

Development of Al-Si based alloys

Author:

Cao, Yi

Publication Date:

2015

DOI:

<https://doi.org/10.26190/unsworks/18581>

License:

<https://creativecommons.org/licenses/by-nc-nd/3.0/au/>

Link to license to see what you are allowed to do with this resource.

Downloaded from <http://hdl.handle.net/1959.4/55260> in <https://unsworks.unsw.edu.au> on 2024-05-01



UNSW
A U S T R A L I A

School of Materials Science and Engineering

A thesis submitted in complete fulfillment of the requirements

for the award of the degree of

Doctor of Philosophy

in

Materials Science and Engineering

“Development of Al-Si based alloys”

Yi Cao

March 2015

PLEASE TYPE

THE UNIVERSITY OF NEW SOUTH WALES
Thesis/Dissertation SheetSurname or Family name: CAOFirst name: YI

Other name/s:

Abbreviation for degree as given in the University calendar: PhDSchool: Materials ScienceFaculty: ScienceTitle: Development of Al-Si Based Alloys

Abstract 350 words maximum: (PLEASE TYPE)

The development of Al-based metallic glasses capable of easily generating an amorphous structure on cooling from the melt is recognized as one of the major challenges in this field of research. Recent findings in Al-rich Al-Ni-Co-La-Y alloys, where a critical casting diameter of ~ 1mm has been reported, has rekindled interest in the possibility of producing Al-based bulk metallic glasses (BMGs). The research outlined in this thesis is focused on the design of Al-Si-based metallic glasses without rare earth elemental additions but having good glass-forming ability (GFA). Based on the underlying thermodynamic and kinetic factors that dictate the retention of a glassy structure in an alloy melt upon cooling, three fundamental concepts were simultaneously adopted in order to identify alloy compositions with the highest propensity for glass-formation in a range of Al-Si-based alloy systems. These incorporate the heat of mixing between alloying elements, the thermodynamic driving force for crystallization within an alloy system and the efficient packing of atoms for maximizing alloy melt viscosity, thereby slowing the kinetics of crystallisation. With this in mind, transition metals Cr, Mo, Mn, Fe, Co, and Ni, were selected as viable additions to the binary Al-Si alloy system.

Compositions that satisfy these criteria were produced by arc-melting and vacuum casting into wedge-shaped copper moulds in order to examine their GFA. The microstructure and morphology of the as-cast alloys were investigated mainly using electron microscopy and x-ray diffraction techniques. Results showed that glass formation is possible within the systems studied, with alloys in the Al-Ni-Si and Al-Co-Si systems forming glasses with a critical casting size of up to 400µm and 195µm, respectively. The GFA of the alloy systems studied in the thesis were found to follow the sequence: Al-Ni-Si > Al-Co-Si > Al-Cr-Si > Al-Mo-Si > Al-Mn-Si > Al-Fe-Si. The results indicate that the nature of the electronic bonding between Al and the transition metal elements strongly affects GFA of a given alloy system and that atomic packing efficiency also contributes to maximizing glass formation.

Declaration relating to disposition of project thesis/dissertation

I hereby grant to the University of New South Wales or its agents the right to archive and to make available my thesis or dissertation in whole or in part in the University libraries in all forms of media, now or here after known, subject to the provisions of the Copyright Act 1968. I retain all property rights, such as patent rights. I also retain the right to use in future works (such as articles or books) all or part of this thesis or dissertation.

I also authorise University Microfilms to use the 350 word abstract of my thesis in Dissertation Abstracts International (this is applicable to doctoral theses only).

Signature

Witness

28/03/2015

Date

The University recognises that there may be exceptional circumstances requiring restrictions on copying or conditions on use. Requests for restriction for a period of up to 2 years must be made in writing. Requests for a longer period of restriction may be considered in exceptional circumstances and require the approval of the Dean of Graduate Research.

FOR OFFICE USE ONLY

Date of completion of requirements for Award:

THIS SHEET IS TO BE GLUED TO THE INSIDE FRONT COVER OF THE THESIS

ORIGINALITY STATEMENT

'I hereby declare that this submission is my own work and to the best of my knowledge it contains no materials previously published or written by another person, or substantial proportions of material which have been accepted for the award of any other degree or diploma at UNSW or any other educational institution, except where due acknowledgement is made in the thesis. Any contribution made to the research by others with whom I have worked at UNSW or elsewhere, is explicitly acknowledged in the thesis. I also declare that the intellectual content of this thesis is the product of my own work, except to the extent that assistance from others in the project's design and conception or in style, presentation and linguistic expression is acknowledged.'

