrystallization occurring; (ii) the Al,Sc precipitates are formed in the alloy before deformation. The first publication about this characteristic was given in a patent [73] which showed the effect of 0.3 wt% Sc on the recrystallization of Al–Mg, Al–Mn and Al–Zn–Mg alloys. The results showed that the addition of Sc increase the temperature for initiation of recrystallization approximately 220 °C. Jones and Humphreys [13] studied the effect of Al,Sc precipitates on recrystallization of Al–Sc alloys. The results showed that the recrystallization in Al–0.25 wt% Sc alloy only occurs at long aging times or temperatures higher than 500 °C. At these temperatures, precipitates coarsen
and lose their full coherency and therefore initiate recrystallization. In deformed supersaturated Al–0.12 wt% Sc alloy, at temperatures below 370 °C, precipitation happens and inhibits recrystallization. Above this temperature recrystallization and precipitation occur simultaneously. Figure 1.13 shows the recrystallization kinetics of Al–0.02 wt% Sc, Al–0.12 wt% Sc, and Al–0.25 wt% Sc alloys.

![Figure 1.13. Isothermal recrystallization kinetics of Al-Sc alloys [13].](image)

Ocenasek and Slamova [87] showed that fully recrystallization occurs in the AlMg3 alloy (AA5754) after 5 min annealing at 360 °C; the addition of 0.25 wt% Sc and 0.08 wt% Zr lead the alloy resist to recrystallization even when annealed for 8 h at 520 °C. The study of Yin et al. [88] had the same conclusion when adding Sc and Zr to Al–8.2Zn–2.1Mg–2.3Cu (wt%) alloy. According to Mirua’s [89], the recrystallization temperature increase 200 °C when adding 0.2 wt% Sc to Al–3 wt% Mg alloy. Some studies have proven that AlSc precipitates promote thermal stability to the deformed microstructures even at high temperatures in deformed Al–Sc alloys [90-92]. Figure 1.14 illustrates the effect of annealing time and temperature on grain size of Al–0.2 wt% Sc alloy deformed by equal channel angular pressing (ECAP) [92].
1.2.4.3 Corrosion resistance

The studies about corrosion behaviour of Al alloys containing Sc reported that addition of Sc increases the corrosion potential (less negative) in pure Al [93,94], Al–Zn alloys [95,96], Al–Mg alloys [97] Al–Zn–Mg–Cu alloys [80,94], Al–Cu–Mg–Mn alloys [94], and Al–Cu–Li–Mg–Ag alloys [94]. Some characteristics were noted. The effect of Sc on the corrosion potential is more evident with the hypereutectic composition Al–Sc alloys [93]. The heat treatment conditions of Al alloys containing Sc can affect corrosion potential [80,97]. The results of corrosion rates and passivation current densities indicated that the addition of Sc enhances the corrosion resistance of wrought Al alloys [80,93,94,97].

Ahmad et al. [98] studied the effect of Al,Sc precipitates on the corrosion behavior of Al–2.5 wt% Mg (5052) alloy adding 0.1–0.3 wt% Sc in 3.5 wt% NaCl. The result showed that Sc does not increase the corrosion rate of Al–Mg alloys. The better corrosion resistance in Al–2.5 wt% Mg–(0.1–0.3) wt% Sc alloys in comparison with commercial aluminium alloys such as 5052, 6063, 6013, 3023, 6061 was indicated. The weight-loss studies showed that the corrosion rate decreased with the exposure period. Table 1.4 summarizes the corrosion rates of Al–Mg–Sc alloys in 3.5 wt% of NaCl (after 400 h) and Table 1.5 shows the corrosion rates of some commercial aluminium alloys.
Table 1.4. Corrosion rate of Al–Mg–Sc alloys in 3.5 wt% of NaCl (after 400 h) [98]

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Corrosion rate</th>
<th>Mdd*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mm/year</td>
<td></td>
</tr>
<tr>
<td>Al–2.5Mg</td>
<td>0.023</td>
<td>1.477</td>
</tr>
<tr>
<td>Al–2.5Mg–0.1Sc</td>
<td>0.031</td>
<td>1.98</td>
</tr>
<tr>
<td>Al–2.5Mg–0.15Sc</td>
<td>0.046</td>
<td>2.914</td>
</tr>
<tr>
<td>Al–2.5Mg–0.3Sc</td>
<td>0.038</td>
<td>2.46</td>
</tr>
</tbody>
</table>

*mdd — milligrams per square decimeter per day.

Table 1.5. Corrosion rates of commercial aluminum alloys [98]

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Corrosion rate (mm/year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6061</td>
<td>0.109 [99]</td>
</tr>
<tr>
<td>5052 (O Zr)</td>
<td>0.071 [100]</td>
</tr>
<tr>
<td>3023</td>
<td>0.075 [100]</td>
</tr>
<tr>
<td>6063</td>
<td>0.109 [100]</td>
</tr>
<tr>
<td>6013</td>
<td>0.089 [98]</td>
</tr>
</tbody>
</table>

The corrosion rate of Al–2.5 wt% Mg–0.1 wt% Sc alloy decreases from 2.4 mdd (0.038 mm/y) to 1.44 mdd (0.023 mm/y) after 800 h exposure. It can be explained by the formation of protective films of either bayerite ($\beta\text{-Al}_2\text{O}_3\cdot3\text{H}_2\text{O}$) or boehmite ($\gamma\text{-Al}_2\text{O}_3\cdot\text{H}_2\text{O}$). Pitting studies by ASTM cyclic-polarization technique showed that age hardening does not affect the pitting potential. The pitting data of Al–2.5 wt% Mg–(0.1–0.3) wt% Sc alloys in 3.5 wt% NaCl and some commercial alloys are shown in Table 1.6 and 1.7.

Table 1.6. Pitting potential ($E_p$) and protection potential ($E_{pp}$) of Al–Mg–S alloy in 3.5 wt% NaCl [98]

<table>
<thead>
<tr>
<th>Alloy</th>
<th>$E_p$ (V)</th>
<th>$E_{pp}$ (V)</th>
<th>$E_{corr}$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al–2.5Mg–0Sc</td>
<td>−0.521</td>
<td>−0.697</td>
<td>−0.643</td>
</tr>
<tr>
<td>Al–2.5Mg–0.1Sc</td>
<td>−0.578</td>
<td>−0.713</td>
<td>−0.659</td>
</tr>
<tr>
<td>Al–2.5Mg–0.15Sc</td>
<td>−0.518</td>
<td>−0.694</td>
<td>−0.628</td>
</tr>
<tr>
<td>Al–2.5Mg–0.3Sc</td>
<td>−0.670</td>
<td>−0.729</td>
<td>−0.742</td>
</tr>
</tbody>
</table>
Table 1.7. $E_p$ values of some selected aluminum alloys in 3.5 wt% NaCl [98]

<table>
<thead>
<tr>
<th>Alloy</th>
<th>$E_p V$ vs SCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>6061</td>
<td>-0.669</td>
</tr>
<tr>
<td>6013</td>
<td>-0.688</td>
</tr>
<tr>
<td>2024</td>
<td>-0.540</td>
</tr>
<tr>
<td>5456</td>
<td>-0.695</td>
</tr>
</tbody>
</table>

The pitting potentials of Al–2.5 wt% Mg–(0.1–0.3) wt% Sc alloys show the more positive values in comparison with those of commercial Al–Mg alloys. It indicates a good pitting resistance of Al–2.5 wt% Mg–(0.1–0.3) wt% Sc alloys. The pitting morphologies of Al–2.5 wt% Mg–(0–0.3) wt% Sc alloys are shown in Figure 1.15. The alloys exhibit irregular crystallographic pits with small pitting depths. Pits on the alloy surface are covered by Al(OH)$_3$ (Figure 1.15 (d)).

![Figure 1.15](image1.png)

Figure 1.15. SEM micrographs showing crystallographic pitting of: (a) Al–2.5Mg, (b) Al–2.5Mg–0.1Sc, (c) Al–2.5Mg–0.15Sc, and (d) SEM micrographs of Al–2.5Mg–0.15Sc showing covering of pits by gelatinous Al(OH)$_3$ [98].

The effect of Al$_3$Sc particles on the initiation and propagation of pitting corrosion in 0.1 M NaCl of Al–Sc alloys was studied by Cavanaugh et al. [101]. The results showed that Al$_3$Sc exhibits a good electrochemical
compatibility with Al alloys and consequently better corrosion resistance than other common dispersoid intermetallic compounds in Al alloys as Al\(_6\)Mn, Al\(_3\)Zr and Al\(_3\)Ti. The comparison of the distribution of corrosion potential between Al\(_3\)Sc and other dispersoid intermetallic compounds is shown in Figure 1.16. Figure 1.17 illustrates the oxygen reduction reaction rate at −950 mV\(_{SCE}\) of dispersoid intermetallic compounds in 0.1 M NaCl solution. This figure shows that oxygen reduction reaction rate of Al\(_3\)Sc is slowest in comparison with others.

![Figure 1.16. Distribution of corrosion potentials of Al\(_3\)Sc, Al\(_3\)Ti, Al\(_3\)Zr and Al\(_6\)Mn [101].](image)

![Figure 1.17. Magnitude of cathodic current sustained by Al\(_3\)Sc, Al (99.9999), Al\(_3\)Zr, Al\(_6\)Mn and Al\(_3\)Ti at a potential of −950 V\(_{SCE}\) in 0.1 M NaCl [101].](image)
1.2.5 Al–Sc–REMs alloys

An element that substitutes for Sc in Al,Sc should have the following characteristics if it is to be effective for high-temperature applications:

- to facilitate precipitation from a solid solution, it should have solubility in $\alpha$–Al on the order of hundreds of ppm at the alloy homogenization temperature, but low solubility at aging and service temperatures [32];
- to limit the rate of precipitate coarsening, it should have a small diffusivity in $\alpha$–Al;
- to increase creep resistance, it should increase the lattice parameter mismatch to maximize elastic interactions between precipitates and dislocations;
- to decrease the price of the alloy, it should be less expensive than Sc.

Many of these characteristics exhibited by the rare-earth metals (REMs) are attractive ternary additions because:

- many REMs substitute for Sc in the Al,Sc precipitates forming Al$_3$(Sc$_{1-x}$REM$_x$) (L1$_2$ structure) with a high solubility, thereby replacing the more expensive Sc [103,104];
- the light REMs have a smaller diffusivity in Al than Sc [105], improving the coarsening resistance of the precipitates;
- however, both the light REMs and ytterbium (Yb) have a larger diffusivity in Al [16] than Zr or Ti [28], so that the REM atoms are incorporated into the L1$_2$ precipitates with faster kinetics than the Zr or Ti atoms;
- unlike Ti or Zr [30], REMs increase the lattice parameter mismatch between $\alpha$–Al and Al$_3$(Sc$_{1-x}$REM$_x$) [103,104], which could increase the creep resistance of the alloy [31];
- from Table 1.8 the electronegativity difference between Al and Sc is small, which suggests that the bonding between the two is predominantly metallic or covalent. Most of the REMs have electronegativity values very similar to Sc, in where Y and Gd through Tm being the closest. This comparability suggests that these metals should strongly resemble Sc in their interaction with Al. The metallic radii of all RE metals are significantly larger than Sc. The closest in size of RE metals with Sc are Y and the series Gd though. This characteristic lead RE metals increase the lattice parameter mismatch between $\alpha$–Al and Al$_3$(Sc$_{1-x}$REM$_x$).
Sawtell and Morris [107,108] found that additions of 0.3 at% Er, Gd, Ho, or Y improve the ambient-temperature tensile strength of Al–0.3 at% Sc by 11-23%. Both Sc and the REMs exceeded their maximum equilibrium solid solubility, which, in the binary alloys, occurs at the eutectic temperatures of 639–655 °C for the various RE elements and 660 °C for Sc [109]. The samples were chill-cast with mildly rapid solidification rates of 10–100 Ks⁻¹. Since the Sc and REMs were supersaturated, the alloys in this study were not homogenized. The peak-aged tensile strength at room temperature, when compared to that of binary Al–0.3 at% Sc, was found to be up to 25% greater. Very small precipitates were observed by TEM after aging, which were assumed to be Al₃(Sc₁₋ₓREMₓ). Therefore, the increased strengthening provided by the addition of 0.3 at% REM was attributed to an increase in volume fraction, strength and stability of Al₃(Sc₁₋ₓREₓ) precipitates.

Dunand and Seidman et al. [30,110-116] have paid a lot of attention to ternary Al–0.06Sc–0.02REM alloys (at%, REM = Y, Sm, Gd, Dy, Er, Yb, Tb, Ho, Tm or Lu). It was shown that REMs substitute for Sc in the nanoscale L1₂ trialuminide precipitates, resulting in an aging Vickers hardness response at 300 °C generally similar to that of a binary Al–0.08Sc alloy with the same solute concentration. The incubation time, peak hardness, and over-aging behaviour were mostly unaffected by the partial replacement of Sc by REM. Several exceptions were noted. First, Al–Sc–Sm and Al–Sc–Gd alloys have

Table 1.8. Radii and electronegativity for various metals [106]

<table>
<thead>
<tr>
<th>Metal</th>
<th>Atomic number</th>
<th>Metallic radius (nm)</th>
<th>Electronegativity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>13</td>
<td>0.143</td>
<td>1.61</td>
</tr>
<tr>
<td>Sc</td>
<td>21</td>
<td>0.162</td>
<td>1.36</td>
</tr>
<tr>
<td>Y</td>
<td>39</td>
<td>0.1802</td>
<td>1.22</td>
</tr>
<tr>
<td>Ce</td>
<td>58</td>
<td>0.182</td>
<td>1.12</td>
</tr>
<tr>
<td>Pr</td>
<td>59</td>
<td>0.182</td>
<td>1.13</td>
</tr>
<tr>
<td>Nd</td>
<td>60</td>
<td>0.182</td>
<td>1.14</td>
</tr>
<tr>
<td>Sm</td>
<td>62</td>
<td>0.182</td>
<td>1.17</td>
</tr>
<tr>
<td>Gd</td>
<td>64</td>
<td>0.1801</td>
<td>1.20</td>
</tr>
<tr>
<td>Tb</td>
<td>65</td>
<td>0.1782</td>
<td>1.20</td>
</tr>
<tr>
<td>Dy</td>
<td>66</td>
<td>0.1773</td>
<td>1.22</td>
</tr>
<tr>
<td>Ho</td>
<td>67</td>
<td>0.1765</td>
<td>1.23</td>
</tr>
<tr>
<td>Er</td>
<td>68</td>
<td>0.1757</td>
<td>1.24</td>
</tr>
<tr>
<td>Tm</td>
<td>69</td>
<td>0.1720</td>
<td>1.25</td>
</tr>
<tr>
<td>Yb</td>
<td>70</td>
<td>0.179</td>
<td>1.10</td>
</tr>
<tr>
<td>Lu</td>
<td>71</td>
<td>0.174</td>
<td>1.27</td>
</tr>
</tbody>
</table>
lower peak strengths than Al–0.08Sc due to the lower solubility of these elements in Al,Sc as compared to the other REMs studied, and due to the precipitation of micron-scale Al–Sm precipitates at the grain boundaries in the Al–Sc–Sm alloy. Second, a very rapid initial increase in the Vickers hardness of Al–Sc–Yb occurred, attributed to the experimentally observed clustering of Yb atoms at early aging times (including the as quenched state). Third, ATP studies demonstrated that Er and Gd (and therefore probably also the other REMs) partitioned to the Al(Sc1-xREMx) precipitates and segregated at their cores [117]. The maximum solid solubilities in α-Al, as measured by APT of Er is 0.0461 ± 0.0006 at% and Yb is 0.0248 ± 0.0007 at% at 640 and at 625 °C, respectively. Both values are smaller than the maximum solubility of Sc in Al (0.23 at%). Hence, the maximum volume fraction of Al2Yb (φ=0.11%) or Al2Er (φ=0.14%) precipitates is smaller than that of Al2Sc (φ=0.95%) in binary alloys. As compared to Sc, two REM Er and Yb have diffusivity in Al (Al–0.045 Er and Al–0.03 Yb alloys, at%) at 300 °C much significantly greater ((4 ± 2) x 10^-19 m^2 s^-1 for Er, (6 ± 2) x 10^-17 m^2 s^-1 for Yb and 9 x 10^-20 m^2 s^-1 for Sc) [110]. The value for diffusivity of Yb in Al is larger in comparison with Er and five lighter lanthanides (La, Ce, Pr, Nd and Sm) which were extrapolated to 300 °C from data obtained above 450 °C [105, 113, 118]. The Al/Al,REM interfacial free energies, γ_{Al/Al,REM}, calculated from the isothermal coarsening data at 300 °C, are γ_{Al/Al,Tb} = -0.4 ± 0.2 and γ_{Al/Al,Er} = -0.6 ± 0.3 J m^-2, both of which are greater than γ_{Al/Al,REM} ≈ 0.2 Jm^-2 [29]. These results lead REM to the rapid decomposition of the supersaturated solid-solution and growth of the precipitates in α-Al.

In the study of Krug et al. [113], four ternary Al–0.08Sc–0.02REM alloys (at.%, REM = Tb, Ho, Tm or Lu) were cast, homogenized at 640 °C, and aged at 300 °C, resulting in nanoscale Al(Sc,REM) precipitates responsible for increases in Vickers hardness. The microstructures of the alloys aged for 10 min and 24 h were investigated by ATP. The incubation times and thus the early age hardening behavior of the present Al–0.06Sc–0.02REM (where REM = Tb, Ho, Tm or Lu) fall between those of Al–0.06Sc–0.02Yb and Al–0.06Sc–0.02Er, suggesting that diffusivity of these REMs stays between Er and Yb [113].

In another aspect, Yb has a lower melting temperature (824 °C) than Er (1497 °C) and the other lanthanides, which increase from 920 to 1545 °C with increasing atomic number, Z, with the exceptions of Ce (795 °C), Eu (826 °C) and Yb. Also, Yb is the only REM with a face-centered cubic crystal structure; all other REMs have a hexagonal close-packed structure except for the body-centered cubic Eu and the trigonal Sm. Finally, Yb has an anomalous valence state in Al compared with the other lanthanides (again except Eu) and has much different enthalpies of formation for the Al,REM and Al,REM phases.
1.2.6 Grain refinement of Al alloys

1.2.6.1 Grain refinement of Al–Sc alloys

A limited-solubility eutectic diagram of Sc with Al was shown in Figure 1.1. The maximum solid solubility of Sc in $\alpha$–Al is 0.38 wt% and the eutectic composition is 0.55 wt% of Sc. The grain refinement effect of Sc occurs in hypereutectic alloys which the Sc content exceeds 0.55 wt%. In these alloys the Al$_3$Sc particles are the first phase to form in the melt during casting process. The lattice parameter of Al$_3$Sc is close to that of Al showing the small lattice parameter mismatch of them. Moreover the L1$_2$ structure of Al$_3$Sc is an ordered structure that based on the FCC structure of $\alpha$–Al with Sc atoms at the face centres of the unit cell. These characteristics conduct Al$_3$Sc particles act as potent sites for the heterogeneous nucleation of $\alpha$–Al grains [44]. Many researches have reported that very fine grains structure in aluminium alloys was obtained by adding Sc [44,45,119-125]. Those studies demonstrated that approximate 0.7 wt% Sc is sufficient to provide excellent grain refinement.

In ternary and higher order systems, the eutectic Sc composition may depend on the present of other alloying elements. In the ternary Al–Mg–Sc system, the eutectic composition of Sc probably decrease with the increase of Mg content [63]. A good grain refinement was observed in Al–7Mg–0.5Sc (wt%) alloy [126]. It is also observed that grain refinement is obtained at low Sc contents by adding Sc together with Zr. The addition of 0.25 wt% Sc + 0.25 wt% Zr provides good grain refinement in pure Al [44]. Adding 0.2 wt% Sc + 0.1 wt% Zr to Al–5 wt% Mg alloys provides a finer grain size structure than adding either 0.2 wt% Sc, 0.6 wt% Sc or 0.1 wt% Zr [127]. Effect of Sc on grain size of Al–Sc and in an Al–Zn–Mg–Sc–Zr alloy is shown in Figure 1.18 [5]. The comparison of grain refinement with Sc content from 0.05 to 1.2 wt% shown in Figure 1.19 was reported by Zhang et al. [125].