Signed 

Date28/03/2015.....

COPYRIGHT STATEMENT

'I hereby grant the University of New South Wales or its agents the right to archive and make available my thesis or dissertation in whole or part in the University libraries in all forms of media, now or here after known, subject to the provisions of the Copyright Act 1968. I retain all proprietary rights, such as patent rights. I also retain the right to use in future works (such as articles or books) all or part of this thesis or dissertation. I also authorize University Microfilms to use the 350 word abstract of my thesis in Dissertation Abstract International (this is applicable to doctoral thesis only). I have either used no substantial portions of copyright material in my thesis or I have obtained permission to use copyright material; where permission has not been granted I have applied/will apply for a partial restriction of the digital copy of my thesis or dissertation.'

Signed 

Date28/03/2015.....

AUTHENTICITY STATEMENT

'I certify that the library deposit digital copy is a direct equivalent of the final officially approved version of my thesis. No emendation of content has occurred and if there are any minor variations in formatting, they are the result of conversion to digital format.'

Signed 

Date28/03/2015.....

Acknowledgements

Firstly, I am very grateful to my supervisor, Professor Michael Ferry, for his prompt and invaluable guidance in this project, giving me enormous amounts of support and encouragement in all aspects. I also appreciate my co-supervisor, Dr. Kevin Laws, for his comprehensive training and professional advice on the alloy design, synthesis, characterization, and analysis during the entire study. I am also thankful to our School of Materials Science in University of New South Wales and ARC Centre of Excellence for Design in Light Metals for providing the conducive environment and novel facilities to explore this exciting research area.

At each stage of this study, I received much help and assistance in learning various techniques and analyzing associated results. I am thankful to:

Dr Quadir Zakaria for training in EPMA and TEM;

Dr Karen Privat for training in EPMA;

Dr George Yang for training in various metallography preparations and micro hardness tests;

Dr Yu Wang for training in X-ray diffraction with a micro-capillary X-ray guide;

Dr Charlie Kong for training in FIB for the preparation of TEM samples;

Ms Leah Koloadin for training in carbon coating, gold coating, and SEM with EDS;

Dr Helen Rutledge for help with laser-ablation mass spectroscopy; and

Dr Thiam Teck Tan for training in differential scanning calorimetry.

Finally, I would like to express my gratitude to my beloved wife and son, Minwan and Jason, my parents, friends, and group members for their help, understanding, and support through this endeavor.

Abstract

The development of Al-based metallic glasses capable of easily generating an amorphous structure on cooling from the melt is recognized as one of the major challenges in this field of research. In the past, the Al-based amorphous alloys could be categorized into four types: (1) Al-LTM-RE; (2) Al- LTM- ETM; (3) Al-LTM-AEM and (4) Al-TM-Metalloid. Recent findings in Al-rich Al-Ni-Co-La-Y alloys, where a critical casting diameter of $\sim 1\text{mm}$ has been reported, has rekindled interest in the possibility of producing Al-based bulk metallic glasses (BMGs). The research outlined in this thesis is focused on the design of Al-Si-based metallic glasses without rare earth elemental additions but having good glass-forming ability (GFA). Based on the underlying thermodynamic and kinetic factors that dictate the retention of a glassy structure in an alloy melt upon cooling, three fundamental concepts were simultaneously adopted in order to identify alloy compositions with the highest propensity for glass-formation in a range of Al-Si-based alloy systems. These incorporate the heat of mixing between alloying elements, the thermodynamic driving force for crystallization within an alloy system and the efficient packing of atoms for maximizing alloy melt viscosity, thereby slow down the kinetics of crystallisation. With this in mind, transition metals Cr, Mo, Mn, Fe, Co, and Ni, were selected as viable additions to the binary Al-Si alloy system.