![Figure 1.18. Grain refinement as a function of Sc addition in pure Al and Al–Zn–Mg–Zr [5].](image-url)
1.2.6.2 Grain refinement mechanisms of Al alloys by adding Al–Ti–B grain refiner

In order to understand the grain refinement mechanism in Sc-containing Al alloys, we summarized the grain refinement mechanism of Al alloys by adding Al–Ti–B grain refiner that is quite similar with Al–Sc system. The proposed mechanisms for grain refinement can be divided into two groups:

- First is “nucleant paradigm” which proposed that the nucleant particle plays the most important role. The nucleant paradigm includes the following theories:
  - Boride/carbide theory
  - Phase diagram/peritectic theory
  - Peritectic hulk theory
  - Hypernucleation theory
  - Duplex nucleation theory

- Second, called “solute paradigm” which assumed that the solute elements will decide a fine grained microstructure. According to the solute paradigm, the grain refinement mechanisms are driven by constitutional undercooling.
(i) Nucleant paradigm

- Boride/carbide theory

The boride/carbide theory was first proposed by Cibula [128]. According to this theory, TiC and/or TiB₂ crystals nucleate solid aluminium by heterogeneous nucleation after the addition of Al–Ti–B master alloy. The added Ti and carbon impurities always present in the melt will react to form TiC. Soon after the addition of the master alloy, the TiAl₃ particles begin to dissolve rapidly, thereby creating a constitutionally favourable growth condition for α-Al to grow on these TiB₂ and TiC particles.

- Phase diagram/peritectic theory

This theory in Al–Sc alloys was known as phase diagram/eutectic theory that was used to explain the grain refinement in hypereutectic Al–Sc alloys.

The peritectic nucleation theory proposed that grain refinement is achieved by a peritectic reaction of transition elements such as Ti, Sc, Zr, Cr, Mo and W with Al. According to Al–Ti phase diagram, the reaction in the melt of Al alloys containing Ti can occur as follows:

\[
\text{Al (liquid)} + \text{TiAl₃} \rightarrow \text{Al (solid with titanium in solid solution)}
\]

The peritectic reaction occurs at approximately 665°C at a minimum concentration of 0.15 wt% Ti. The TiAl₃ particles will act as nuclei sites for heterogeneous nucleation of α-Al grain. A layer of α-Al then forms and completely encloses the surface of the particle. Figure 1.20 shows the aluminium-rich side of the Al–Ti phase diagram with the peritectic point at 1.2 wt% Ti and 665°C.

The big problem of this theory is that could not explain the grain refinement in Al alloys when the content of Ti is lower than 0.15 wt%. Delamore and Smith [129] suggested that probably TiAl₃ nucleates aluminium heterogeneously without any peritectic reaction. Marcantino and Mondolfo [130] proposed that, the existence of boron can shift in the peritectic reaction to a composition below 0.15 wt% Ti. They suggested the ternary Al–Ti–B peritectic reaction as follows [130]:

\[
\text{Liquid} \rightarrow (\text{Al, Ti})\text{B}_{2} + \text{TiAl}_3 + \text{Solid}
\]
Figure 1. Detail of Al–Ti phase diagram showing the minimum Ti content for the peritectic reaction at 0.15% and 665°C [131].

However, there is no experimental record that can prove those suggestions. Theoretical thermodynamic analyses from Jones and Pearson [132] and Sigworth [131,133] study has shown that ternary peritectic does not occur. Another problem came from Johnsson and Backerud [134] study that indicated that Al₃Ti would dissolve into the melt. They suggested that Al₃Ti would take less than 1 minute to dissolve at 775 ± 10 °C. According Backerud et al. [135], a spherical Al₃Ti with size of 20 µm would dissolve into the melt in 3–4 seconds.

**Peritectic Hulk theory**

The peritectic hulk theory was proposed by Backerud et al. [135] and Vader and Noordegraaf [136]. This theory suggested that Al₃Ti is a more powerful nucleant than TiB₂. According to the peritectic hulk theory, TiB₂ shell will be formed around the Al₃Ti and therefore slow down the dissolution of Al₃Ti. The Al₃Ti dissolves inside of TiB₂ shell to form the liquid with the higher content of Ti than other sites. The peritectic reaction occurs and α-Al could be nucleated and grown [137]. However, TiB₂ shells existed more often in Al grains than at the centre of grains at hypopretectic concentrations [138]. Indeed, the peritectic hulk theory is not evident to explain the grain refinement properly.

**The hyper-nucleation Theory**

The hyper-nucleation theory was proposed by Jones [139] which suggested that:

- melt solutes can segregate stably to the interface of the melt-inoculants;
- with the right conditions, stable pseudo-crystals can be created even above the liquidus;
- immediately below the liquidus these pseudo crystals allow nucleation and growth of α-Al;
- the atomic size of the segregant element relative to aluminium is a key factor in hyper nucleation;
- competitive segregation of solutes with mismatching size can poison the process.

According this theory, TiB₂ creates an activity gradient that leads Ti atoms to segregate at the TiB₂/melt interface. The preitectic reaction would occur and a thin layer of TiAl₃ could be formed on the TiB₂ particles that can act as nuclei sites for α-Al grains. But the main problem of this theory is that there is no evident experimental result to prove it.

### **Duplex nucleation theory**

This theory was proposed by Mohanty et al. [34,140] and further convincing evidence has been provided by Greer and Schumacher and co-workers [141,142]. The theory suggested that at a hyperperitectic composition of Ti, Al₃Ti layer was formed on the surface of TiB₂ and around which was an α-Al layer. However, at a hypoperitectic concentration of Ti, Al₃Ti layer existed in between the TiB₂ and α-Al. The formation of Al₃Ti could be due to the adsorption effect at the boride/aluminide interface but the stability of this layer has not been confirmed. Johnsson et al. [143] measured the nucleation and growth temperature across the Al-Ti phase diagram and mentioned that the liquid adjacent to the Al₃Ti needs to be 0.15 wt% Ti which means the nucleation temperature should correspond to the nucleation temperature at the peritectic concentration. For an alloy containing 0.05 wt% Ti this means the nucleation temperature should be 3 °C above the liquidus temperature and the duplex nucleation theory would fail to explain this.

#### (ii) **Solute paradigm**

This theory was proposed by Johnsson et al. [143] which suggested that nucleants and segregating solutes are two main factor to control grain refinement. The solute paradigm was based on the constitutional undercooling mechanism. The equiaxed crystal can nucleate in the solute-enriched liquid ahead of a growing solid/liquid interface. Solute elements like Ti, Si and Fe have a restrictive effect on the solidifying metal. They segregate to the nucleant/melt interface and restrict the growth of dendrites. They build up a constitutionally undercooled zone in front of the interface [137] that facilitates nucleation and produce nuclei for α-Al grains. A schematic of constitutional undercooled zone in front of the interface mechanism was shown in Figure 1.21.
The growth-restricting factor (GRF) measures the growth restricting effect of solute elements on the growth of the solid-liquid interface of the new grains in the melt. It was used to evaluate the segregation potential of elements. Solute elements like Ti, Si and Fe have been found to restrict dendrite growth and their GRFs prove more clearly for that observation. Particularly, Ti showed a strong tendency to segregate that lead to more effective on grain refinement.

Many researches have studied the effect of solute elements on grain refinement through controlling the growth with the growth–restriction parameter $Q$ [144-146]. Maxwell and Hellawell [146] investigated the effect of the number of nucleant particles and the amount of solute on grain refinement. The evaluation was based on the nucleant potency, cooling rate, nucleant particle size and segregating potency of the solute elements. They predicted that GRF has the largest effect on grain size of alloys. The effect of GRF on grain size was shown in Figure 1.22. This paradigm could explain why TiB$_2$ has no grain refinement effect when adding into the alloys. Because there are no segregating elements and constitutionally undercooled zone to promote nucleation in front of the interface does happen.

Figure 1.21. Constitutional undercooled zone in front of the interface. The size of the zone depends on the nucleant and the constitution of the melt [137].

Figure 1.22. Graph from Spittle and Sadli’s grain size data plotted against the GRF [137].
(iii) Summary

Table 1.9 summarises all theories above and describes the nucleating substrate and the effect of solute on grain refining in each case. However, the mechanism of grain refinement is still not clear and considerable controversy still surrounds this issue.

<table>
<thead>
<tr>
<th>Theory</th>
<th>Nucleating substrate</th>
<th>Effect of solute in grain refining performance</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>The nucleant paradigm</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Boride diagram theory</td>
<td>On borides or carbides</td>
<td>None, except some suggest Ti as a powerful segregant restricts growth of grains, which allows for further nucleation events.</td>
</tr>
<tr>
<td>Phase diagram theories</td>
<td>Via peritectic reaction</td>
<td>Ti is present to form Al$_3$Ti, which acts as nucleant.</td>
</tr>
<tr>
<td>Peritectic hulk</td>
<td>In a Ti-rich boride shell via the peritectic reaction</td>
<td>Ti present in the boride shell after Al$_3$Ti dissolution at the peritectic concentration.</td>
</tr>
<tr>
<td>Hypernucleation</td>
<td>On borides</td>
<td>Ti segregates down an activity gradient to the boride to provide a suitable interface for nucleation of $\alpha$-Al</td>
</tr>
<tr>
<td>Duplex nucleation</td>
<td>On Al$_3$Ti, which is formed on the surface of TiB$_2$ particles</td>
<td>Ti is present to segregate to TiB, down an activity gradient to form Al$_3$Ti on the surface, which then nucleates Al.</td>
</tr>
<tr>
<td><strong>The solute paradigm</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Undercooling-driven mechanism</td>
<td>Borides (or other particles)</td>
<td>Solute affects dendrite growth and builds up constitutionally undercooled zone in front of the interface. This undercooled zone facilitates nucleation and the new grain does the same to the next grain. The shape and magnitude of the constitutionally undercooled zone depend upon the dendrite growth, which is affected by solute, which in turn affects the subsequent nucleation behaviour.</td>
</tr>
</tbody>
</table>
1.2.6.3 Grain refinement mechanism by ultrasonic treatment

Three mechanisms have been proposed to explain for grain refinement by ultrasonic treatment:

- Cavitation-enhanced heterogeneous nucleation.
- Cavitation-induced dendrite fragmentation.
- Vibration-stimulated separation of wall crystals.

i) Cavitation-enhanced heterogeneous nucleation

The cavitation-enhanced heterogeneous nucleation was explained through three mechanisms:

- The first mechanism is based on the promotion of the wetting behaviour of second phase particles with the melt due to cavitation bubbles collapse. When ultrasonic vibration was applied into the melt, a large number of cavitation bubbles were formed and dispersed in the whole of the melt. The collapse of cavitation bubbles in the vicinity of second phase particles leads to produce locally high temperature, pressures and melt flows [147]. The pressures pulse promotes filling of the cracks (capillaries) on the surface of second phase particles by the melt and improves the wetting of those particles with the melt [148]. According to Easton and StJohn [149], the higher wettability of substrates with the melt leads to the smaller free energy barrier for nucleation even at relatively low undercooling. As a consequence, these substrates will acts as effective nucleation sites and enhance the nucleation [147].

- The second mechanism is based on the pressure pulse melting point where the pressure pulse generated from the cavitation bubbles collapse conducts the increasing of melting point according to the Clausius-Clapeyron equation [147,150]. Consequently, the localized undercooling occurs that leads to promote nucleation throughout the melt.

- The third mechanism explained that the expansion of gas inside the cavitation bubbles leads to increase the bubble size and decrease the bubble temperature [150,151]. This phenomenon resulted in undercooling of the melt and form nuclei on the surface of bubbles. When these bubbles collapsed, a significant number of nuclei were produced into the melt and promoted heterogeneous nucleation in the melt.

ii) Cavitation-induced dendrite fragmentation

In the cavitation-induced dendrite fragmentation mechanism, fragmentation of dendrites occurred by the shock waves that were generated from bubbles collapse. These fragments were distributed throughout the melt by acoustic streaming which leads to increase the number of solidification sites [147,152,153].
### iii) Vibration-stimulated separation of wall crystals

The ultrasonic treatment increased the wettability of the mould wall with the melt that resulted in the promotion of nucleation on the mould wall [154]. The local shaking and/or shearing during ultrasonic vibration conducted the separation of the nuclei from the mould wall into the whole of the melt. Due to this trend, the number of nucleation sites was increased and hence grain refinement was obtained.

### 1.2.7 Application of Sc-containing Al alloys

Sc-containing Al alloys have been used in a wide range of applications. They are potentially applied in automotive and aerospace for wheels, running gear, seat tracks, bumpers, frames, pistons and fuel and exhaust systems. Some of Sc-containing Al alloys are used in MiG 29 fighter aircrafts. Al–Mg–Sc and Al–Mg–Li–Sc alloys have been evaluated to use in structural applications of Airbus airplanes. AirLite ScTM handgun produced by Smith & Wesson is made by Sc–containing Al alloys. Due to a good corrosion resistance, Sc–containing Al alloys can be used in a saltwater environment as heat exchanger tubes in desalination plants.

Ashurst Technology has succeeded to produce sports equipment by Sc–containing Al alloys as bicycle frames, baseball/softball bats, and lacrosse sticks. Using Sc–containing Al alloys in bicycle frames lead to reduce 12% of weight, increase 50% of yield strength and 24% of fatigue in comparison with best-selling aluminium bicycle. Alloy designated Sc7000 and Sc 61.10 A have been used in bicycle frame tubing by Easton Bicycle Products Group and Dedacciai (Italian bicycle tubing manufacturer), respectively. Aluminium alloys designated Sc500 by Ashurst Technology and Sc777 by Kaiser Aluminium have been used in baseball/softball bats by Easton. Sc777 is used three new lines of baseball/softball bats: Sc777 Triple Seven series, Sc777 Z-Core series and Sc777 ConneXion series. Sc containing Al alloys designated C555 was produced by Alcoa that was used in baseball/softball bats by DeMarini, Louisville Slugger and Worth manufacturers. All of those alloys above are Al–Zn–Mg–Sc alloys. Hawk series of baseball/softball bats from Nike also are made from Sc containing alloy designated ScX. STX is a major Lacrosse equipment manufacturer. They produced Lacrosse stick handles from Sc–containing Al alloys provided by Ashurst Technology and Kaiser Aluminium. Birdland, an outdoor equipment manufacturer, have introduced a series of lightweight tents, Colibri made from Sc-containing Al alloys that is designated Alu–SC.
References


[91] Ferry M, Burhan N. Microstructural evolution in a fine-grained Al-0.3wt% Sc alloy produced by severe plastic deformation. Scri. Mater. 2007;56:525-8.


[106] JCPDS-International Centre for Diffraction Data


[112] van Dalen ME, Dunand DC, Seidman DN. Microstructural evolution and creep properties of precipitation-strengthened Al–0.06Sc–0.02Gd and Al–0.06Sc–0.02Yb (at.%) alloys. Acta Mater. 2011;59:5224-37.

[114] Knipling KE, Karnesky RA, Lee CP, Dunand DC, Seidman DN. Precipitation evolution in Al–0.1Sc, Al–0.1Zr and Al–0.1Sc–0.1Zr (at.% alloys during isochronal aging. Acta Mater. 2010;58:5184-95.


[116] Dalen ME, Dunand DC, Seidman DN. Nanoscale precipitation and mechanical properties of Al-0.06 at.% Sc alloys microalloyed with Yb or Gd. J. Mater. Sci. 2006;41:7814-23.


Effects of substituting rare earth metals for scandium on the microstructure and properties of Al-Sc and Al-Mg-Sc alloys

CHAPTER 2 - EXPERIMENTAL PROCEDURES
Chapter 2 – Experimental Procedures

The following chart (Figure 2.1) outlines the experimental procedures of research.

**Starting materials:**
- pure Al, pure Yb, master alloys of Al–2% wt% Sc, Al–20% wt%Mg

**Composition of processed alloys (wt%)**
1) Al–0.28Sc
2) Al–0.24Sc–0.07Yb
3) Al–(1, 4)Mg
4) Al–(1, 4)Mg–0.3 Sc
5) Al–4Mg–0.24Sc–0.06Yb

**Casting**
- Pouring Temperature: 720 °C in air. For grain refinement study, pouring temperature varies from 680–800 °C
- Copper mold and water cooling

**Isochronal Aging**
- Ambient: In air
- Temperature: increments 50 °C
- Period time: 2h
- Vickers hardness

**Isothermal Aging**
- Ambient: In air
- Temperature: 300, 325, 350 °C
- Holding time: 10 min. – 1 week

**Microstructure and mechanical characterization**
- Microstructural characterization: OM, FEG-SEM/EDS, TEM, HRTEM
- Mechanical properties: Vickers hardness

**Corrosion tests**
- Immersion test: Open Circuit potential (OCP) measurement
- Potentiodynamic polarization

*Figure 2.1. Outline of the research experimental procedure.*
2.1 Alloys processing

2.1.1 Al–Sc and Al–Sc–Yb alloys

Al–0.28Sc and Al–0.24Sc–0.07Yb (wt%) alloys were cast by using commercially pure Al (99.83 wt% purity), Al–2 wt% Sc master alloy and pure Yb (99.99 wt% purity). The alloys were melted in a graphite crucible using a high frequency induction furnace. For each alloy, pure Al was firstly melted at 720 °C ± 5. Then the Al–2 wt% Sc master alloy and pure Yb were added into the melt. The melt was kept at this temperature for 30 minutes and stirred with an alumina rod to ensure homogeneity. The molten alloys were poured into cylindrical copper moulds with 16 mm in diameter and 80 mm in length and water cooled. All the ingots were cut into several samples with size of 16 mm in diameter and 6 mm in length. Position of the analysed sections on the sample was shown in Figure 2.2. Samples from the centre of each ingot were used for microstructure characterization.

\[
\begin{align*}
\text{(I)} & \quad \text{Top View} \\
\text{(II)} & \quad \text{Cut Plane}
\end{align*}
\]

Figure 2.2. Position of the analysed sections on the sample.

The composition of the as-cast alloy was measured by X-ray Fluorescence Spectrometry (Bruker S8 Tiger). The chemical composition of the as-cast alloys is given in Table 2.1.

| Table 2.1. Chemical composition of the Al–0.28Sc and Al–0.24Sc–0.07Yb as-cast alloys |
|-----------------|------|------|------|------|------|------|------|------|------|------|
| Alloy           | Sc   | Yb   | Si   | Fe   | Ni   | Cu   | Ba   | Mn   | Ti   | Al   |
| Al–Sc           | wt%  | 0.283| -    | 0.383| 0.130| 0.010| 0.007| 0.060| 0.010| 0.009| Bal  |
|                 | at%  | 0.170| 0.369| 0.063| 0.005| 0.003| 0.012| 0.005| 0.005| Bal  |
| Al–Sc–Yb        | wt%  | 0.243| 0.068| 0.328| 0.208| 0.040| 0.032| 0.015| -    | -    | Bal  |
|                 | at%  | 0.146| 0.011| 0.316| 0.101| 0.018| 0.014| 0.003| -    | -    | Bal  |
2.1.2 Al–Mg–Sc and Al–Mg–Sc–Yb alloys

Al–4Mg, Al–4Mg–0.3Sc, and Al–4Mg–0.24Sc–0.06Yb (wt%) alloys were cast by using commercially pure Al (99.83 wt% purity), Al–2 wt% Sc and Al–20 wt% Mg master alloys as melting stock. The proper weights of these starting materials were melted in an electrical resistance furnace equipped with a SiC crucible. For each alloy pure Al was firstly melted at 800 ± 5 °C followed by addition of the master alloys. The melt was kept at this temperature for 30 minutes and stirred with an alumina rod to ensure homogeneity. The melt was then cooled down and poured at 720 ± 5 °C. Before pouring, the melt was degassed by argon gas purging. Casting was carried out in the same copper mould above and immediately cooled to room temperature by immersion into water. The composition of the as-cast alloy was measured by X-ray spectrometer (X'Unique II, Philips). The chemical compositions of the as-cast alloys are given in Table 2.2.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Mg</th>
<th>Sc</th>
<th>Yb</th>
<th>Si</th>
<th>Fe</th>
<th>Cu</th>
<th>Zn</th>
<th>Cr</th>
<th>Mn</th>
<th>Ti</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al–4Mg</td>
<td>3.93</td>
<td>-</td>
<td>-</td>
<td>0.128</td>
<td>0.228</td>
<td>0.024</td>
<td>0.015</td>
<td>-</td>
<td>0.008</td>
<td>-</td>
<td>Bal</td>
</tr>
<tr>
<td>Al–4Mg–0.3Sc</td>
<td>3.86</td>
<td>0.291</td>
<td>-</td>
<td>0.15</td>
<td>0.325</td>
<td>0.031</td>
<td>0.018</td>
<td>0.03</td>
<td>-</td>
<td>0.011</td>
<td>Bal</td>
</tr>
<tr>
<td>Al–4Mg–0.24Sc–0.06Yb</td>
<td>3.91</td>
<td>0.235</td>
<td>0.071</td>
<td>0.177</td>
<td>0.358</td>
<td>0.029</td>
<td>0.023</td>
<td>0.022</td>
<td>0.012</td>
<td>0.007</td>
<td>Bal</td>
</tr>
</tbody>
</table>

2.1.3 Casting for grain refinement study

**Step 1:** In order to study the effect of Mg and Sc on grain refinement of Al–Mg–Sc alloys, Al–1Mg, Al–4Mg, Al–0.3Sc, Al–1Mg–0.3Sc and Al–4Mg–0.3Sc (wt%) alloys were cast by using commercially pure Al (99.83 wt% purity), Al–2 wt% Sc and Al–20 wt% Mg master alloys as melting stock. The casting in this step was performed by the same procedure referred in Section 2.1.2. The different thing is pouring temperature which was 700 ± 5 °C.

**Step 2:** The effect of pouring temperature on grain refinement of Al–1Mg–0.3Sc (wt%) alloy was performed. Al–1Mg–0.3Sc alloys were prepared by the same procedure referred above (Step 1) and poured at different temperatures ranging from 680 ± 5 °C to 800 ± 5 °C.

**Step 3:** In step, the effect of ultrasonic treatment on grain refinement of Al–1Mg–0.3Sc (wt%) alloy at a wide range of pouring temperatures was evaluated. The experimental set-up (Figure 2.3) used in this work consisted of a novel MMM (Multi-frequency, Multimode, Modulated technology) ultrasonic power supply.
unit, a high power ultrasonic converter (1200W), a 30mm diameter and 150mm long acoustic waveguide and the acoustic load itself which consists on a 20mm diameter and 75mm long Nb acoustic radiator and the melt.

![Figure 2.3. Schematic representation of the experimental setup used in the experiments ((1) SiC Crucible, (2) the melt and (3) Acoustic radiator).](image)

Melting stocks of Al–1Mg–0.3Sc consisted of commercially pure Al (99.83 wt% purity), Al–2 wt% Sc and Al–20 wt% Mg master alloys. Suitable masses of these starting materials were melted in a SiC crucible, using an electrical resistance furnace. For each alloy, pure Al was firstly melted at 800 ± 5 °C. Then the master alloys were added into the melt. The melt was kept at this temperature for 30 minutes and stirred with an alumina rod to ensure homogeneity. The melt was cooled down to different temperatures ranging from 800 ± 5 °C to 700 ± 5 °C and the sonotrode was preheating to avoid a drop in temperature of the melt when applying ultrasonic vibration. Ultrasonic frequency of 20.3 ± 0.25 kHz at electric power of 30 % for 30 s was applied for each processing condition. After ultrasonic treatment, the molten alloy was poured into a copper mould and immediately cooled to ambient temperature by immersion in water.

### 2.2 Heat treatments

Samples for this step were taken from section I and II (Figure 2.2).

The effect of homogenization treatment and aging temperature on precipitation behaviour and age hardening response of Al–0.28Sc and Al–0.24Sc–0.07Yb was investigated. Two separate studies were conducted: in one, the as-cast alloys were treated at 640 °C for 72 h for homogenization and water quenched to room temperature. The samples were subsequently treated at various temperatures within the
range 150 to 375 °C for 2 h, followed by water quenching to ambient room temperature; in the other, the same procedure without homogenization treatment was carried out.

In order to evaluate the aging kinetics of Al–Sc, Al–Sc–Yb, Al–Mg–Sc, and Al–Mg–Sc–Yb alloys, isothermal aging without homogenization treatment of the cast samples was carried out. The samples were aged at different temperatures between 300 and 350 °C for times ranging from 10 minutes to 7 days.

Vickers hardness was used to monitor the hardening behaviour. Vickers hardness measurements were performed at room temperature using 30 kg load and 20 second dwell time. Eight measurements were performed on each sample.

### 2.3 Microstructural characterization of the alloys

Several techniques were used to characterize the microstructure of the alloys. Prior for all analysis the sample were metallographic prepared,

#### 2.3.1 Optical microscopy and scanning electron microscopy

Samples for microstructural characterization were taken from each cast sample by sectioning them perpendicularly to its longitudinal axis (S1 in Figure 2.2). The samples were ground with SiC paper, polished down using non-crystallizing colloidal silica suspension.

For optical microscopy analysis the samples were anodised at a voltage of 30 V in a 2.5 % aqueous solution of fluoroboric acid (HBF₄) to reveal grain size. The overall microstructure morphology was analysed by optical microscopy using a Leica DM 2500 M and Image-Pro Plus software was used to quantify the average grain size and grain size distribution.

Scanning electron microscopy (SEM) and Energy Dispersive Spectroscopy (EDS) analysis were done to the as-cast alloys as well as to homogenised alloys in a FEG-SEM equipment (Nano-SEM-FEI Nova 200/EDAX–Pegasus X4 M).

#### 2.3.2 Transmission electron microscopy and high resolution electron microscopy

Transmission electron microscopy (TEM) and high resolution electron microscope (HRTEM) were used to determine the structure, distribution and morphological characteristics of the precipitates. Discs of 3 mm diameter were prepared and mechanically ground to 100 µm. The foils were prepared by double-jet electropolishing in a solution of 25% nitric acid and 75% methanol solution. The specimens were examined by FEI TECNAI G20 or JEOL JEM-2200FS operating at 200 kV. Thin foils for TEM and HRTEM observations were sectioned from the alloys under different conditions.
In order to determine the average diameter and evaluate the number of precipitates, the TEM micrographs were analysed by Image J software. For each condition, four TEM micrographs at various positions of sample with more than 200 precipitates were selected to measure the precipitate size. Image-Pro Plus software was used to quantify precipitates size distribution. Gatan Digital Micrograph software was used to analyse HRTEM images.

2.4 Electrochemical tests

Prior to the electrochemical tests the samples were polished with colloidal silica (0.3 μm) and cleaned ultrasonically 10 min in propanol followed by 5 min in distilled water. The electrochemical tests consisted in open circuit potential (OCP) and potentiodynamic polarisation tests. All electrochemical tests were performed using a conventional three-electrode electrochemical cell adapted from ASTM standard practice G3-89, where 3.5 wt% NaCl (sea water) was used as the electrolyte. A saturated calomel electrode (SCE) was used as the reference electrode, Pt electrode used as the counter electrode, and the samples used as the working electrode, having an exposure area of 0.07 cm². All potentials are given with respect to SCE. All electrochemical tests were performed by using a Gamry Instruments Reference 600™ Potentiostat controlled by the Gamry Instruments Framework™ software (Gamry Instruments, Warminster, PA, USA).

The immersion tests were performed during 96 h (4 days). OCP was measured just after immersion during 30 min and after that, for 15 min during the following each 4 days. Potentiodynamic polarisation measurements started from a cathodic potential of −1.5 V up to the anodic domain (0 V vs. SCE) with a scan rate of 0.5 mV/s. The samples after electrochemical tests were ultrasonically cleaned in hot water to remove the corrosion products. Each test was repeated at least three times and the average value of corrosion potential ($E_{\text{cor}}$), pitting potential ($E_p$), corrosion current density ($i_{\text{cor}}$) were determined by using the software program Gamry Echem Analyst (Version 5.61). The $i_{\text{cor}}$ and $E_{\text{cor}}$ ($E_{\text{p-corr}}$) were determined by extrapolation of the Tafel lines of each polarisation curve.

---

Effects of substituting rare earth metals for scandium on the microstructure and properties of Al-Sc and Al-Mg-Sc alloys

CHAPTER 3 - EFFECT OF Yb SUBSTITUTING FOR Sc ON THE MICROSTRUCTURE AND AGE-HARDENING BEHAVIOUR OF AL–Sc ALLOY

Chapter 3 – Effect of substituting Yb for Sc on the microstructure and age-hardening behaviour of Al-Sc alloys

Introduction

Al–Sc alloys have excellent mechanical properties at ambient and elevated temperatures due to the presence of a high number density (as high as $10^{22}$ m$^{-3}$) of elastically-hard Al$_3$Sc ($L1_2$ structure) precipitates [1-4]. The Al$_3$Sc precipitates remain fully coherent with the $\alpha$–Al matrix at elevated temperatures [1,5]. Among alloying elements of Al alloys, Sc has one of the greatest strengthening effect on a per-atom basis [6]. The Al$_3$Sc precipitates are very stable with respect to coarsening, even for long aging times at 350 °C [1], while in commercial age-hardening 2xxx and 6xxx series alloys containing Cu, Mg and Si, the precipitates coarsen rapidly at temperatures above 250 °C [6]. At ambient temperature the lattice parameters of Al and Al$_3$Sc are 0.40496 and 0.4105 nm, respectively, showing a small lattice parameter mismatch of Al$_3$Sc precipitates with the $\alpha$–Al matrix [7-9]. A good interfacial strength between the Al$_3$Sc precipitates and the $\alpha$–Al matrix will hinder dislocation motion and prevent grain growth [10]. In addition, the high thermal stability of the Al$_3$Sc precipitates will improve the strength of these alloys at high temperature [11,12]. Therefore Al–Sc alloys are widely used in the fabrication of sports equipment, aerospace components and in a range of structural applications.

Although Al–Sc alloys are very attractive, their use is limited by the cost and availability of Sc. A possible solution for this problem could be replacing part of the Sc by other alloying elements similar in nature in order to reduce the Sc content without decreasing properties. Among them, REMs are attractive ternary additions to substitute Sc. Karnesky et al. [13] showed that the Vickers hardness of Al–0.06 at% Sc–0.02 at% REM alloys (REM = Dy, Er, Gd, Sm, Y, or Yb) aging at 300 °C are generally similar to that of Al–0.08 at% Sc alloy. The Al–0.06 at% Sc alloys microalloyed with Yb or Gd have much improved creep resistance when compared to binary Al–Sc or ternary Al–Sc–Zr alloys with the same composition and precipitate radius [14]. According to Sawtell and Morris [15,16], addition of 0.3 at% Er, Gd, Ho, or Y improves the tensile strength of Al–0.3 at% Sc alloys at room temperature.

In this chapter, the microstructure and mechanical properties of Al–0.24Sc–0.07Yb in comparison with Al–0.28Sc alloys were presented. The aging behaviour, precipitate morphologies, precipitate coarsening and precipitation hardening of both alloys were discussed. The average diameter and the size distribution of nanoscale Al,Sc and Al,(Sc,Yb) precipitates at various aging conditions were measured. TEM and HRTEM were used to understand the precipitate evolution.
3.1 Results and discussion

3.1.1 Age Hardening Behaviour of the as-cast Alloys

3.1.1.1 Effect of homogenization treatment and aging temperatures on ageing behaviour

The Vickers hardness curves of Al–0.28Sc and Al–0.24Sc–0.07Yb alloys aged at various temperatures within the range 150 to 375 °C for 2 h with and without homogenization treatment are shown in Figure 3.1. It is evident that the hardness values of the alloys aged in the as-cast condition are significantly higher than those of the alloys homogenized and aged. In the as-cast alloys, Sc and Yb exist in α–Al supersaturated solid solution due to the high cooling rate during solidification. The precipitation of intermetallic particles occurs during the homogenization treatment, reducing the supersaturation level of Sc and Yb in α–Al solid solution. As a consequence, homogenized alloys will have the lower hardening effect due to the lower fraction volume/density of precipitates. Figure 3.2 shows SEM micrographs of as-cast and homogenized Al–0.24Sc–0.07Yb samples. In the homogenized samples, several large particles of intermetallic precipitates were formed and heterogeneously distributed in α–Al.

![Figure 3.1. Vickers hardness curves of Al–0.28Sc, Al–0.24Sc–0.07Yb alloys at various aging temperatures with and without previous homogenization treatment.](image)

Also shown in Figure 3.1 is the effect of substituting 0.07Yb for Sc of Al–0.28Sc alloy on aging behaviour at various temperatures. The onset of age hardening for both alloys occurs at 200 °C. The precipitates form most rapidly at the temperature range of 300-350 °C, for which the highest hardness values were obtained. In the aging process without homogenization treatment, the Vickers hardness value peaks of Al–0.28Sc and Al–0.24Sc–0.07Yb alloys are 72 HV at 325 °C and 68 HV at 350 °C, respectively. A decreasing in Vickers hardness is observed for both alloys for temperatures higher than 375 °C due to the
precipitate coarsening. The results showed that the partial replacement of Sc by Yb did not significantly affect either the kinetics or the peak hardness. Karnesky et al. [17] reported similar effect of Yb on the hardening response of an Al-0.08 at% Sc based alloy.

Figure 3.2. SEM micrographs of Al–0.24Sc–0.07Yb alloy: (a) as-cast and (b) homogenization treated.

The alloys used in this work present in their composition small contents of other elements, namely Si and Fe that may have some small influence on the alloys mechanical properties, namely hardness. Nevertheless, the difference between both alloys is very small, suggesting that the relative hardness values have not been influenced by the presence of those elements.

3.1.1.2 Isothermal aging behaviour

The age hardening behaviour of Al–0.28Sc and Al–0.24Sc–0.07Yb alloys at aging temperatures of 300, 325 and 350 °C is shown in Figure 3.3. It is quite evident that the Al–0.24Sc–0.07Yb alloy shows the similarity of Vickers hardness and aging behaviour with the Al–0.28Sc alloy. All the curves exhibits four different regions: (a) an incubation period; (b) a period with a rapid increase in hardness values where the precipitates nucleate from a supersaturated solid solution and grow; (c) a period of maximum hardness values (peak aging); and (d) over-aging, characterized by a slow decrease in hardness by the precipitates coarsening. The time to reach the hardness value peak decreases when the aging temperature increases from 300 to 350 °C. The Al–0.28Sc and Al–0.24Sc–0.07Yb alloys reach the hardness value peak after 20, 5, and 1 h when aging at 300, 325, and 350 °C, respectively. Higher temperature leads to earlier occurrence of over-aging. In Figure 3.3(a), there is no significantly softening due to over-aging for both alloys aged at 300 °C after 7 days. However, Figure 3.3 (b) and (c) show a fast over-aging for both alloys
aged at 325 and 350 °C. At these aging temperatures, the hardness drop becomes obviously after reaching the peak values. Higher aging temperature conducts to higher diffusion rate for precipitates nucleation and growth. It accelerates the over-aging stage.

![Graphs showing isothermal ageing curves](image)

Figure 3.3. Isothermal ageing curves of Al–0.28Sc and Al–0.24Sc–0.07Yb alloys at: (a) 300 °C; (b) 325 °C; (c) 350 °C.

### 3.1.2 Evolution of precipitates

#### 3.1.2.1 Precipitate morphologies

The aging behaviour presented above is controlled by the alloys microstructure. In order to correlate the observed hardening with microstructures, TEM and HRTEM observations were performed on samples at different processing states to reveal the evolution of the precipitates.
The TEM micrographs of Al–0.28Sc and Al–0.24Sc–0.07Yb alloys aged at 325 °C for 5 h, 325 °C for 7 days, and 350 °C for 7 days are shown in Figure 3.4, respectively.

Figure 3.4. TEM micrographs of Al–0.28Sc (a–b–c) and Al–0.24Sc–0.07Yb (d–e–f) alloys aged at 325 °C for 5 h, 325 °C for 7 days, and 350 °C for 7 days.

In order to observe more clearly the morphology of precipitates, higher magnification of TEM micrographs with bright-field and dark-field techniques are exhibited in Figure 3.5. The micrographs show the approximately spheroidal Al₃Sc and Al₃(Sc,Yb) precipitates, uniformly distributed throughout the α-Al matrix.
The Al\textsubscript{(Sc,Yb)} precipitates in Al–0.24Sc–0.07Yb alloy could be Al\textsubscript{3}Sc, Al\textsubscript{3}(Sc\textsubscript{1–x}Yb\textsubscript{x}) \textit{(Sc-rich composition)}, Al\textsubscript{3}(Yb\textsubscript{1–x}Sc\textsubscript{x}) \textit{(Yb-rich composition)}, or Al\textsubscript{3}Yb precipitates. There are no signs of coherency loss that can be observed in Figure 3.4 and Figure 3.5. The precipitates in both alloys aged at the higher temperature (350 °C) for long holding time (7 days) still remain coherent with $\alpha$–Al matrix.

![Figure 3.5. TEM micrographs of Al–0.28Sc (a) and Al–0.24Sc–0.07Yb (b–c) alloys aged at 350 °C for 7 days: (a), (b) bright-field TEM image; and (c) dark-field TEM image.](image)

The precipitate diameter of both alloys at the different aging conditions was measured and the corresponding results are presented in Table 3.1. After aging at 300°C for 7 days the average diameter of Al\textsubscript{3}Sc precipitate is 5.6 nm and that of Al\textsubscript{3}(Sc,Yb) precipitate is 5.9 nm. The presence of very small precipitates after long aging time indicates that coarsening occurred very slowly at 300 °C. In combination with hardness results presented in section 3.2, it can be seen that the strongest hardening effects of both alloys was achieved at aging temperature of 300 °C. When alloys were aged at 325 °C, the average
diameter is 4.3 nm for the Al$_3$Sc precipitate and 4.5 nm for the Al$_3$(Sc,Yb) precipitates at the aging peak. With prolonged aging times, after 7 days the average diameter of Al$_3$Sc and Al$_3$(Sc,Yb) precipitates slowly increase to 8.4 and 8.8 nm, respectively. At the temperature of 350 °C and 7 days aging, the average diameter of Al$_3$Sc and Al$_3$(Sc,Yb) precipitates are 13.7 and 15.4 nm, respectively. The TEM images show a smaller number of larger size precipitates due to the coarsening process. The average precipitates size of Al–0.24Sc–0.07Yb alloy is slightly higher than that of Al–0.28Sc alloys for all aging conditions. Thus, it suggests that Yb did not affect the coarsening rate of Al–Sc alloy.