Compositions that satisfy these criteria were produced by arc-melting and vacuum casting into wedge-shaped copper moulds in order to examine their GFA. The microstructure and morphology of the as-cast alloys were investigated mainly using electron microscopy and x-ray diffraction techniques. Results showed that glass formation is possible within the systems studied, with alloys in the Al-Ni-Si and Al-Co-Si systems forming glasses with a critical casting size of up to $400\mu\text{m}$ and $195\mu\text{m}$, respectively. The GFA of the alloy systems studied in the thesis were found to follow the sequence: $\text{Al-Ni-Si} > \text{Al-Co-Si} > \text{Al-Cr-Si} > \text{Al-Mo-Si} > \text{Al-Mn-Si} > \text{Al-Fe-Si}$. The results indicate that the nature of the electronic bonding between Al and the

transition metal elements strongly affects GFA of a given alloy system and that atomic packing efficiency also contributes to maximizing glass formation. The optimized compositions in the Al-Ni-Si alloys contained three types of efficiently packed clusters, which suggested a self-consistence principle that the compositions with all elements efficiently packed by their first-shell atoms are crystallization resistant and more likely to form a glass. Wider featureless regions were observed in the Al-rich lower liquidus temperature regions, indicating a lower crystallization driving force, which is a positive factor in potential glass formation. By carefully design and synthesis, the GFA in the Al-Si based alloys was explored, providing an insight towards the development of Al-based alloys free of rare-earth elements.

Table of Contents

Acknowledgements	i
Abstract	ii
Chapter 1 Introduction	1
Chapter 2 Literature Review	3
2.1 Introduction	3
2.2 Overview of Glass Formation in Al-based Alloys	3
2.3 Processing Methods for Al-based Metallic Glasses	5
2.3.1 Melt Spinning.....	5
2.3.2 Copper Mould Casting	6
2.3.3 Laser Surface Melting.....	6
2.3.4 Thermoplastic Forming.....	7
2.4 Types of Al-based Metallic Glasses	7
2.4.1 Type A: Al-LTM-RE	7
2.4.2 Type B: Al-LTM-ETM	14
2.4.3 Type C: Al-LTM-AEM.....	15
2.4.4 Type D: Al-TM-Metalloid	16
2.5 Design Criteria for Al-based Metallic Glasses	20
2.5.1 Inoue Selection Criteria.....	20
2.5.2 Efficiently Packed Clusters (EPC) Model.....	21
2.5.3 Cluster Line Criterion	23
2.5.4 Driving Force Criterion.....	24
2.5.5 Inverse Monte Carlo Method	25

2.5.6	Topological Instability Criteria	26
2.5.7	Cluster plus glue atom model assisted with electron per atom ratio....	28
2.6	Summary and Scope of Thesis	29
Chapter 3 Experimental Procedure		31
3.1.	Introduction.....	31
3.2	Alloy Design Principles.....	31
3.2.1	Heat of Mixing Criterion.....	31
3.2.2	Driving Force Criterion.....	32
3.2.3	Composition Design.....	33
3.3	Alloy Synthesis.....	35
3.3.1	Initial Induction Furnace Melting	35
3.3.2	Arc Melting of the Alloys	36
3.4	Metallographic Preparation	37
3.5	Structural Characterisation	38
3.5.1	Mono-Capillary X-Ray Diffraction.....	38
3.5.2	Scanning Electron Microscopy	38
3.5.3	Transmission Electron Microscopy	39
3.6	Composition Analysis	40
3.6.1	Laser Ablation Inductively Coupled Plasma Mass Spectrometry	40
3.6.2	Electron Probe Microanalysis	41
3.7	Thermal Analysis	42
3.8	Microhardness Testing	42
Chapter 4 Glass Formation in Al-Early Transition Metal-Metalloid Alloys		44
4.1	Introduction	44
4.2	Al-Mn-Si-Ge Alloy System.....	44
4.2.1	Introduction to Al-Mn-Si Alloys.....	44
4.2.2	Composition Design and X-Ray Diffraction of the Al-Mn-Si Alloys .	45
4.2.3	Scanning Electron Microscopy of the Al-Mn-Si Alloys.....	47