Table 3.1. Average precipitate diameter and hardness of Al–0.28Sc and Al–0.24Sc–0.07Yb alloys

<table>
<thead>
<tr>
<th>Aging condition</th>
<th>Al–0.28Sc</th>
<th></th>
<th>Al–0.24Sc–0.07Yb</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Precipitate diameter (nm)</td>
<td>Hardness (HV$_{30}$)</td>
<td>Precipitate diameter (nm)</td>
<td>Hardness (HV$_{30}$)</td>
</tr>
<tr>
<td>300 °C, 7 days</td>
<td>5.6 ± 0.5</td>
<td>73 ± 2</td>
<td>5.9 ± 0.7</td>
<td>67 ± 2</td>
</tr>
<tr>
<td>325 °C, 5h</td>
<td>4.3 ± 0.2</td>
<td>72 ± 3</td>
<td>4.5 ± 0.8</td>
<td>74 ± 3</td>
</tr>
<tr>
<td>325 °C, 7 days</td>
<td>8.4 ± 0.9</td>
<td>61 ± 2</td>
<td>8.8 ± 1.8</td>
<td>58 ± 2</td>
</tr>
<tr>
<td>350 °C, 7 days</td>
<td>13.7 ± 1.9</td>
<td>52 ± 3</td>
<td>15.4 ± 1.8</td>
<td>50 ± 1</td>
</tr>
</tbody>
</table>

The precipitates size distribution (PSDs) of Al–0.28Sc and Al–0.24Sc–0.07Yb alloys aged at 325 °C and 350 °C for 7 days is illustrated in Figure 3.6. The PSDs of Al–0.28Sc aged at 325 °C for 7 days showed more narrow width in comparison with Al–0.24Sc–0.07Yb alloys at the same aging condition. The precipitates diameter ranges of Al–0.28Sc and Al–0.24Sc–0.07Yb alloys are 7–10.5 and 5–12 nm, respectively. The PSDs of both alloys aged at 350 °C for 7 days exhibited a similar width. The precipitates diameter ranges of Al–0.28Sc and Al–0.24Sc–0.07Yb alloys at this aging condition are 10–18 and 12–20 nm, respectively.
Precipitates in Al–0.28Sc and Al–0.24Sc–0.07Yb alloys at aging peak and the most coarsened stage were studied by HRTEM technique. The HRTEM images of both alloys aged at 325 °C for 5 h and 350 °C for 7 days are shown in Figure 3.7. Through fast Fourier transform (FFT) analysis, the [011] zone axis orientation was found to fit well to the simulation of the reciprocal lattice section at the orientation. The FFT images show the reflections from (100) and (011) of Ll$_2$ Al$_3$Sc and Al$_3$(Sc,Yb) precipitates and the reflections from (200), (022), and (111) of α–Al. The interface between the precipitates and the α–Al matrix remained coherent in both alloys even after aging at 350 °C for 7 days. There are no interfacial misfit dislocations in the HRTEM images, which conducts fully coherency of precipitates. Figure 3.7(a, b) shows the precipitates morphology of Al–0.28Sc and Al–0.24Sc–0.07Yb alloys aged at 325 °C for 5 h. The images show small precipitates with diameter less than 5 nm. The larger size and more obvious morphologies of precipitates are observed in Figure 3.7(c, d) corresponding to both alloys aged at 350 °C for 7 days. The Al$_3$Sc precipitates in Al–0.28Sc alloy have a facetted shape that corresponds to a great rhombicuboctahedron predicted by Marquis et al. [1]. Facets are parallel to the (100) and {011} planes. The precipitates average diameter is 18.1 nm, while the Al$_3$(Sc,Yb) precipitate in Al–0.24Sc–0.07Yb alloy

**Figure 3.6.** Precipitates size distribution of Al–0.28Sc and Al–0.24Sc–0.07Yb alloys at different aging conditions: $d_{16}$, $d_{50}$, and $d_{84}$ are the precipitate diameters corresponding to 16, 50, and 84 % cumulative undersize particle size distribution.

Precipitates size distribution of Al–0.28Sc and Al–0.24Sc–0.07Yb alloys at different aging conditions: $d_{16}$, $d_{50}$, and $d_{84}$ are the precipitate diameters corresponding to 16, 50, and 84 % cumulative undersize particle size distribution.
exhibits an approximately spheroidal shape with 18.5 nm diameter. The presence of Yb decreases the amount of faceting parallel to the \{100\} and \{0\bar{1}1\} and changes the morphology of precipitates into a more spheroidal shape.

![Figure 3.7](image)

Figure 3.7. High-resolution TEM images of Al–0.28Sc (a–c) and Al–0.24Sc–0.07Yb (b–d) alloys aged at 325°C for 5 h and 350°C for 7 days.

The equilibrium morphology of the precipitate is achieved by minimizing the sum of the interface energy and the elastic strain energy at constant volume [17,18]. The interface energy is caused by the existence of precipitate–matrix interfaces and the elastic strain energy is due to the lattice misfit between the precipitate and matrix. The relative contribution of the elastic strain and interfacial energies is evaluated using the parameter L given by Thompson et al. [18] according to the following equation:

\[
L = \frac{\varepsilon^2 C_{44} l}{\sigma}
\]

where \(\varepsilon\) is the precipitate–matrix lattice parameter mismatch, \(C_{44}\) is an elastic constant of the matrix, \(l\) is the measured precipitate dimension, and \(\sigma\) is interfacial energy. The lattice parameter mismatches of AlSc and AlYb with \(\alpha\)-Al are 1.36 and 3.65 %, respectively [8,19]. According to the studies of Marquis et al. [1], the
elastic constant of α-Al is 28.5 GPa and the interfacial energy $\sigma^{\alpha/Al_3Sc}$ approximates 0.2 J m$^{-2}$. The interfacial energy $\sigma^{Al/Al_3Yb}$ was obtained by Van Dalen et al. [20] and the result showed the value of 0.6 ± 0.3 J m$^{-2}$.

For the Al$_3$Sc precipitate shown in Figure 3.7(c) (diameter is 18.1 nm), L approximates 0.4 suggesting that the interfacial energy is dominant to control the precipitate morphology. The precipitate morphology in this case showed a great rhombicuoboctahedron shape predicted by Marquis et al. [1].

For the Al$_3$(Sc,Yb) precipitate shown in Figure 3.7(d) (diameter is 18.5 nm) L value is 1.17 ± 0.585. In this case the precipitate morphology was governed by both the elastic strain energy and interfacial energy. Various studies proposed 2D and 3D equilibrium morphology of a misfit, coherent precipitate as a function of L [21-23]. The results showed that the equilibrium morphology of precipitate for a cuboid with smoothly curvature faces, rounded edges and corners. The degree of curvature varies with the value of L. Three-dimensional equilibrium morphology of precipitate at low value of L (L = 1–2) was exhibited in Figure 3.8. This predicted morphology is nearly spheroidal shape and fits with the morphology of Al$_3$(Sc,Yb) precipitate shown in Figure 3.7(d).

![Figure 3.8. Three-dimensional equilibrium morphology for L = 1-2 viewed along: (a) [100] direction and (b) [111] direction [23].](image)

### 3.1.2.2 Coarsening behaviour

The coarsening behaviour of spherical precipitates in binary alloys was predicted by The Lifshitz–Slyozov–Wagner (LSW) model base on volume diffusion theory [24,25]. The Ostwald ripening of spherical precipitates was developed in concentrated multicomponent alloys by Umantsev and Olsan [26] and more detailed in ternary alloys, allowing for capillary effects by Kuehmann and Voorhees (KV) [27].
According to the KV model, the coarsening behaviour of precipitates was analysed through the following equation:

\[
\langle R(t) \rangle^n - \langle R(t_0) \rangle^n = K (t - t_0)
\]  

(3.1)

where \(K\) is a coarsening rate constant, \(\langle R(t) \rangle\) is the average precipitate radius at time \(t\), \(\langle R(t_0) \rangle\) is the average precipitate radius at the onset of quasi-stationary coarsening at time \(t_0\), and \(n\) is the inverse time exponent. Eq. (1) could be applied for both binary alloy (Al–0.28Sc) and ternary alloy (Al–0.24Sc–0.07Yb) with different coarsening rate constant. It was assumed that \(\langle R(t_0) \rangle^n\) and \(t_0\) is much smaller than \(\langle R(t) \rangle^n\) and \(t\), the Eq. (1) became [28,29]:

\[
\langle R(t) \rangle^n = K t
\]  

(3.2)

A log–log plot of Eq. (2) reveals a slope of \(\frac{1}{n}\) as following equation:

\[
\log \langle R(t) \rangle = \frac{1}{n} \log t + \frac{1}{n} \log K
\]  

(3.3)

This slope is known as a time exponent of coarsening and often reported to indicate the coarsening behaviour of precipitates. By applying the KV model to the Al–0.28Sc and Al–0.24Sc–0.07Yb alloys aged at 325 °C, the time exponents of coarsening \(\frac{1}{n}\) was calculated and showed the same value of 0.19 for both alloys. This value indicated that the precipitate coarsening behaviour of both investigated alloys is similar to the Al–0.18 at% Sc alloy aged at 300 °C \(\frac{1}{n} = 0.18\) referred by Marquis et al. [1,28] and Al–0.06 at% Sc–0.02 at% Yb alloy aged at 300 °C \(\frac{1}{n} = 0.18\) referred by Van Dalen et al. [30].

### 3.1.3 Precipitation hardening mechanisms

The evolution of precipitates and corresponding hardness at different aging conditions is presented in Table. 2. According to Hyland et al. [31] and Marquis et al. [2], the volume fraction of precipitate is approximately constant for Al–Sc alloys aged at various temperatures from 275 °C to 400 °C after long enough aging time (longer than 10000 s at 288 °C and 2000 s at 343 °C). On this work the alloys were aged at 300, 325, and 350 °C for 5h and 7 days. For these conditions and according to the findings of Hyland and Marquis we can assume that the volume fraction of precipitates is constant. The precipitation hardening is typically understood through the cutting mechanism which dislocations cut through precipitates and the Orowan bypass mechanism which dislocations bow or loop precipitates. According to the experimental data from the
study about precipitation strengthening in Al–0.3 wt% Sc alloy, Marquis et al. [2] predicted a transition from cutting mechanism to Orowan bypass mechanism at a precipitate diameter of 4.2 nm. The strength of alloy is controlled by the cutting mechanism for smaller sizes, and the Orowan bypass mechanism for larger sizes of precipitates which higher precipitate diameter results in lower hardness. Table 3.1 showed a maximum hardness around 73 (HV$_30$) at a precipitate diameter from 4.3 to 5.6 nm for both alloys. It sharply decreases to HV$_{30} = 50$ when the average diameter of precipitate increases to 13.7–15.4 nm. This result is in a good agreement with above theory and the result of Marquis et al. [2].

3.2 Conclusions

The similarity of microstructure, hardness and aging behaviour of Al–0.24Sc–0.07Yb alloy in comparison with Al–0.28Sc alloy was shown in this investigation. It indicates that the substitution of 0.07 wt% Yb for more expensive Sc in the Al–0.28Sc alloy is possible. Some final characteristics of Al–0.28Sc and Al–0.24Sc–0.07Yb alloys were concluded below:

- The hardness values of both alloys aged without homogenization treatment are significantly higher than those of alloys aged after homogenization treatment.

- The approximately spheroidal Al$_3$Sc and Al$_3$(Sc,Yb) precipitates were uniformly distributed throughout the $\alpha$–Al matrix. The precipitates remain fully coherent with $\alpha$–Al matrix even after aging at high temperature for long time.

- With the aging temperature of 325 °C, the average diameter is 4.3 nm for Al$_3$Sc precipitates and 4.5 nm for Al$_3$(Sc,Yb) precipitates at the aging peak. At the temperature of 350 °C and 7 days aging, the average diameter of Al$_3$Sc and Al$_3$(Sc,Yb) precipitates are 13.7 and 15.4 nm, respectively.

- The Al$_3$Sc precipitates of Al–0.28Sc alloy show the faceted shape that are similar with great rhombicuboctahedron shape, while the Al$_3$(Sc,Yb) precipitates of Al–0.24Sc–0.07Yb alloy show an approximately spheroidal shape.
References


[14] Dalen ME, Dunand DC, Seidman DN. Nanoscale precipitation and mechanical properties of Al-0.06 at.% Sc alloys microalloyed with Yb or Gd. J Mater Sci. 2006;41:7814-23.


[30] van Dalen ME, Dunand DC, Seidman DN. Microstructural evolution and creep properties of precipitation-strengthened Al–0.06Sc–0.02Gd and Al–0.06Sc–0.02Yb (at.%) alloys. Acta Mater. 2011;59:5224-37.

Effects of substituting rare earth metals for scandium on the microstructure and properties of Al-Sc and Al-Mg-Sc alloys

CHAPTER 4: PRECIPITATION AND AGE-HARDENING

BEHAVIOUR OF Al–Mg–Sc AND Al–Mg–Sc–Yb ALLOYS
Chapter 4: Precipitation and age-hardening behaviour of Al–Mg–Sc and Al–Mg–Sc–Yb alloys

Introduction

In Sc–containing Al alloys, the Al–Mg–Sc alloys have attracted more attention due to their wide range application in automotive, aerospace, ship building and structural fields. The combination between of solid-solution hardening and precipitation hardening leads Al–Mg–Sc alloys have excellent properties of both Al–Mg and Al–Sc alloys. According to Sawtell and Jensen [1], the properties of Al–Mg–Sc alloys appear to reflect a superposition of the characteristics of Al–Sc alloys and Al–Mg alloys. Formation of the A1Sc precipitate appears to be unaltered by the presence of Mg. Magnesium increases the strength and strain-hardening exponent of the Al–Sc base alloy in direct proportion to the amount of Mg present in solution. The increased strain hardening significantly improves crack initiation toughness resulting in a better overall combination of strength and toughness for alloys containing Mg. The addition of Mg also reduces the subgrain size during fabrication through their influence on deformation mode and thus improves superplastic performance as measured by maximum superplastic elongation or strain rate/temperature to achieve a given elongation. Lathabai and Lloyd [2] studied the microstructure, mechanical properties and weld hot cracking behaviour of a cast Al–Mg–Sc alloy containing 0.17 wt% Sc in comparison with those of a Sc-free alloy of similar chemical composition. The results showed that the Al–Mg–Sc alloy had significantly higher 0.2% proof stress (~55% higher) and tensile strength (~20% higher) as well microhardness (~30% higher) and a slightly lower ductility than the cast Al–Mg alloy. The higher levels of Sc should improve the weld hot cracking resistance of alloys by enhanced grain refinement of both the casting and the weld metal. The previous researches have proven that Yb can substitute a part of Sc in binary Al–Sc alloy in order to reduce their cost without decreasing of alloy properties [3-5]. There was not any study showing the effect of Yb on properties of Al–Mg–Sc alloy.

In this chapter, in this study the precipitation and age-hardening behaviour of Al–4Mg–0.3Sc and Al–4Mg–0.24Sc–0.06Yb alloys were investigated. The aging behaviour, precipitate morphologies, precipitate coarsening and precipitation hardening of both alloys were discussed. The average diameter and the size distribution of nanoscale Al3Sc and Al(Sc,Yb) precipitates at various aging conditions were measured. Transmission electron microscopy (TEM) and high-resolution TEM were used to understand the precipitate behaviour.
4.1 Results and discussion

4.1.1 Age hardening behaviour of the as-cast alloys

4.1.1.1 Isochronal aging behaviour

The Vickers hardness of Al–4Mg–0.3Sc and Al–4Mg–0.24Sc–0.06Yb alloys aged at various temperatures from 200–450 °C for 2 h were shown in Figure 4.1. The onset of age hardening for both alloys occurs at 250 °C. The Vickers hardness increases rapidly when aging at 300 °C and obtains the hardness peaks of 110 HV for Al–4Mg–0.3Sc alloy and 103 HV for Al–4Mg–0.24Sc–0.06Yb alloy at 325 °C. The Vickers hardness was decreased sharply at 400 °C and 450 °C due to the precipitate coarsening. The partial replacement of Sc by Yb did not significantly affect either the kinetics or the peak hardness. In order to compare with Al–4Mg–0.3Sc and Al–4Mg–0.24Sc–0.06Yb alloys, the Vickers hardness curves of Al–0.28Sc and Al–0.24Sc–0.07Yb alloys aged at various temperatures from 150–375 °C for 2 h also presented in Figure 4.1. It can be seen that solid solution strengthening by adding Mg has significantly increased the hardness of Al–Sc–(Yb) alloys.

![Figure 4.1](image)

*Figure 4.1. Isochronal aging curves of Al–4Mg–0.3Sc and Al–4Mg–0.24Sc–0.06Yb alloys in comparison with Al–0.28Sc and Al–0.24Sc–0.07Yb alloys.*

4.1.1.2 Isothermal aging behaviour

The age hardening behaviour of Al–0.28Sc, Al–0.24Sc–0.07Yb, Al–4Mg–0.3Sc, and Al–4Mg–0.24Sc–0.06Yb alloys at aging temperatures of 300, 325 and 350 °C were shown in Figure 4.2.
Figure 4.2. Isothermal ageing curves of Al–4Mg–0.3Sc and Al–4Mg–0.24Sc–0.06Yb alloys in comparison with Al–0.28Sc and Al–0.24Sc–0.07Yb alloys aged at 300 °C, 325 °C, and 350 °C.

The curves show that Al–4Mg–0.24Sc–0.06Yb alloy has a similar aging behaviour with Al–4Mg–0.3Sc alloy with four distinguished regions: an incubation period, a period with a rapid increase in hardness values, a period of maximum hardness values (peak aging), and over-aging. The aging rate increases with the increasing of aging temperature. Higher temperature leads to earlier occurrence of over-aging. Higher aging temperature conducts to higher diffusion rate for precipitates nucleation and growth that consequently accelerates the over-aging stage. The Al–4Mg–0.3Sc and Al–4Mg–0.24Sc–0.06Yb alloys reach the hardness value peak after 1 day, 5 h, and 30 minutes when aging at 300, 325, and 350 °C, respectively. At aging temperature of 300 °C, the Vickers hardness of Al–4Mg–0.3Sc and Al–4Mg–0.24Sc–0.06Yb alloys reach peak values of 112 ± 6 and 104 ± 3 HV, and slightly decreases to 98 ± 6 and 97 ± 1 HV after 7 days aging respectively. At aging temperature of 325 °C, the Vickers hardness of Al–4Mg–0.3Sc and Al–4Mg–0.24Sc–0.06Yb alloys reach the peak values of 112 ± 2 and
104 ± 5 HV, and decreases to 94 ± 2 and 89 ± 3 HV after 7 days aging, respectively. At aging temperature of 350 °C, the Vickers hardness of Al–4Mg–0.3Sc and Al–4Mg–0.24Sc–0.06Yb alloys reach the peak values of 108 ± 5 and 102 ± 4 HV, and substantial decreases to 77 ± 1 and 72 ± 2 HV after 7 days aging respectively. It can be seen that both alloys show a slow over-aging at 300 and 325 °C and much faster at 350 °C.

In comparison with Al–0.28Sc and Al–0.24Sc–0.07Yb alloys, the evolutions of hardness of Al–4Mg–0.3Sc, and Al–4Mg–0.24Sc–0.06Yb alloys with time are similar and the values are significantly higher that of Al–0.28Sc and Al–0.24Sc–0.07Yb alloys at every aging conditions. Addition of Mg increases the hardness of Al–Sc–(Yb) alloys but did not change the aging kinetic of those alloys.

4.1.2 Precipitate behaviour

4.1.2.1 Precipitate morphologies and distributions

The TEM micrographs of Al–4Mg–0.3Sc and Al–4Mg–0.24Sc–0.06Yb alloys aged at 325 °C for 5 h, 325 °C for 7 days, and 350 °C for 7 days are shown in Figure 4.3, respectively. The micrographs show the spheroidal Al₃Sc and Al₃(Sc,Yb) precipitates, uniformly distributed throughout the α–Al matrix.

The precipitate diameter of both alloys at different aging conditions was measured and the corresponding results are presented in Table 4.1. At hardness peak when aging at 325 °C, the average diameter of Al₃Sc and Al₃(Sc,Yb) precipitates in both alloys are 3.5 ± 0.6 nm. After 7 days aging at 325 °C, the average diameter of Al₃Sc in Al–4Mg–0.3Sc alloy slowly increases to 6.3 ± 1.4 nm that lead to slightly decreasing of hardness. The Al₃(Sc,Yb) precipitate in Al–4Mg–0.24Sc–0.06Yb alloy shows a faster coarsening rate than Al₃Sc in Al–4Mg–0.3Sc alloy when aging at 325 °C. The average diameter of Al₃(Sc,Yb) in Al–4Mg–0.24Sc–0.06Yb alloy is 9.5 ± 1.4 nm. At the temperature of 350 °C and 7 days aging, the average diameter of Al₃Sc and Al₃(Sc,Yb) precipitates are 13.0 ± 1.6 and 12.6 ± 1.9 nm, respectively. This result is in accordance with the conclusion in the Section 3.2.3 for precipitation hardening in Al–0.28Sc and Al–0.24Sc–0.07Yb alloys. The maximum hardness was achieved at a precipitate diameter around 4–6 nm. The hardness sharply decreases when the average diameter of precipitate above 12 nm. In comparison with Al–0.28Sc and Al–0.24Sc–0.07Yb alloys (Section 3.1.2.1), at the same aging condition the average sizes of precipitates in Al–4Mg–0.3Sc and Al–4Mg–0.24Sc–0.06Yb alloys were slightly lower.
Figure 4.3. TEM micrographs of Al–4Mg–0.3Sc (a–b–c) and Al–4Mg–0.24Sc–0.06Yb (d–e–f) alloys aged at 325 °C for 5 h, 325 °C for 7 days, and 350 °C for 7 days.
Table 4.1. Average precipitate diameter and hardness of Al–4Mg–0.3Sc and Al–4Mg–0.24Sc–0.06Yb alloys

<table>
<thead>
<tr>
<th>Aging condition</th>
<th>Al–4Mg–0.3Sc</th>
<th>Al–4Mg–0.24Sc–0.06Yb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Precipitate</td>
<td>Hardness</td>
<td>Precipitate</td>
</tr>
<tr>
<td>diameter (nm)</td>
<td>(HV)</td>
<td>diameter (nm)</td>
</tr>
<tr>
<td>325 °C, 5h</td>
<td>3.5 ± 0.6</td>
<td>112 ± 2</td>
</tr>
<tr>
<td>325 °C, 7 days</td>
<td>6.3 ± 1.4</td>
<td>94 ± 2</td>
</tr>
<tr>
<td>350 °C, 7 days</td>
<td>13.0 ± 1.6</td>
<td>77 ± 1</td>
</tr>
</tbody>
</table>

The precipitates size distribution (PSDs) of Al–4Mg–0.3Sc and Al–4Mg–0.24Sc–0.06Yb alloys aged at 325 °C for 5 h, 325 °C for 7 days, and 350 °C for 7 days are shown in Figure 4.4, respectively.

![Figure 4.4](image.png)

**Figure 4.4.** Precipitates size distribution of Al–4Mg–0.3Sc (a–b–c) and Al–4Mg–0.24Sc–0.06Yb (d–e–f) alloys aged at 325 °C for 5 h, 325 °C for 7 days, and 350 °C for 7 days: $d_{16}$, $d_{50}$, and $d_{84}$ are the precipitate diameters corresponding to 16, 50, and 84 % cumulative undersize particle size distribution.
The results show that the Al₃Sc precipitates in Al–4Mg–0.3Sc alloy are more uniformly distributed than Al₃(Sc,Yb) precipitates in Al–4Mg–0.24Sc–0.06Yb alloy at the same aging condition. The precipitates diameter ranges in Al–4Mg–0.3Sc alloy aged at 325 °C for 5 h, 325 °C for 7 days, and 350 °C for 7 days are 2.5–5.5, 4–11, and 10–17 nm, respectively. The precipitates diameter ranges in Al–4Mg–0.24Sc–0.06Yb alloy aged at 325 °C for 5 h, 325 °C for 7 days, and 350 °C for 7 days are 1.5–5.5, 6.5–13, and 10–19 nm, respectively.

4.1.2.2 High resolution TEM study

Precipitates in Al–4Mg–0.3Sc and Al–4Mg–0.24Sc–0.06Yb alloys aged at 325 °C for 5 h, 325 °C for 7 days, and 350 °C for 7 days were studied by high resolution TEM technique.

According to selected area (electron) diffraction (SAD) analysis, the [011] and [112] (Figure 4.5) zone axis orientation was found to fit well to the simulation of the reciprocal lattice section at the orientation. Al₃Sc and Al₃(Sc,Yb) precipitates with cubic lattice L1₂ (cP4) structure in HRTEM images can be identified by using Digital Micrograph software. The reflections from (100) and (01̅1) of L1₂, Al₃Sc and Al₃(Sc,Yb) precipitates were determined by using a fast Fourier transform (FFT) analysis. The inverse fast Fourier transform (IFFT) obtained by applying masks near reflections from (100) and (01̅1) could show much better contrast for precipitates identification.

![Figure 4.5. SAD taken along the [100] or [110] crystallographic directions.](image)

High-resolution TEM images, FFT and IFFT of precipitates in Al–4Mg–0.3Sc and Al–4Mg–0.24Sc–0.06Yb alloys aged at 325 °C for 5 h are shown in Figure 4.6. A clear lattice cross-grating contrast of precipitates is not clearly defined in HRTEM images. Very fine, fully coherent precipitates (3–4 nm) distributed throughout the α-Al matrix were detected by using IFFT analysis. There are no misfits between the precipitates and the matrix appearing in the structure.
Figure 4.6. High-resolution TEM images, FFT and IFFT of precipitates in Al–4Mg–0.3Sc (a) and Al–4Mg–0.24Sc–0.06Yb (b) alloys aged at 325 °C for 5 h.

High-resolution TEM images, FFT and IFFT of precipitates in Al–4Mg–0.3Sc and Al–4Mg–0.24Sc–0.06Yb alloys aged at 325 °C for 7 days and 350 °C for 7 days are shown in Figure 4.7.

Figure 4.7. High-resolution TEM images, FFT and IFFT of precipitates in Al–4Mg–0.3Sc (a–c) and Al–4Mg–0.24Sc–0.06Yb (b–d) alloys aged at 325 °C for 7 days (a–b) and 350 °C for 7 days (c–d).
The precipitate sizes of Al–4Mg–0.3Sc and Al–4Mg–0.24Sc–0.06Yb alloys were measured and show the values of 10 and 9 nm when aging at 325 °C for 7 days and 14 and 18 nm when aging at 350 °C for 7 days, respectively. All precipitates remain fully coherent with the α–Al matrix. The morphology of Al₃Sc and Al₃(Sc,Yb) precipitates in Al–4Mg–0.3Sc and Al–4Mg–0.24Sc–0.06Yb alloys aged at 350 °C for 7 days is clearly spheroidal shape.

4.2 Conclusions

The precipitation and age-hardening behaviour of Al–4Mg–0.3Sc and Al–4Mg–0.24Sc–0.06Yb alloys were investigated. Some final conclusions were summarized below:

- The spheroidal Al₃Sc and Al₃(Sc,Yb) precipitates were uniformly distributed throughout the α–Al matrix. The precipitates remain fully coherent with α–Al matrix even after aging at high temperature for long time.

- The maximum hardness was achieved at a precipitate diameter around 4–6 nm. The hardness sharply decreases when the average diameter of precipitate above 12 nm.

- The hardness of Al–4Mg–0.3Sc and Al–4Mg–0.24Sc–0.06Yb alloys were significantly higher than that of Al–0.28Sc and Al–0.24Sc–0.07Yb alloys at the same aging condition due to the solid solution strengthening of Al–Mg. The average size of precipitates in Al–4Mg–0.3Sc and Al–4Mg–0.24Sc–0.06Yb alloys was slightly lower than that of Al–0.28Sc and Al–0.24Sc–0.07Yb alloys at the same aging conditions.
References


[4] Dalen ME, Dunand DC, Seidman DN. Nanoscale precipitation and mechanical properties of Al-0.06 at.% Sc alloys microalloyed with Yb or Gd. J. Mater. Sci. 2006;41:7814-23.

Effects of substituting rare earth metals for scandium on the microstructure and properties of Al-Sc and Al-Mg-Sc alloys

CHAPTER 5 – GRAIN REFINEMENT OF Al-Mg-Sc ALLOYS

The work presented in this chapter was based on the paper accepted for publication: N.Q. Tuan, H. Puga, J. Barbosa, A.M.P. Pinto, “Grain refinement of Al-Mg-Sc alloy by ultrasonic treatment”, Metals and Materials International (will be published in Vol.21 & No.1. (Jan, 2015))
Chapter 5 - Grain refinement of Al–Mg–Sc alloys

Introduction

In foundry practice of aluminium alloys, several processes have been applied to achieve a fine, equiaxed and uniform grain microstructure. Grain refinement plays an important role to enhance mechanical properties as toughness, fracture resistance, fatigue strength and isotropic behaviour of the cast alloys. Two methods are usually used for microstructure refinement: chemical and physical techniques with particular emphasis to first. There are three major mechanisms for grain refinement during solidification process those are heterogeneous nucleation, restricting the grain growth and breaking the solidified crystals.

The chemical method is widely applied in industry by grain refiner inoculation [1-4]. Through adding grain refiners as Al–Ti or Al–Ti–B master alloys, the particles of TiAl₃, TiB₂ phases in the molten alloy will act as nuclei, promoting heterogeneous nucleation, nucleating solid particles during solidification [3]. However, only 1% of the refiner particles are active for nucleation of solid grain [1,3]. The rest of them contaminate the casting alloy and have detrimental effects on the final microstructure and mechanical properties.

Another approach to achieve grain refinement is some kind of physical method that may promote nucleation, obtaining grain multiplication by dendrite fragmentation under mechanical force or external physical field without further chemical addition [5]. Dramatic grain refinement has been obtained in Al–10 wt% Mg and AA7449 alloys by applying intensive melt shearing above liquidus temperature [6,7]. Other techniques have been successfully applied for grain refinement, such as mechanical stirring, electromagnetic stirring [8], and gas bubbling [9,10]. However those techniques are time consuming, can promote low fluidity and are high costly.

During the last years an effort has been done to develop reliable ultrasonic techniques to control the microstructure of several engineering alloys, with particular emphasis to Al and Mg based ones, to overtake the problems associated to traditional refinement techniques. Khalifa et al. [11] and Jian et al. [12] demonstrated that it is possible to obtain non dendritic and globular grains of primary α–Al phase smaller than 100 µm by supplying acoustic energy to molten AlSi7Mg, isothermally and during solidification, respectively. Ultrasonic vibration can also be used to refine hypereutectic Al–Si alloys, as demonstrated by Feng et al. [13], who obtained equiaxed, α–Al crystals of around 40 µm and homogeneously distributed primary Si phase with average size of 180 µm in AlSi23 alloy.
Puga et al. [14,15] studied the influence of ultrasonic power and treatment temperature on the microstructure and mechanical properties of an AlSi9Cu3 alloy by applying ultrasound to the melt during the first stages of solidification. The results showed that ultrasound promoted the formation of refined globular structures and globular α-Al grain sizes decreased with increasing of treatment temperature and electric power. Moreover, uniform distribution of fine particles of the β-Al5FeSi intermetallic phase was also obtained. Ultrasonic treated alloys showed better mechanical properties in comparison with non-ultrasonic treated alloys.

It is important to notice that until now the capability of ultrasound as microstructure refinement technique of metallic alloys has been evaluated for a very narrow range of alloys. Most of the studies have been directed to magnesium alloys [16-20] and aluminium-silicon alloys [11-15,21-23]. Besides, in foundry practice cast alloys must not be poured at low temperature because consequent low fluidity often leads to premature solidification, cold shuts and incomplete castings. On the other hand, high pouring temperatures usually promote grain coarsening, oxide formation and gas porosity. Ultrasonic treatment is a potential process to obtain grain refinement within a wide temperature range, decreasing or even eliminating the traditional defects associated to high or low refining and pouring temperatures.

Al–Mg–Sc alloys have received a lot of attention due to their excellent mechanical behaviour [24-26]. However, there are no available studies concerning grain refinement of these alloys. Almost studies of Al–Mg–Sc alloys concentrated on strengthening mechanism with Al,Sc precipitates and effect of Mg on it. Grain refinement and its mechanism of Al–Mg–Sc alloys, especially with hypoeutectic composition of Sc (the content of Sc is lower than 0.55 wt%) have not been studied. In this chapter, the role of Mg and Sc as well as the influence of pouring temperature on grain refinement of Al–1Mg–0.3Sc (wt%) was presented. In another work, the effect of ultrasonic treatment on grain refinement of Al–1Mg–0.3Sc alloy at a wide range of pouring temperatures was evaluated. The microstructures of Al–1Mg–0.3Sc alloy at various pouring temperatures with ultrasonic treatment were evaluated. The mechanism of grain refinement was proposed and understood.

5.1 Results and discussion

5.1.1 Grain refinement of Al–Mg–Sc alloys without ultrasonic treatment

5.1.1.1 Grain refinement results

i) Effect of Mg and Sc on grain refinement of Al–Mg–Sc alloys

Figure 5.1 shows the optical micrographs of Al–1Mg, Al–0.3Sc, Al–4Mg, Al–1Mg–0.3Sc, and Al–4Mg–0.3Sc alloys cast at 700 ± 5 °C. It is clear that the microstructure of
Al–4Mg, Al–1Mg–0.3Sc and Al–4Mg–0.3Sc alloys have a uniform, equiaxed and finer grain size in comparison with Al–1Mg and Al–0.3Sc alloys.

![Figure 5.1. Optical micrographs of as-cast alloys cast at 700 °C: (a) Al–1Mg, (b) Al–0.3Sc, (c) Al–4Mg, (d) Al–1Mg–0.3Sc, (e) Al–4Mg–0.3Sc.](image)

Figure 5.2 presents the average grain sizes of those as-cast alloys. The average grain size of the Al–1Mg alloy is 439 ± 21 µm and it decreases to 95 ± 2 µm in the Al–4Mg alloy. The average grain size of the Al–0.3Sc alloy is 410 ± 15 µm and it decreases to 103 ± 2 and 56 ± 1 µm in Al–1Mg–0.3Sc and Al–4Mg–0.3Sc alloys, respectively. Besides, it can also be inferred that the grain size of Al–1Mg can be significantly reduced by adding a small content of Sc (0.3 wt% in this case). In fact, according to Figures 5.1(a) and 1(d), the average grain size of Al–1Mg alloy decreases from 439 ± 21 µm to 103 ± 2 µm in Al–1Mg–0.3Sc alloy.

![Figure 5.2. Average grain size and hardness of Al–1Mg, Al–0.3Sc, Al–4Mg, Al–1Mg–0.3Sc, Al–4Mg–0.3Sc as-cast alloys cast at 700 °C.](image)
**ii) Effect of pouring temperature on grain refinement of Al–1Mg–0.3Sc alloy**

Figure 5.3 shows the optical micrographs of as-cast Al–1Mg–0.3Sc alloys without ultrasonic treatment poured at 800 and 770 °C ± 5 °C. The microstructure exhibits columnar zones (present in the centre of the samples) with elongated grains and dendritic features and the outer chill zones (present in the border of samples) with finer and more equiaxed grains. The average grain size of Al–1Mg–0.3Sc samples poured at 800 and 770 °C ± 5 °C is 487 ± 20 and 394 ± 14 µm. The different morphology of coarse grains in the different zones can be explained by the different solidification rate and interfacial temperature gradient [27]. In the chill zone, under the large supercooling that occurs as soon as the molten alloy contacts the cold mould wall a large number of nuclei forms and grow as equiaxed shaped grains. After pouring, the temperature gradient at the mould walls decreases and the grains in the chill zone grow dendritically side by side in the direction of the heat flow which is perpendicular to the mould walls. They stop growing when they meet grains growing out from the opposite wall. This process leads to the formation of elongated grains and creates the columnar zone.

![Optical Micrographs](image)

*Figure 5.3. Optical micrographs of Al–1Mg–0.3Sc alloy cast at pouring temperatures: (a–b) 800 °C, (c–d) 770 °C: (a), (c) in the border of samples; (b), (d) in the centre of samples.*

Figure 5.4 shows the optical micrographs of as-cast Al–1Mg–0.3Sc alloys without ultrasonic treatment poured at 740, 720 and 700 °C ± 5 °C. It is evident that grain size gradually decreases with decreasing of pouring temperature. The average grain size of Al–1Mg–0.3Sc samples poured at 740, 720, and 700 °C are at 269 ± 8, 197 ± 5 and 103 ± 2 µm, respectively. It is evident to conclude that the pouring temperature has a strong influence on the grain size of the Al–1Mg–0.3Sc alloy.
Figure 5.4. Optical micrographs of Al–1Mg–0.3Sc alloy cast at pouring temperatures: (a) 740 °C, (b) 720 °C, (c) 700 °C.

The grain size distribution of Al–1Mg–0.3Sc alloy poured at 800, 770, 740, 720 and 700 ± 5 °C is illustrated in Figure 5.5. The grain size of those samples is within the range of 200–1000, 200–800, 100–500, 50–400, and 50–270 µm, respectively. It is evident that the most fine and uniform equiaxed grains were achieved on the sample cast at 700 °C.

Figure 5.5. Grain size distribution of Al–1Mg–0.3Sc cast samples for different pouring temperatures.
5.1.1.2 Grain refinement mechanism

i) Nucleation mechanism

According to research reviews of Murty et al. [28] it is easily perceptible that grain refinement is very far from fully understood and is still object of discord between researchers. According to Li et al. [29] MgAl₂O₄ particles that form in Al–Mg melt can act as potential sites for heterogeneous nucleation of α–Al grains. MgAl₂O₄ oxide has a perfect lattice matching with α–Al at the {1 1 1} plane that promotes high potency for heterogeneous nucleation. In this experiment, when the melt was heated up to 800 °C, MgAl₂O₄ oxide formed due to the high affinity of Mg with oxygen. The oxidation process was followed by two consecutive steps: Mg + 1/2O₂ → MgO, and then MgO + 2Al + 3/2O₂ → MgAl₂O₄. MgAl₂O₄ is present as oxide films in Al–Mg alloy with low Mg content and as dispersed discrete particles in alloys with high content of Mg [29]. This is the reason why Al–1Mg and Al–4Mg present so different microstructures (Figures 5.1(a) and 5.1(c)) even having been processed on the same conditions. The higher density of MgAl₂O₄ particles in the melt due to the higher content of Mg in Al–4Mg alloy promotes more nuclei sites for α–Al nucleation, leading to a more refined and homogeneous microstructure with smaller grain size.

The much lower average grain size of Al–1Mg–0.3Sc in comparison with Al–1Mg and Al–0.3Sc alloys suggested that grain refinement was achieved in aluminium alloys containing both Sc and Mg. The theory proposed by Johnsson et al. [30] described the influence of nucleants and segregating solutes on grain refinement. Solute elements like Sc, Mg, Si, Cu and Fe segregate to the nucleant/melt interface and restrict the growth of dendrites, so there is more time for nucleation to occur [28,30]. Moreover, segregating elements would lead to constitutional undercooling in front of the interface. This constitutionally undercooled zone activates the nucleant agent in front of the interface. In case of Al–1Mg–0.3Sc alloy, the nucleant particles could be MgAl₂O₄ oxide or impurity particles. Segregating Sc can lead to form Al₃Sc that has L1₂ structure, a small lattice parameter mismatch and fully coherent with α–Al at elevated temperatures [31]. This characteristic makes Al₃Sc an ideal nucleating agent for grain refinement of Al alloys. In addition, Alexander Pisch et al. [32] indicated that the eutectic composition of Sc decreases with increasing Mg content in the Al–Mg–Sc alloy. This characteristic facilitates the formation of Al₃Sc. The increasing of nucleant potency and segregating potency due to the existence of both Sc and Mg improves grain refinement in Al–1Mg–0.3Sc alloy. The finest grain size observed in the microstructure of Al–4Mg–0.3Sc alloy could be understood through combination of those mechanisms.
Figure 5.6 shows the SEM micrographs and EDS spectra of Al–0.3Sc alloy cast at 700 °C. Intermetallic particles containing Al, Sc, Si, and Fe in this alloy exhibit a rod-like shape, which cannot act as nuclei sites for $\alpha$–Al nucleation.