4.2.4	Electron Probe Microanalysis of the Al-Mn-Si Alloys.....	48
4.2.5	Differential Scanning Calorimetry of the Al-Mn-Si Alloys	49
4.3.	Al-Mo-Si Alloy System	50
4.3.1	Composition Design in the Al-Mo-Si Alloys	50
4.3.2	Copper Mould Casting of the Al-Mo-Si Alloys.....	52
4.3.3	Scanning Electron Microscopy of the Al-Mo-Si Alloys.....	53
4.4.	Al-Cr-Si Alloy System.....	56
4.4.1	Composition Design in the Al-Cr-Si Alloys	56
4.4.2	Copper Mould Casting of the Al-Cr-Si Alloys	58
4.4.3	Scanning Electron Microscopy of the Al-Cr-Si Alloys	59
Chapter 5 Glass Formation in Al-Fe-Si and Al-Co-Si Alloys		65
5.1	Introduction	65
5.2	Al-Fe-Si Alloy System	65
5.2.1	Composition Design of the Al-Fe-Si Alloys.....	65
5.2.2	Copper Mould Casting of the Al-Fe-Si Alloys	67
5.2.3	Scanning Electron Microscopy of the Al-Fe-Si Alloys	68
5.2.4	X-Ray Diffraction of the Al-Fe-Si Alloys	71
5.3	Al-Co-Si Alloy System	74
5.3.1	Composition Design of the Al-Co-Si Alloys	74
5.3.2	Copper Mould Casting of the Al-Co-Si Alloys	76
5.3.3	Scanning Electron Microscopy of the Al-Co-Si Alloys.....	77
5.3.4	X-Ray Diffraction of the Al-Co-Si Alloys.....	81
5.3.5	Bi-clusters Composition of the Al-Co-Si Alloys	85
Chapter 6 Glass Formation in Al-Ni-Si and Al-Ni-Co-Si Alloys.....		86
6.1	Introduction	86
6.2	Al-Ni-Si Alloys	86
6.2.1	Composition Design of Al-Ni-Si Alloys.....	86
6.2.2	Copper Mould Casting of the Al-Ni-Si Alloys	89

6.2.3 Scanning Electron Microscopy of Al-Ni-Si Alloys	89
6.2.4 X-Ray Diffraction for Al-Ni-Si Alloys	97
6.2.5 Focused Studies on the Al _{74.13} Ni _{7.69} Si _{18.18} Amorphous Alloy.....	102
6.3 Al-Ni-Co-Si Alloys	105
6.3.1 Quaternary Alloy Design and Processing	105
6.3.2 Scanning Electron Microscopy of Al-Ni-Co-Si Alloys	106
Chapter 7 Discussion	112
7.1 Introduction	112
7.2 Glass Forming Ranges.....	113
7.2.1 Al-Mn-Si/Ge alloys.....	113
7.2.2 Al-Cr-Si alloys	114
7.2.3 Al-Mo-Si alloys.....	116
7.2.4 Al-Fe-Si alloys	118
7.2.5 Al-Co-Si alloys	120
7.2.6 Al-Ni-Si alloys	121
7.2.7 Summary	122
7.3 Atomic Packing Efficiency.....	123
7.4 Heat of Mixing Criterion	128
7.5 Driving Force Criterion	130
7.5.1 Al-Cr-Si alloys	130
7.5.2 Al-Mo-Si alloys.....	131
7.5.3 Al-Fe-Si alloys	132
7.5.4 Al-Co-Si alloys	133
7.5.5 Al-Ni-Si alloys	134
7.5.6 Summary	135
7.6 Reasons for Poor Glass-formation Al-LTM-Si-base Alloys.....	135
7.7 Means of Improving GFA of Al-Si-base Alloys	137
Chapter 8 Concluding Summary	139

Chapter 9 References	142
Appendix A The Efficiently Packed Cluster Model	149
A.1 Introduction	149
A.2 Example Calculation for Efficiently Packed Clusters	150

Chapter 1

Introduction

Metallic glasses are non-crystalline or amorphous alloys that possess many interesting and often unique properties. For example, the absence of dislocations in metallic glasses means that they deform by different mechanisms to their crystalline counterparts, which usually equates to a much greater strength but lower ductility. A glassy alloy is often difficult to generate from the melt because, below its melting point, the Gibbs free energy of the crystalline phase/s is much lower than that of the amorphous state; this leads to a very high driving force for crystallization. Indeed, it was not until 1960 that the first metallic glass was produced in an $\text{Au}_{75}\text{Si}_{25}$ binary alloy (Klement et al. 1960).

In the early development of metallic glasses, the glass-forming ability (GFA) was so low because crystallization occurs so easily even during rapid cooling from the melt. Hence, thin glassy foils could only be obtained by extremely rapid quenching, where the cooling rate needed to suppress crystallization is at least 10^6 K/s (Wang et al. 2004). Later, Chen (1974) produced the first so-called “bulk metallic glass” (BMG) of Pt-based alloy cylinders by water quenching the melt in a quartz capillary. The critical cooling rate was estimated to be as low as 10^3 K/s, which distinguished the intrinsic high GFA in this Pt alloy from that of conventional metallic glasses. Due to the large dimensions of these glassy alloys components (i.e. >1 mm in either diameter or thickness), they are usually termed BMGs.