![Figure 5.6. SEM micrograph and EDS spectra of intermetallic phase in Al–0.3Sc alloy cast at 700 °C.](image)

Figure 5.7 presents the SEM micrograph and EDS spectra of Al–1Mg–0.3Sc alloy cast at 700 °C. Oxide nucleus (Z2), intermetallic nucleus containing Al, Mg, Sc, Si, Fe, and Cu (Z1) and intermetallic nucleus containing Al, Mg, Sc, Si, and Fe (Z3) were detected in the microstructure of this alloy.

![Figure 5.7. SEM micrograph and EDS spectra of intermetallic phases in Al–1Mg–0.3Sc alloy cast at 700 °C.](image)

Figure 5.8 shows the SEM micrograph and EDS spectra of Al–4Mg–0.3Sc alloy cast at 700 °C. Oxide nucleus (Z1 particle) was detected in this micrograph.
ii) Effect of pouring temperature on grain refinement in Al–1Mg–0.3Sc alloy

When the alloy is melted and poured at high temperature, the melt is quite homogeneous and consequently reduces the segregating potency of solute elements. The constitutional undercooling in front of the nucleant/melt interface will not happen and Al$_3$Sc cannot form. The low segregating potency and nucleant potency result in very coarse grains in the microstructure of as-cast alloy. At lower pouring temperature, the segregating potency and nucleant potency are higher that leads to better refining effect promoting the development of finer and more homogeneous equiaxed grains in the microstructure of as-cast alloy. Figure 5.9 shows the SEM micrograph and EDS spectra of Al–1Mg–0.3Sc alloy cast at 770 °C. Almost second phase particles are intermetallic phase of Al, Mg, and Fe with a rod-like morphology. Those particles cannot act as heterogeneous nuclei sites to form α–Al grain.

The mechanism of grain refinement that bases on heterogeneous nucleation above liquidus and dendrite growth restriction was proposed. In general, MgAl$_2$O$_4$ oxide and Al$_3$Sc are the main possibilities of nuclei site for α–Al nucleation. Figure 5.10 sketches the mechanisms of α–Al nucleation that probably happen during solidification of those alloys.
5.1.2 Grain refinement of Al–Mg–Sc alloys with ultrasonic treatment

5.1.2.1 Effect of ultrasonic treatment at various temperatures on grain size of Al–1Mg–0.3Sc alloy

Figure 5.11 and 5.12 show the optical micrographs and the grain size distribution of Al–1Mg–0.3Sc cast samples with ultrasonic treatment at the temperatures of 800, 770, 740, 720, and 700 ± 5 °C.
Figure 5.11. Optical micrographs of Al–1Mg–0.3Sc alloy ultrasonic treated at different temperatures:
(a) 800 °C, (b) 770 °C, (c) 740 °C, (d) 720 °C, (e) 700 °C.

Figure 5.12. Grain size distribution of Al–1Mg–0.3Sc samples ultrasonic treated at different temperatures.
It is obvious that the impact of ultrasonic treatment on grain refinement depends on the treatment temperature. The influence of ultrasonic treatment on grain refinement is most effective within the temperature range of 700–740 °C. The average grain size of cast samples is 98 ± 2, 83 ± 1, 93 ± 2 µm for 740, 720, and 700 °C ultrasonic treatment temperatures, respectively. When the alloy was treated by ultrasonic vibration at 770 and 800 °C, the grains tend to be larger, with average size of 166 ± 4 and 169 ± 4 µm, respectively. At the temperature of 720 °C, the grains are finer and more uniform than at any other treatment temperature.

The quantitative results of the average grain size of Al–1Mg–0.3Sc alloys are summarized and presented in Figure 5.13 to compare the grain size of alloys with and without ultrasonic treatment. The strong refinement effect of ultrasound is quite clear, especially if the treatment is conducted within the temperature range 700–740 °C.

![Figure 5.13. Effect of ultrasonic treatment on the average grain size of Al–1Mg–0.3Sc alloys.](image)

Figure 5.14 shows the grain size distribution of the most refined samples with and without ultrasonic treatment. It is evident that ultrasonic vibration not only decreases the average grain size but also homogenizes grain size distribution, as can be inferred by the higher frequency of grains with less than 100 µm. These results suggest that ultrasonic treatment can be applied to foundry practice of the Al–1Mg–0.3Sc alloy at a wide range of temperatures ensuring both fluidity of the melt and grain refinement.
5.1.2.2 Grain refinement mechanism

We propose that cavitation-enhanced heterogeneous nucleation is the main mechanism of grain refinement by ultrasonic treatment in Al–1Mg–0.3Sc alloy. When the ultrasonic treatment was applied directly into the melt, a large number of cavitation bubbles were formed throughout the melt. These cavitation bubbles grow and the bubbles temperature decreases due to the expansion of the gas inside them. At critical size of bubbles, they will collapse and generate the pressure pulse. The increase of the local pressure in the melt leads to transiently increase of the melting point of the alloy according to the Clausius-Clapeyron equation. The decrease of bubble temperature and the increase of melting point lead to high localized undercooling at the bubble/melt interface. As a consequence, a large number of nuclei are formed at the surface of existing bubbles. These bubbles will collapse and disperse nuclei into the melt. Through acoustic streaming, the nuclei are homogeneously distributed throughout the melt. Moreover, the cavitation phenomenon cleans the surfaces of nuclei, improves their wettability and consequently increases the nucleant potency.

High ultrasonic treatment temperatures will shorten the life time of cavitation bubbles and decrease undercooling in the melt. Therefore, the number of nuclei formed in the melt will decrease which results in less grain refinement. This mechanism explains the increase in average grain size when the ultrasonic treatment temperature increases from 720 to 800 ºC. The slightly higher grain size of the alloy treated at 700 ºC in comparison with 720 ºC can be explained by a decrease in melt fluidity. The lower fluidity of the melt reduces the dispersion of nuclei that results in less grain refinement.
5.2 Conclusions

5.2.1 Grain refinement of Al–Mg–Sc alloys without ultrasonic treatment

- The average grain size of Al–Mg alloy remarkably decreases from 439 ± 21 to 95 ± 2 μm when the content of Mg increases from 1 to 4 wt% at the pouring temperature of 700 °C.
- The average grain size of Al–1Mg sharply decreases from 439 ± 21 μm to 103 ± 2 μm by adding 0.3 wt% of Sc.
- The pouring temperature has a strong effect on the microstructure of Al–1Mg–0.3Sc alloy. Lower pouring temperature leads to smaller grain size and more homogeneous microstructure in this alloy. The fine equiaxed grains in microstructure can be achieved at pouring temperature range from 680–710 °C.
- The mechanism of grain refinement that bases on heterogeneous nucleation above liquidus and dendrite growth restriction by segregating solute elements was proposed. MgAl₂O₄ oxide and Al₃Sc possibly act as nuclei sites for α–Al nucleation.

5.2.2 Grain refinement of Al–Mg–Sc alloys with ultrasonic treatment

- Ultrasonic vibration proved to be a potential grain refinement technique of Al–1Mg–0.3Sc. Significant grain refinement was obtained by applying ultrasonic treatment within the temperature range from 700 to 740 °C. This fact makes more flexible to decide the pouring temperature in the foundry practice of this kind of alloy. The best grain refinement and uniform grain size are obtained by ultrasonic treatment at 720 °C.
- Grain refinement of Al–1Mg–0.3Sc alloy by ultrasonic treatment can be explained by the cavitation-enhanced heterogeneous nucleation mechanism.
References


Effects of substituting rare earth metals for scandium on the microstructure and properties of Al-Sc and Al-Mg-Sc alloys

CHAPTER 6: THE EFFECT OF SUBSTITUTING Yb FOR Sc ON CORROSION BEHAVIOUR OF HEAT TREATED Al–Sc AND Al–Mg–Sc ALLOYS


**Chapter 6: The effect of substituting ytterbium for scandium and aged-hardening heat treatment on corrosion behaviour of Al–Sc and Al–Mg–Sc alloys**

**Introduction**

Sc–containing Al alloys are potentially to apply in saltwater environment due to a good corrosion resistance. However, almost works have been focused on microstructure and mechanical properties while limited research is focused on corrosion behaviour of Sc–containing Al alloys. The effect of Sc on corrosion behaviour has been investigated in various Al alloys [1-15], pure Al [1], Al–Zn alloys [12,14], Al–Mg alloys [2-4], Al–Zn–Mg alloys [5-7,15], and Al–Cu–Li–Mg–Ag alloys [15]. These researches indicated that Sc has a positive effect on the corrosion properties of Al alloys. The results of corrosion rates and passivation current density indicated that the addition of Sc enhances the corrosion resistance of Al alloys [1,2,5]. The electrochemical properties of coarse Al,Sc particle were investigated by Cavanaugh *et al.* [8] where the influence of these particles on the initiation and propagation of pitting corrosion in Al–2.05 wt% Sc alloy exposed to dilute chloride solution was evaluated. The authors reported that Al,Sc is slightly cathodic to the α–Al matrix and spontaneously passivates with a low self-dissolution rate in dilute chloride solution. Al,Sc showed slower oxygen reduction reaction kinetics than other dispersoid intermetallic phases as Al,Zr, Al,Mn and Al,Ti. Ganiev [1] and Vyazovikina [15] proposed that the passive film in Sc–containing Al alloys consists of duplex layer of scandium oxide and aluminium oxide. Sc,O, layer was formed by the presence of oxygen in the solution, deposited and accumulated on the surface of alloys. In comparison with the less defective Al,O, layer, the duplex layer in Sc–containing Al alloys has more protective property. As a consequence, the corrosion resistance in these alloys was improved.

Another results for Al,Sc,Zr, phases in Al–Zn–Mg–Cu alloys was shown by Wloka *et al.* [7]. The authors indicated that these coarse particles disturb the grain structure near the particle/matrix interface and initiate localized corrosion. Moreover, mass loss measurements showed that the addition of scandium increases the mass loss during the initial period. Ahmad and Aleem [16] studied the effect of Sc on mechanical properties and corrosion resistance of Al–2.5 Mg alloys doped with Sc and Zr. The authors reported that the homogeneous coherent nano Al(Sc,Zr) precipitates increase the passivation tendency and improve the corrosion resistance of alloys. It was also suggested that the formation of protective Sc,O, reinforced Al,O, films that enhanced the passivity of Al–Mg–Sc alloys. The film is very coherent with the matrix due to the coherency of the nano-precipitates without any discontinuities at the oxide/electrolyte interface. However, experimental proofs are needed to confirm this hypothesis.
To the best of our knowledge there was no research showing details of corrosion behaviour and its mechanisms of Sc–containing Al alloys.

In the present work, the corrosion behaviour of Al–0.28Sc and Al–0.24Sc–0.07Yb, Al–4Mg, Al–4Mg–0.3Sc and Al–4Mg–0.24Sc–0.06Yb alloys in 3.5 wt% of sodium chloride was investigated by immersion and potentiodynamic polarisation studies. The effect of the addition of Sc and Yb, impurity intermetallic phases, and heat treatment on corrosion behaviour of these alloys was studied.

6.1 Results and discussion

6.1.1 Effects of substituting ytterbium for scandium on corrosion behaviour of Al–Sc alloy

6.1.1.1 Impurity intermetallic particles

The morphologies of intermetallic particles in Al–0.28Sc and Al–0.24Sc–0.07Yb alloys were observed and the representative SEM images are given in Fig. 6.1. Chemical compositions of selected intermetallic particles were determined by EDS and the results are listed in Table 6.1. It can be seen that the intermetallic particles with rod-like and rounded shapes are uniformly distributed throughout the matrix in both Al–0.28Sc and Al–0.24Sc–0.07Yb alloys. The size range of rod-like particles is 7–15 μm in length whereas the size range of rounded particles is 1–3 μm. Two intermetallic phases were detected in Al–0.28Sc alloy: Al–Sc–Si–Fe (particles marked as “A1” and “A2”) and Al–Fe (particle marked as “A3”) containing intermetallic phases. Al–Sc–Yb–Si–Fe–Cu (particles marked as “B1”, “B2”, and “B3”), Al–Sc–Yb–Fe–Cu (particle marked as “B4”) containing intermetallic phases were observed in Al–0.24Sc–0.07Yb alloy. The age-hardening heat treatment did not affect significantly these intermetallic particles, thus they were also detected in heat treated samples of both alloys.
Figure 6.1. SEM micrographs of Al–0.28Sc alloy (a–b–c) and Al–0.24Sc–0.07Yb alloy (d–e–f).
### Table 6.1. Chemical compositions of intermetallic particles in Al–0.28Sc and Al–0.24Sc–0.07Yb alloys

<table>
<thead>
<tr>
<th>Intermetallic Particle</th>
<th>Al (wt%)</th>
<th>Sc (wt%)</th>
<th>Yb (wt%)</th>
<th>Fe (wt%)</th>
<th>Si (wt%)</th>
<th>Cu (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Al–0.28Sc</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A1</td>
<td>87.31</td>
<td>1.97</td>
<td>-</td>
<td>8.06</td>
<td>2.67</td>
<td>-</td>
</tr>
<tr>
<td>A2</td>
<td>89.92</td>
<td>1.31</td>
<td>-</td>
<td>7.49</td>
<td>1.28</td>
<td>-</td>
</tr>
<tr>
<td>A3</td>
<td>91.9</td>
<td>-</td>
<td>-</td>
<td>8.1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td><strong>Al–0.24Sc–0.07Yb</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B1</td>
<td>78.28</td>
<td>0.67</td>
<td>5.24</td>
<td>9.7</td>
<td>2.33</td>
<td>3.77</td>
</tr>
<tr>
<td>B2</td>
<td>79.27</td>
<td>0.8</td>
<td>4.0</td>
<td>10.14</td>
<td>2.93</td>
<td>2.86</td>
</tr>
<tr>
<td>B3</td>
<td>76.76</td>
<td>1.31</td>
<td>6.64</td>
<td>9.01</td>
<td>3.94</td>
<td>2.35</td>
</tr>
<tr>
<td>B4</td>
<td>83.36</td>
<td>0.55</td>
<td>3.27</td>
<td>9.97</td>
<td>-</td>
<td>2.86</td>
</tr>
</tbody>
</table>

#### 6.1.1.2 Corrosion test

**i) Immersion tests**

Fig. 6.2 shows the evolution of the OCP with immersion time for Al–0.28Sc and Al–0.24Sc–0.07Yb alloys (as-cast and heat treated samples) in 3.5 wt% NaCl solution.

![Figure 6.2. Evolution of OCP with time for Al–0.28Sc and Al–0.24Sc–0.07Yb alloys (as-cast and heat treated samples).](image)

After exposing all samples to 3.5 wt% NaCl solution the OCP starts to decrease as a consequence of the initiation of pits. After 4 days of immersion, the OCP of Al–0.28Sc (as-cast and heat treated samples)
and Al–0.24Sc–0.07Yb (as-cast sample) were measured as $-883 \pm 41$, $-901 \pm 35$, and $-904 \pm 39$ mV vs. SCE, respectively. There was no significant difference between these values suggesting the similarity in thermodynamic tendency of these alloys to electrochemical oxidation in 3.5 wt% NaCl solution. The OCP of Al–0.24Sc–0.07Yb heat treated sample stabilized quickly at $-755 \pm 30$ mV vs. SCE after 4 hours of immersion. The OCP of Al–0.24Sc–0.07Yb heat treated sample is more noble (shift to positive value) than that of other samples. It indicated that the addition of Yb and age-hardening heat treatment decreases the susceptibility to corrosion in Al–Sc alloy.

Fig. 6.3 shows the representative SEM micrographs of Al–0.28Sc as-cast and heat treated samples exposed for 4 days in 3.5 wt% NaCl solution. Chemical compositions of three selected intermetallic particles were determined by EDS and listed in Table 6.2. The particles marked as “C1” contain Al and Fe, the particle “C2” contains Al, Sc, and Fe, and the particle “C4” contain Al, Sc, Fe, and Si. The dissolution of the matrix surrounding these Fe–containing intermetallic phases was observed. These particles are more noble in comparison with the matrix that can act as cathodes that may cause galvanic coupling with the surrounding matrix as well as an increase on pH due to hydroxyl ions forming during oxygen reduction reaction [17,18]. As a consequence, the dissolution of the matrix at the periphery of these particles may occur. The composition in the grain boundary (the area marked as “C3”) was also analyzed. Fe and Sc segregated on the grain boundary and promoted a slight dissolution of the matrix at these sites. Previous studies have demonstrated that Fe-containing intermetallic particles (such as Al$_6$Fe, Al$_3$Fe and Al$_{12}$Fe$_3$Si$_2$, etc...) can act as cathodes compared to the matrix and promote the preferential dissolution of the surrounding matrix [17-25]. The corrosion product still remained after cleaning the surface of Al–0.28Sc as-cast sample (Fig. 6.3(c)) that was detected as Al(OH)$_3$ [3]. Many pit cavities were observed in the microstructure of Al–0.28Sc heat treated sample. The presence of Al$_3$Sc nano-precipitates in Al–0.28Sc heat treated sample can accelerate the pitting propagation and therefore increase the pit growth rate and number of pit cavities.
Figure 6.3. SEM micrographs of Al–0.28Sc alloy after immersion in 3.5 wt% NaCl solution for 4 days: (a–b–c) as-cast samples; (d–e–f) heat treated samples; (a–b–d–f) BSE images and (c–e) SE image.
Table 6.2. Chemical compositions of intermetallic particles in Al–0.28Sc alloy after immersion in a 3.5 wt% NaCl solution for 4 days

<table>
<thead>
<tr>
<th>Particle</th>
<th>Al</th>
<th>Sc</th>
<th>Fe</th>
<th>Si</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>wt%</td>
<td>78.77</td>
<td>0.88</td>
<td>3.69</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>at%</td>
<td>71.52</td>
<td>-</td>
<td>1.62</td>
<td>-</td>
</tr>
<tr>
<td>C2</td>
<td>wt%</td>
<td>82.17</td>
<td>0.67</td>
<td>0.98</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>at%</td>
<td>74.47</td>
<td>0.36</td>
<td>0.43</td>
<td>-</td>
</tr>
<tr>
<td>C3</td>
<td>wt%</td>
<td>72.71</td>
<td>1.27</td>
<td>1.75</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>at%</td>
<td>63.09</td>
<td>0.66</td>
<td>0.73</td>
<td>-</td>
</tr>
<tr>
<td>C4</td>
<td>wt%</td>
<td>74.15</td>
<td>0.72</td>
<td>7.53</td>
<td>0.49</td>
</tr>
<tr>
<td></td>
<td>at%</td>
<td>69.37</td>
<td>0.41</td>
<td>3.41</td>
<td>1.34</td>
</tr>
</tbody>
</table>

Fig. 6.4 shows SEM micrographs taken on Al–0.24Sc–0.07Yb as-cast and heat treated samples exposed for 4 days in 3.5 wt% NaCl solution at OCP. Chemical compositions of the particles labelled as “D1” (Al–Sc–Fe–Si intermetallic phase), “D2” (Al–Sc–Yb–Fe–Si intermetallic phase), “D3” (Al–Sc–Yb–Fe intermetallic phase), “D4” (Al–Sc–Fe intermetallic phase) and “C5” (grain boundary containing Al–Sc–Fe) after EDS analysis were given in Table 6.3. The dissolution of the matrix was observed clearly in the vicinity of the particles “D1”, “D2” and slightly at the periphery of the particles “D3”, “D4”, and “D5”. Some pit cavities present in the microstructure of Al–0.24Sc–0.07Yb heat treated sample. It can be seen the corrosion product (Al(OH)₃) deposited in the vicinity of pit cavities. In comparison with Al–0.28Sc heat treated sample, the number of pit cavities in the Al–0.24Sc–0.07Yb heat treated sample was much lower.
Figure 6.4. SEM micrographs of Al–0.24Sc–0.07Yb alloy after immersion in 3.5 wt% NaCl solution for 4 days: (a–b–c) as-cast samples; (d–e–f) heat treated samples.
Table 6.3. Chemical compositions of intermetallic particles in Al–0.24Sc–0.07Yb alloy after immersion in a 3.5 wt% NaCl solution for 4 days

<table>
<thead>
<tr>
<th>Particle</th>
<th>Al  (wt%)</th>
<th>Sc  (wt%)</th>
<th>Yb  (wt%)</th>
<th>Fe  (wt%)</th>
<th>Si  (wt%)</th>
<th>O  (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D1</td>
<td>76.32</td>
<td>0.99</td>
<td>-</td>
<td>10.57</td>
<td>1.28</td>
<td>10.84</td>
</tr>
<tr>
<td></td>
<td>75.16</td>
<td>0.59</td>
<td>-</td>
<td>5.03</td>
<td>1.21</td>
<td>18.01</td>
</tr>
<tr>
<td>D2</td>
<td>53.60</td>
<td>1.52</td>
<td>13.16</td>
<td>4.39</td>
<td>3.22</td>
<td>24.10</td>
</tr>
<tr>
<td></td>
<td>52.24</td>
<td>0.89</td>
<td>2.01</td>
<td>2.07</td>
<td>3.03</td>
<td>39.76</td>
</tr>
<tr>
<td>D3</td>
<td>65.57</td>
<td>0.53</td>
<td>5.46</td>
<td>4.44</td>
<td>-</td>
<td>24.00</td>
</tr>
<tr>
<td></td>
<td>59.96</td>
<td>0.29</td>
<td>0.78</td>
<td>1.96</td>
<td>-</td>
<td>37.01</td>
</tr>
<tr>
<td>D4</td>
<td>67.80</td>
<td>0.60</td>
<td>-</td>
<td>6.34</td>
<td>-</td>
<td>25.26</td>
</tr>
<tr>
<td></td>
<td>57.57</td>
<td>0.32</td>
<td>-</td>
<td>2.69</td>
<td>-</td>
<td>37.42</td>
</tr>
<tr>
<td>D5</td>
<td>81.05</td>
<td>0.49</td>
<td>-</td>
<td>1.97</td>
<td>-</td>
<td>16.49</td>
</tr>
<tr>
<td></td>
<td>73.61</td>
<td>0.27</td>
<td>-</td>
<td>0.87</td>
<td>-</td>
<td>25.26</td>
</tr>
</tbody>
</table>

ii) Potentiodynamic polarization behaviour

Representative potentiodynamic polarization curves of Al–0.28Sc and Al–0.24Sc–0.07Yb alloys (as-cast and heat treated samples) in 3.5 wt% NaCl solution are shown in the Fig. 6.5. Corrosion potential (E_{corr}), corrosion current density (i_{corr}) and pitting potential (E_p) are listed in Table 6.4.

![Potentiodynamic polarization curves](image-url)

Figure 6.5. Potentiodynamic polarization curves obtained in 3.5 wt% NaCl solution for Al–0.28Sc and Al–0.24Sc–0.07Yb alloys (as-cast and heat treated samples).
### Table 6.4. Summary of results of potentiodynamic polarization

<table>
<thead>
<tr>
<th>Alloys</th>
<th>$E_{corr}$ (mV)</th>
<th>$i_{corr}$ ($\mu A cm^{-2}$)</th>
<th>$E_{pit}$ (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-0.3Sc, as-cast</td>
<td>-956 ± 30</td>
<td>0.296 ± 0.139</td>
<td>-632 ± 42</td>
</tr>
<tr>
<td>Al-0.3Sc, aging325 -C, 5h</td>
<td>-1038 ± 8</td>
<td>1.913 ± 0.596</td>
<td>-679 ± 33</td>
</tr>
<tr>
<td>Al-0.24Sc-0.06Yb, as-cast</td>
<td>-884 ± 6</td>
<td>0.110 ± 0.02</td>
<td>-565 ± 24</td>
</tr>
<tr>
<td>Al-0.24Sc-0.06Yb, aging325 -C, 5h</td>
<td>-982 ± 9</td>
<td>3.281 ± 0.968</td>
<td>-521 ± 19</td>
</tr>
</tbody>
</table>

It can be seen that after the addition of Yb, the corrosion potential ($E_{corr}$) of Al–0.24Sc–0.07Yb as-cast and heat treated samples were more positive than Al–0.28Sc as-cast and heat treated samples. It indicates that Al–0.24Sc–0.07Yb alloy presents lower tendency to corrosion in 3.5 wt% NaCl solution than Al–0.28Sc alloy. Yb addition and age-hardening heat treatment had strong effect on the polarization behavior in the anodic domain of Al–Sc alloy. The polarization curve in the anodic domain of Al–0.28Sc as-cast sample show the active corrosion followed by induced pitting. Al–0.28Sc heat treated samples presented active corrosion and passivation followed by induced pitting. On the other hand, Al–0.24Sc–0.07Yb as-cast and heat treated samples exhibited an active region due to metal oxidation with the increasing of current density as applied potential increases. Then, the current density tends to decrease with the increasing of applied potential to reach the passive current density. In the heat treated sample, the passive region was observed before a localized breakdown of passivity due to transpassive dissolution and pitting corrosion. At pitting potential, the current density rapidly increases. The pitting potentials of Al–0.28Sc as cast and heat treated samples are -632 ± 42 and -679 ± 33 mV vs. SCE, respectively. The pitting potentials of Al–0.24Sc–0.07Yb as cast and heat treated samples are -565 ± 24 and -521 ± 19 mV vs. SCE, respectively. The pitting potentials of Al–0.24Sc–0.07Yb alloy (both as-cast and heat treated samples) were more positive than that of Al–0.28Sc alloy. Thus, it can be stated that the addition of Yb improved the resistance to pitting corrosion of Al–0.28Sc alloy.

After age-hardening heat treatment, the corrosion potentials of Al–0.28Sc and Al–0.24Sc–0.07Yb alloys moved to negative direction and the corrosion current density increased significantly. The presence of Al₃Sc or Al₃(Sc,Yb) precipitates can increase the susceptibility to corrosion and corrosion rate of these alloys. However, the passive plateau was clearly observed in the polarization curve of heat treated samples for both alloys. It is suggested that the age-hardening heat treatment enhances the passivation tendency of Al–0.28Sc and Al–0.24Sc–0.07Yb alloys during exposure to 3.5 wt% NaCl solution. This result is supported by the hypothesis proposed by Ahmad and Aleem [16]. The existence of a high
number density of nano–sized Al₃Sc or Al₃(Sc,Yb) precipitates, which fully coherent with the matrix, leads to improvement of the passivity of heat treated samples.

Pitting corrosion in aluminium alloys is a complex process that depends on many factors such as temperature, pH, solution or the characteristics of microstructure and passive layer [26]. In this section, the pitting corrosion mechanisms in Al–0.28Sc and Al–0.24Sc–0.07Yb alloys exposure to 3.5 wt% NaCl solution were proposed. Aluminium alloys are susceptible to pitting corrosion due to the presence of intermetallic phases more noble than the matrix [20,21,23,27,28]. These particles can act as cathodes and cause the preferential dissolution of the surrounding matrix. In addition, the reduction reaction of water and oxygen leads to increase the local pH. The presence of OH⁻ ion can dissolve the protective oxide layer and promotes the formation of pits in the vicinity of these intermetallic particles (localized alkaline corrosion). Besides, the adsorption of aggressive Cl⁻ ion into the defective sites of the passive layer can trigger the pitting process [29]. Figure 6.6(a) shows the schematic view of the proposed corrosion process due to the presence of intermetallic phase and Cl⁻ ions aggression into the defective sites. The first image exhibits the cross-section of sample before immersion containing the intermetallic phases and a thin oxide layer. The second image shows cathodic and anodic possible reactions of corrosion process in the sample during exposure to the NaCl solution. The anodic reactions are the oxidation of Al and Sc and consequently lead to the preferential dissolution of the matrix. The cathodic reactions are water and oxygen reductions that cause the localized alkaline medium. The third image shows the pits at the periphery of intermetallic particles and a cavity in the sample after immersion. The surface of sample in the vicinity of intermetallic particles and cavities is covered by corrosion production depositions. Besides, the localized alkaline corrosion could completely occur in the surrounding matrix of the intermetallic particles and cause a cavity due to the detachment of these particles [29]. The schematic of this hypothesis is shown in Figure 6.6 (b).
Figure 6.6. (a) Schematic view of the corrosion process: sample before immersion, corrosion reactions in the NaCl solution, and sample after exposure to the solution; (b) Schematic view of the cavity formation by localized alkaline corrosion.
6.1.2 The effect of Sc and Yb microalloying additions and aged-hardening heat treatment on corrosion behaviour of Al–Mg alloys

6.1.2.1 Impurity intermetallic particles

Iron, copper and silicon are common impurities in aluminium alloys. Intermetallic particles could be formed by alloying elements and those impurity elements play a crucial role in localized corrosion of Al alloys. Before exposure of samples to the 3.5 wt% NaCl solution, their microstructure was characterized by SEM and EDS. The morphologies and chemical elements of intermetallic particles were observed and analysed. Fig. 6.7 shows the SEM micrographs and EDS spectra of Al–4Mg alloy. Two second phase intermetallic particles were detected: bright particles (particle marked as “Z1”) with needle-like shape contain Al, Mg, Si, and Fe and Chinese script dark particles (particle marked as “Z2”) contain Mg, Al, and Si.

![SEM micrographs and EDS spectra of intermetallic phases in Al–4Mg alloy.](image)

Chinese script dark particles were observed in the grain boundaries. Fig. 6.8 and Fig. 6.9 exhibit the SEM micrographs and EDS spectra of Al–4Mg–0.3Sc and Al–4Mg–0.24Sc–0.06Yb alloys, respectively. The size of the impurity intermetallic particles dramatically decreased to 0.5–4 μm when adding Sc and Yb to Al–4Mg alloy. Three types of second-phase particles with different chemical compositions were detected in Al–4Mg–0.3Sc alloy: Al–Mg–Si–Fe (particle marked as “Z3”), Al–Mg–Sc–Si–Fe (particle marked as “Z4”) containing intermetallic particle and oxide particle (particle marked as “Z5”). Oxide
particle could be MgAl₂O₄ that was formed during casting due to the high affinity of Mg with oxygen [30]. Another intermetallic particle containing Al, Mg, Sc, Si, Fe, and Yb (“Z6” particle) was observed in Al–4Mg–0.24Sc–0.06Yb alloy. These intermetallic phases were also detected in the microstructures of heat treated alloys because these phases are generally unaffected by heat treatment.

Figure 6.8. SEM micrographs and EDS spectra of intermetallic phases in Al–4Mg–0.3Sc alloy.

Figure 6.9. SEM micrographs and EDS spectra of intermetallic phases in Al–4Mg–0.24Sc–0.06Yb alloy.
6.1.2.2 Corrosion tests

i) Immersion tests

The OCP indicates the thermodynamic tendency of a material to electrochemical oxidation in a corrosive environment. During immersion, the nature of the sample surface changes due to oxidation or passive film formation and consequently alters the OCP of sample. The OCP will stabilize around a stationary value after a period of immersion. Fig. 6.10 shows the evolution of the OCP with time for Al–4Mg, Al–4Mg–0.3Sc and Al–4Mg–0.24Sc–0.06Yb alloys (as-cast and heat treated samples) immersed in 3.5 wt% NaCl solution.

![Figure 6.10](image)

*Figure 6.10. Evolution of OCP values with time for Al–4Mg, Al–4Mg–0.3Sc and Al–4Mg–0.24Sc–0.06Yb alloys (as-cast and heat treated samples).*

In the beginning period of immersion, the OCP values presented large oscillations. Over longer periods of exposure, the OCP decreased and reached relatively stable values. The OCP becomes less and less noble can be explained by the initiation of pitting. Al alloys tend to pitting corrosion in presence of chlorides ions at a pH close to neutrality. The passive film dissolves to form Al³⁺ and reduces its protection ability. The OCP decreases with the increase of the dissolution rate. The OCP of Al–4Mg, Al–4Mg–0.3Sc and Al–4Mg–0.24Sc–0.06Yb as-cast samples stabilized at −774 ± 33, −923 ± 17, and −945 ± 19 mV vs. SCE after 8, 24, and 24 hours of immersion, respectively. The OCP of Al–4Mg–0.3Sc and Al–4Mg–0.24Sc–0.06Yb heat treated samples stabilized at −789 ± 27 and −864 ± 26 mV vs. SCE after 48 hours of immersion, respectively. It can be seen that the OCP of Al–4Mg became less noble (more negative) by adding Sc and Yb. This indicated that Al–4Mg–0.3Sc and Al–4Mg–0.24Sc–0.06Yb as-cast alloy have a higher susceptibility to corrosion in comparison with Al–4Mg alloy. However, the OCP of Al–4Mg–0.3Sc and Al–4Mg–0.24Sc–0.06Yb heat treated alloys was more positive than the as-cast
alloys, indicating higher tendency to corrosion in heat treated alloys than as-cast alloys. The presence of high number density of Al,Sc precipitates as a result of age-hardening heat treatment increases the cathodic reactivity of the surface, thereby increasing the OCP of heat treated alloys.

Fig. 6.11 shows representative SEM micrographs at the corroded surfaces taken on Al–4Mg sample exposed for 4 days in 3.5 wt% NaCl solution at OCP.

Figure 6.11. SEM micrographs of Al–4Mg alloy after immersion in 3.5 wt% NaCl solution for 4 days: (a–b) BSE images and (c) SE image.

Chemical compositions of three selected intermetallic particles were determined by EDS and the results are given in Table 6.5.

<table>
<thead>
<tr>
<th>Particle</th>
<th>Al</th>
<th>Mg</th>
<th>Fe</th>
<th>Si</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>wt%</td>
<td>61.04</td>
<td>2.76</td>
<td>6.44</td>
<td>17.72</td>
</tr>
<tr>
<td></td>
<td>at%</td>
<td>58.39</td>
<td>2.93</td>
<td>2.98</td>
<td>16.28</td>
</tr>
<tr>
<td>A2</td>
<td>wt%</td>
<td>59.28</td>
<td>1.21</td>
<td>16.17</td>
<td>12.84</td>
</tr>
<tr>
<td></td>
<td>at%</td>
<td>60.19</td>
<td>1.37</td>
<td>7.93</td>
<td>12.53</td>
</tr>
<tr>
<td>A3</td>
<td>wt%</td>
<td>68.86</td>
<td>10.11</td>
<td>-</td>
<td>8.37</td>
</tr>
<tr>
<td></td>
<td>at%</td>
<td>62.91</td>
<td>10.25</td>
<td>-</td>
<td>7.34</td>
</tr>
</tbody>
</table>

The particles labelled as “A1” and “A2” contain Al, Mg, Fe, and Si whereas the particle labelled as “A3” contain Al, Mg, and Si. It is evident to observe the dissolution of the matrix at the periphery of the
Al–Mg–Fe–Si containing particles. These particles are nobler than the matrix thus can act as cathodes and support oxygen reduction to form hydroxyl ions. The galvanic coupling between the noble particles and the surrounding matrix was established. Furthermore, it has been reported that a local pH at these particles can increase and promotes grooving of the surrounding matrix by alkaline dissolution \cite{17,18}. On the other hand, corrosion was not observed in the vicinities of the Al–Mg–Si containing particles. Birbilis and Buchheit \cite{18} reported a survey of corrosion potentials and electrochemical characteristics for intermetallic particles commonly present in high-strength aluminium-based alloys. Corrosion potentials of Mg–containing intermetallic phases are between corrosion potential of pure Al (−823 mV vs. SCE in 0.1 M NaCl solution) and pure Mg (−1586 mV vs. SCE in 0.1 M NaCl solution). According to Birbilis and Buchheit, corrosion potentials of Mg–containing intermetallic phases are more negative than Al matrix and other intermetallic phases. Therefore, these phases are active to the matrix and can act as anode leading to dissolution or Mg dealloying when exposed in NaCl solution. This mechanism has also been confirmed by some previous researches \cite{28,31,32}. However different Mg–containing intermetallic phases show the different phenomena due to the different dissolution rates and the presence of noble elements.

Mg–containing intermetallic phases with high self-dissolution rates lead to an anodic dissolution at high rates. The local alkalization appears and can dissolve the Al matrix in the vicinity of intermetallic particles \cite{28}. In the Mg–containing intermetallic particle with a noble elemental such as Al\textsubscript{1}CuMg, Mg and Al selectively dissolve and the dealloying particle remnant can act as cathode. The peripheral pits around the particle occur due to the alkaline dissolution or galvanic corrosion \cite{28}. In the present study, the Al–Mg–Si containing particles in Al–4Mg alloy are not any case listed above. We proposed that Al–Mg–Si containing phase has a low self-dissolution rate. Therefore, there is no preferential dissolution of the matrix surrounding Al–Mg–Si containing particles.

Fig. 6.12 shows representative SEM micrographs taken on Al–4Mg–0.3Sc as-cast and heat treated samples exposed for 4 days in 3.5 wt% NaCl solution at OCP. Two intermetallic phases were detected. The Al–Mg–Sc–Si–Fe containing intermetallic particle labelled as “B1”, “B2”, “B4” and Al–Mg–Sc–Fe containing intermetallic particle labelled as “B3”. Both phases are Fe–containing intermetallic phases. The Al–Mg–Fe–Si containing intermetallic phase was not detected on the samples.
Chemical compositions of these intermetallic particles were determined by EDS and the results are listed in Table 6.6. It can be observed that the matrix dissolved heavily in the vicinity of the particles “B1” and “B2”. A slight anodic dissolution of the matrix at the periphery of the particle “B3” was observed. No preferential dissolution of the matrix was detected around the particle “B4”. Table 6.6 shows that the Mg content in these intermetallic particles increases gradually from the particles “B1” and “B2” to “B3” and maximum in the particle “B4”. The presence of Mg in the Fe–containing intermetallic phases can reduce both anodic and cathodic rates, thus, the high content of Mg makes the Fe–containing intermetallic particle less noble to the matrix.
Table 6.6. Chemical compositions of intermetallic particles in Al–4Mg–0.3Sc alloy after immersion in 3.5 wt% NaCl solution for 4 days

<table>
<thead>
<tr>
<th>Particle</th>
<th>Al</th>
<th>Mg</th>
<th>Sc</th>
<th>Fe</th>
<th>Si</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1</td>
<td>wt%</td>
<td>42.1</td>
<td>2.73</td>
<td>0.95</td>
<td>17.32</td>
<td>1.35</td>
</tr>
<tr>
<td></td>
<td>at%</td>
<td>36.52</td>
<td>2.62</td>
<td>0.49</td>
<td>7.26</td>
<td>1.12</td>
</tr>
<tr>
<td>B2</td>
<td>wt%</td>
<td>58.17</td>
<td>1.72</td>
<td>0.83</td>
<td>14.12</td>
<td>1.11</td>
</tr>
<tr>
<td></td>
<td>at%</td>
<td>53.36</td>
<td>1.76</td>
<td>0.45</td>
<td>6.26</td>
<td>0.98</td>
</tr>
<tr>
<td>B3</td>
<td>wt%</td>
<td>69.20</td>
<td>3.54</td>
<td>0.39</td>
<td>9.12</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>at%</td>
<td>64.25</td>
<td>3.65</td>
<td>0.22</td>
<td>4.09</td>
<td>-</td>
</tr>
<tr>
<td>B4</td>
<td>wt%</td>
<td>74.83</td>
<td>5.63</td>
<td>0.56</td>
<td>10.46</td>
<td>1.18</td>
</tr>
<tr>
<td></td>
<td>at%</td>
<td>74.84</td>
<td>6.25</td>
<td>0.33</td>
<td>5.06</td>
<td>1.13</td>
</tr>
</tbody>
</table>

Fig. 6.13 shows representative SEM micrographs taken on Al–4Mg–0.24Sc–0.06Yb as-cast and heat treated samples exposed for 4 days in 3.5 wt% NaCl solution at OCP.

Figure 6.13. SEM micrographs of Al–4Mg–0.24Sc–0.06Yb alloy after immersion in 3.5 wt% NaCl solution for 4 days: (a–b–c) as-cast samples; (d–e–f) heat treated samples; (a–c–d–f) BSE images and (b–e) SE image.

Chemical compositions of the particles labelled as “C1” and “C4” (Al–Mg–Sc–Yb intermetallic phase), “C2” (Al–Mg–Sc–Yb–Fe–Si intermetallic phase), “C3” (Al–Mg–Sc–Fe–Si intermetallic phase), and “C5”
(Al–Mg–Sc–Yb–Fe intermetallic phase) and the results are given in Table 6.7. It can be seen that the Yb–containing intermetallic phases did not lead to corrosion in the vicinity of their particles (“C1”, “C4”, and “C5”) or a slight dissolution of the surrounding matrix was observed (“C2”). However, the high content of Fe in the particle “C3” (Al–Mg–Sc–Fe–Si intermetallic phase) promote heavily dissolution of the matrix in the vicinity of this particle. The pitting cavities were observed in both as-cast and heat treated samples of Al–4Mg–0.24Sc–0.06Yb alloy. The number of pitting cavities was significantly increased in heat treated sample.

### Table 6.7. Chemical compositions of intermetallic particles in Al–4Mg–0.24Sc–0.06Yb alloy after immersion in 3.5 wt% NaCl solution for 4 days

<table>
<thead>
<tr>
<th>Particle</th>
<th>wt%</th>
<th>Mg</th>
<th>Sc</th>
<th>Yb</th>
<th>Fe</th>
<th>Si</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>71.77</td>
<td>14.08</td>
<td>0.41</td>
<td>10.55</td>
<td>-</td>
<td>-</td>
<td>3.19</td>
</tr>
<tr>
<td>at%</td>
<td>75.81</td>
<td>16.51</td>
<td>0.26</td>
<td>1.74</td>
<td>-</td>
<td>-</td>
<td>5.68</td>
</tr>
<tr>
<td>C2</td>
<td>74.40</td>
<td>4.08</td>
<td>0.41</td>
<td>9.04</td>
<td>1.19</td>
<td>0.38</td>
<td>10.5</td>
</tr>
<tr>
<td>at%</td>
<td>74.98</td>
<td>4.56</td>
<td>0.25</td>
<td>1.42</td>
<td>0.58</td>
<td>0.37</td>
<td>17.84</td>
</tr>
<tr>
<td>C3</td>
<td>60.85</td>
<td>4.06</td>
<td>0.53</td>
<td>-</td>
<td>12.16</td>
<td>0.65</td>
<td>21.76</td>
</tr>
<tr>
<td>at%</td>
<td>55.90</td>
<td>4.14</td>
<td>0.29</td>
<td>-</td>
<td>5.39</td>
<td>0.57</td>
<td>33.70</td>
</tr>
<tr>
<td>C4</td>
<td>71.50</td>
<td>10.74</td>
<td>0.36</td>
<td>15.49</td>
<td>-</td>
<td>-</td>
<td>1.91</td>
</tr>
<tr>
<td>at%</td>
<td>80.09</td>
<td>13.35</td>
<td>0.24</td>
<td>2.71</td>
<td>-</td>
<td>-</td>
<td>3.61</td>
</tr>
<tr>
<td>C5</td>
<td>78.29</td>
<td>4.92</td>
<td>0.45</td>
<td>12.19</td>
<td>2.42</td>
<td>-</td>
<td>1.73</td>
</tr>
<tr>
<td>at%</td>
<td>86.98</td>
<td>6.07</td>
<td>0.30</td>
<td>2.11</td>
<td>1.30</td>
<td>-</td>
<td>3.24</td>
</tr>
</tbody>
</table>

**ii) Potenciodynamic polarization behaviour**

Representative potentiodynamic polarization curves of Al–4Mg, Al–4Mg–0.3Sc and Al–4Mg–0.24Sc–0.06Yb alloys (as-cast and heat treated samples) in 3.5 wt% NaCl solution are shown in the Fig. 6.15 and corrosion potential ($E_{corr}$), corrosion current density ($i_{corr}$), and pitting potential ($E_p$) are listed in the Table 6.8.
Figure 6.14. Potentiodynamic polarization curves obtained in 3.5 wt% NaCl solution for Al–4Mg, Al–4Mg–0.3Sc and Al–4Mg–0.24Sc–0.06Yb alloys (as-cast and heat treated samples).

Table 6.8. Summary of results of potentiodynamic polarization

<table>
<thead>
<tr>
<th>Alloys</th>
<th>$E_{i=0}$ (mV)</th>
<th>$i_{cor}$ (μA cm$^{-2}$)</th>
<th>$E_{pit}$ (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al–4Mg, as-cast</td>
<td>-851 ± 17</td>
<td>1.99 ± 0.83</td>
<td>-530 ± 45</td>
</tr>
<tr>
<td>Al–4Mg–0.3Sc, as-cast</td>
<td>-1100 ± 33</td>
<td>1.9 ± 0.61</td>
<td>-643 ± 57</td>
</tr>
<tr>
<td>Al–4Mg–0.3Sc, aging 325 °C, 5h</td>
<td>-1110 ± 7</td>
<td>3.06 ± 0.55</td>
<td>-527 ± 52</td>
</tr>
<tr>
<td>Al–4Mg–0.24Sc–0.06Yb, as-cast</td>
<td>-1123 ± 13</td>
<td>1.68 ± 0.33</td>
<td>-670 ± 52</td>
</tr>
<tr>
<td>Al–4Mg–0.24Sc–0.06Yb, aging 325 °C, 5h</td>
<td>-1125 ± 9</td>
<td>4.29 ± 0.50</td>
<td>-591 ± 29</td>
</tr>
</tbody>
</table>

It can be seen that corrosion potential of Al–4Mg alloy is more positive than Al–4Mg–0.3Sc and Al–4Mg–0.24Sc–0.06Yb alloys (as-cast and heat treated samples). The addition of Sc and Yb increased the corrosion tendency of Al–4Mg alloy in 3.5 wt% NaCl solution. The heat treatment did not change the corrosion potential of Al–4Mg–0.3Sc and Al–4Mg–0.24Sc–0.06Yb alloys significantly. It is known that Sc is electrochemically active in both solid solution and the Al$_3$Sc intermetallic form [33]. This characteristic can promote the active dissolution of alloys. The presence of new impurity intermetallic phases in Al–4Mg–0.3Sc and Al–4Mg–0.24Sc–0.06Yb alloys also plays an important role by increasing the corrosion tendency. The cathodic current density increased significantly by the addition of Sc and Yb to Al–4Mg alloy and by the heat treatment of Al–4Mg–0.3Sc and Al–4Mg–0.24Sc–0.06Yb alloys, whereas, the corrosion current density was not significantly affected by the addition of Sc and Yb.
However, the heat treatment increased the corrosion current density of Al–4Mg–0.3Sc and Al–4Mg–0.24Sc–0.06Yb alloys. Faraday’s law indicated that the electrochemical corrosion rate is proportional with the corrosion current density. Thus, the corrosion rate of Al–4Mg–0.3Sc and Al–4Mg–0.24Sc–0.06Yb alloys was increased after heat treatment. The highest corrosion current density was observed in the Al–4Mg–0.24Sc–0.06Yb heat treated sample. This value is in accordance with the high amount of pits that was observed in the SEM micrographs of Al–4Mg–0.24Sc–0.06Yb heat treated sample after immersion for 4 days in 3.5 wt% NaCl solution (Fig. 6.13(d) and Fig. 6.13(e)).

The polarization curve in the anodic domain of as-cast Al–4Mg alloy shows the active corrosion followed by induced pitting where a passive plateau was not observed. The polarization curves of Al–4Mg–0.3Sc and Al–4Mg–0.24Sc–0.06Yb alloys (as-cast and heat treated samples) show a spontaneous passivation before a distinctly breakdown by pitting corrosion. The dissolution in a neutral solution is given by [28]:

\[
Al \rightarrow Al^{3+} + 3e^- \quad (1)
\]

\[
Mg \rightarrow Mg^{2+} + 2e^- \quad (2)
\]

\[
Sc \rightarrow Sc^{3+} + 3e^- \quad (3)
\]

\[
Al + 3OH^- \rightarrow Al(OH)_3 \quad (4)
\]

\[
Sc + 3OH^- \rightarrow Sc(OH)_3 \quad (5)
\]

And the cathodic reactions are given by:

\[
2H_2O + 2e^- \rightarrow H_2 \uparrow + 2OH^- \quad (6)
\]

\[
O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad (7)
\]

In Al–4Mg alloy, the films of bayerite and boehmite (AlO$_2$.3H$_2$O, AlO$_2$H$_2$O) can be formed but it is not stable and easy to breakdown by the presence of large impurity intermetallic particles (Fig. 6.7). In Al–4Mg–0.3Sc and Al–4Mg–0.24Sc–0.06Yb alloys, hydrated Sc$_2$O$_3$ is accumulated to form the duplex film with bayerite and boehmite [1,9,16,33]. This duplex film is less defective and more stable than bayerite and boehmite films. Therefore it enhances the passivity of Al–4Mg–0.3Sc and Al–4Mg–0.24Sc–0.06Yb alloys.

In comparison with the as-cast samples, the passive domain of the heat treated samples dramatically increased. It indicated that the passive film formed in the heat treated samples is more stable than the as-cast samples. This behaviour can explain by the more noble OCP values of the heat treated samples in comparison with the as-cast samples (Section 6.2.2.2(a)). The pitting potentials of Al–4Mg, Al–4Mg–0.3Sc, and Al–4Mg–0.24Sc–0.06Yb as-cast samples are $-530 \pm 45$, $-643 \pm 57$, and $-670 \pm 52$ mV vs. SCE, respectively. The values for Al–4Mg–0.3Sc and Al–4Mg–0.24Sc–0.06Yb heat treated samples are
−527 ± 52 and −591 ± 29 mV vs. SCE, respectively. The pitting potential of Al–4Mg alloy decreased with the addition of Sc and continues decreasing with adding Yb. However, the pitting potentials of Al–4Mg–0.3Sc and Al–4Mg–0.24Sc–0.06Yb alloys after heat treatment shifted to more positive values and are close to the value of Al–4Mg alloy. Thus, the addition of Sc and Yb to Al–4Mg tended to increase the pitting corrosion tendency, whereas heat treatment lead to an improvement of the resistance to pitting corrosion of Al–4Mg–0.3Sc and Al–4Mg–0.24Sc–0.06Yb alloys. After heat treatment, a high number density (as high as $10^{22}$ m$^{-3}$) of nano-sized Al$_3$Sc or Al$_3$(Sc,Yb) precipitates that fully coherent with the matrix were formed [34]. The duplex film of Sc$_2$O$_3$ reinforced Al$_2$O$_3$ is formed throughout the samples even on the precipitates sites. This passive film formed on the precipitates also coherent with the matrix. It was observed that the nanosized precipitates did not introduce any discontinuities in the passive film. It is well known that the localized corrosion will attack at the interface between intermetallic particles and matrix. These intermetallic particles must be noble and cathodic to the matrix. In Al–4Mg–0.3Sc and Al–4Mg–0.24Sc–0.06Yb alloys, these intermetallic particles are Fe–containing intermetallic phases (Section 6.2.2.2(a)). Cavanaugh et al. [8] indicated that Al$_3$Sc precipitates are inert to corrosion and slightly cathodic to the Al matrix. The presence of high number density of nano-sized Al$_3$Sc or Al$_3$(Sc,Yb) precipitates around the Fe–containing intermetallic particles can increase the electrochemical compatibility of Fe–containing intermetallic particles with the matrix. As a consequence, it reduces the tendency to pitting corrosion in heat treated samples.

Finally, it can be seen that in comparison with Al–4Mg–0.3Sc and Al–4Mg–0.24Sc–0.06Yb as-cast samples, the heat treated samples have more stable passive film, higher pitting corrosion resistance but higher corrosion rate and pit growth rate. It can be acceptable according to the findings of Frankel et al. [35] where it has been indicated that the passive film does not play a fundamental role in pitting, it has a low contribution in pit growth resistance and pit growth depends on events occurring within pits.
6.2 Conclusions

The corrosion behaviour of Al–0.28Sc and Al–0.24Sc–0.07Yb, Al–4Mg, Al–4Mg–0.3Sc and Al–4Mg–0.24Sc–0.06Yb alloys in 3.5 wt% of NaCl solution was investigated by immersion and potentiodynamic polarisation analysis. Based on the results obtained from the present research, the following conclusions can be drawn:

a) For Al–0.28Sc and Al–0.24Sc–0.07Yb alloys:

- The OCP evolution of these alloys during immersion in 3.5 wt% NaCl showed the lowest corrosion tendency in Al–0.24Sc–0.07Yb heat treated alloy.
- The presence of Fe–containing intermetallic phases in these alloy promoted pitting corrosion.
- The presence of a high number density of fully coherent nano–sized Al$_3$Sc or Al$_3$(Sc,Yb) precipitates in heat treated alloy enhanced the passivity of these alloys.

b) For Al–4Mg, Al–4Mg–0.3Sc and Al–4Mg–0.24Sc–0.06Yb alloys:

- The addition of Sc and Yb to Al–4Mg alloy reduced the size and changed the morphology of impurity intermetallic particles. The Fe–containing intermetallic particles are cathodic with respect to the matrix and can act as pitting initiation sites.
- The high content of Mg makes the Fe–containing intermetallic particle less noble to the matrix. Yb–containing intermetallic particles did not show any dissolution of the matrix at the periphery of these particles.
- The addition of Sc and Yb can decrease the susceptibility to corrosion of the heat treated Al–4Mg–0.3Sc and Al–4Mg–0.24Sc–0.06Yb alloys.
- The active dissolution and pitting are dominant corrosion mechanisms in Al–4Mg alloy. More stable passive plateau and less susceptibility to pitting corrosion was observed in the polarization curves of Al–4Mg–0.3Sc and Al–4Mg–0.24Sc–0.06Yb alloys after heat treatment.
References


CHAPTER 7: FINAL CONCLUSIONS AND FUTURE WORK
Chapter 7: Final Conclusions and Future Work

7.1 Final Conclusions

The Al–Sc and Al–Mg–Sc alloys with microalloying additions of Yb were investigated. The effects of substituting Yb for Sc on the microstructure and on the mechanical properties of Al–Sc alloy were studied by using SEM, TEM, HRTEM and Vickers hardness. The ageing behaviour, precipitate morphologies, precipitate coarsening and precipitation hardening of these alloys were investigated. The grain refinement in Al–Mg–Sc alloys with and without ultrasonic treatment at various pouring temperatures and the corrosion behaviour in 3.5 wt% of NaCl solution were also investigated.

The results showed the similarities of microstructure, hardness and aging behaviour of Al–0.24Sc–0.07Yb and Al–4Mg–0.24Sc–0.06Yb alloys in comparison with Al–0.28Sc and Al–4Mg–0.3Sc alloys were shown in this investigation, respectively. The hardness values of both alloys aged without homogenization treatment are significantly higher than those of alloys aged after homogenization treatment. The approximately spheroidal Al,Sc and Al,(Sc,Yb) precipitates were uniformly distributed throughout the α–Al matrix. The precipitates remain fully coherent with α–Al matrix even after aging at high temperature for long time. The maximum hardness was achieved at a precipitate diameter around 4–6 nm. The hardness sharply decreases when the average diameter of precipitate is above 12 nm. The hardness of Al–4Mg–0.3Sc and Al–4Mg–0.24Sc–0.06Yb alloys were significantly higher than that of Al–0.28Sc and Al–0.24Sc–0.07Yb alloys at the same aging condition due to the solid solution strengthening of Al–Mg.

Mg, Sc and the pouring temperature have strong effect on the microstructure of Al–Mg–Sc alloy. The average grain size of Al–Mg alloy remarkably decreases from 439 ± 21 to 95 ± 2 µm when the content of Mg increases from 1 to 4 wt% at the pouring temperature of 700 °C. The average grain size of Al–1Mg sharply decreases from 439 ± 21 µm to 103 ± 2 µm by adding 0.3 wt% of Sc. Lower pouring temperature leads to smaller grain size and more homogeneous microstructure. Ultrasonic vibration proved to be a potential grain refinement technique for Al–1Mg–0.3Sc. Significant grain refinement was obtained by applying ultrasonic treatment within the temperature range of 700-740 °C. This fact makes more flexible to determine the pouring temperature in the foundry practice of this kind of alloy. The best grain refinement and uniform grain size are obtained by ultrasonic treatment at 720 °C.

Regarding the corrosion behaviour of Al–0.28Sc and Al–0.24Sc–0.07Yb alloys in 3.5 wt% of NaCl solution, the evolution the OCP with time showed the lowest tendency to corrosion in Al–0.24Sc–0.07Yb heat treated alloy. The presence of Fe–containing intermetallic phases in these alloy promote the pitting corrosion. Yb has strong effect on the polarization behaviour of Al–Sc alloys. The addition of Yb decreases the
corrosion tendency and improves the pitting corrosion resistance of this alloy. The presence of a high number density of fully coherent nano–sized Al,Sc or Al,(Sc,Yb) precipitates in heat treated alloy enhances the passivity of these alloys.

The immersion and potentiodynamic polarisation properties of Al–4Mg, Al–4Mg–0.3Sc and Al–4Mg–0.24Sc–0.06Yb alloys were also shown in this study. The addition of Sc and Yb to Al–4Mg alloy reduced the size and changed the morphology of impurity intermetallic particles. The Fe–containing intermetallic particles are cathodic with respect to the matrix and can act as pitting initiation sites. The high content of Mg makes the Fe–containing intermetallic particle less noble to the matrix. Yb–containing intermetallic particles did not cause any dissolution of the matrix at the periphery of these particles. The addition of Sc and Yb can decrease the tendency to corrosion of the heat treated Al–4Mg–0.3Sc and Al–4Mg–0.24Sc–0.06Yb alloys. The active dissolution and pitting are dominant corrosion mechanisms in Al–4Mg alloy. While the polarization curves of Al–4Mg–0.3Sc and Al–4Mg–0.24Sc–0.06Yb alloys showed the spontaneous passivation followed by pitting corrosion. More stable passive plateau and less susceptibility to pitting corrosion was observed in the polarization curves of Al–4Mg–0.3Sc and Al–4Mg–0.24Sc–0.06Yb alloys after heat treatment.

7.2 Future work

- This thesis research can be continued to fully understand the precipitate coarsening, precipitation hardening and its mechanism in Al–Sc and Al–Mg–Sc alloys with microalloying additions of Yb. In combination with modeling, the formation of precipitates in these alloys can be simulated.

- To fully understand the grain refinement mechanism by ultrasonic treatment, the size and distribution of cavitation should be investigated with various ultrasonic frequency, power, acoustic radiator position and shape, treatment time, the dynamic of cavitation (bubble growth and collapse), the dynamic interaction between cavitation and the melt during solidification can be studied. Modelling of these processes using the finite element commercial software should be performed.

- The corrosion behaviour of Al–Mg–Sc alloys after ultrasonic treatment can be investigated to clarify the idea about the improvement of corrosion resistance of Al–Mg–Sc alloys by applying ultrasonic treatment.