Meanwhile, several different methods were developed in the 1980s to produce metallic glasses, such as radiation-induced amorphization, hydrogen-induced amorphization and ball milling (Johnson 1986). The diversity of processing methods led to searches for multicomponent alloys based on commodity metals such as Zr, Fe,

Cu, Mg, Al etc. During this research boom in metallic glasses, Al-based metallic glasses were discovered by melt spinning, which included Al-TM-Metalloid, Al-ETM-LTM, and Al-TM-RE metallic glasses (TM = transition metals, ETM = early transition metals, LTM = late transition metals, RE = rare earth elements). Al-TM-Metalloid metallic glasses were first generated in an $\text{Al}_{70}\text{Fe}_{13}\text{Si}_{17}$ alloy composition by melt spinning in a helium atmosphere (Legresy et al. 1986), Al-ETM-LTM metallic glasses were first synthesized in Al-Cu-V alloys by melt spinning (Tsai et al. 1988a), and Al-TM-RE metallic glasses were first produced in melt-spun $\text{Al}_{90}(\alpha_{1-x}\beta_x)_{10}$ and $\text{Al}_{87}(\alpha_{1-x}\beta_x)_{13}$ ribbons, where $\alpha=\text{Fe, Co, Ni, Rh}$ and $\beta=\text{Y, Ce, Gd}$ (He et al. 1988).

In the last 30 years, considerable effort has been devoted to understanding the GFA of Al-TM-RE alloys, such as Al-Fe-Nb (He et al. 1988), Al-Ni-Fe-Gd (He et al. 1993), Al-Fe-Y (Perepezko et al. 2010), Al-Ni-Y-(Co)-(Fe) (Hong et al. 2001, Inoue et al. 1990, Wang et al. 2013), Al-Ni-Y-Co-La (Li et al. 2013, Yang et al. 2009), Al-Ni-Sm (Aliaga et al. 2011), Al-Ni-Ce (Zhang et al. 2012), and Al-Tb (Ovun et al. 2014). These Al-based glasses exhibited ultra-high specific strength, double that of conventional crystalline Al alloys, and the fracture strength was improved in the absence of an intermetallic Al-rich compounds in the amorphous matrix (Zhuo et al. 2009). It was not until 2009 that the first Al-rich BMGs with diameters of $\sim 1\text{mm}$ were produced by copper mould casting (Yang et al. 2009). One of their successful compositions was the RE-containing $\text{Al}_{86}\text{Ni}_7\text{Y}_5\text{Co}_1\text{La}_1$ alloy. The high GFA of these Al-TM-RE alloys has inspired the current study on Al-TM-Metalloid alloys free of expensive RE elements. The Al-TM-Metalloid system has been the least studied, and glassy ribbons have been produced for only a few alloys, such as Al-Fe-Si-(Co) (Kiliçaslan et al. 2013), Al-Cr-Si (Kimura et al. 1988), and Al-Ni-Si (Inoue et al. 1988). Therefore, the aim of the current thesis is to explore the GFA of Al-Si-based alloys containing low-cost elements by the lower cooling-rate method of copper mould wedge casting. Here, both early transition metals and late transition metals were selected as potential additions to the Al-Si binary system, whereby the GFA of carefully selected alloy compositions was investigated in detail using a systematic alloy design approach that combines several contemporary selection criteria.

Chapter 2

Literature Review

2.1 Introduction

Metallic glasses consisting of a fully amorphous structure have attracted considerable research interest since their discovery over fifty years ago. Over the last three decades, many metallic glasses have been produced with at least one dimension greater than 1mm, which is termed a bulk metallic glass (BMG). They are usually multicomponent alloys containing at least three elements, and a wide variety of base elements have been used, including gold, platinum, palladium, magnesium, zirconium, titanium, iron, copper, cobalt, nickel, calcium etc. As aluminium is the most widely used light metal, there has been an intense pursuit of Al-based BMGs since the initial discovery of BMGs. Recent studies have shown that fully amorphous rods with diameters over 1mm are possible in the Al-transition metal-rare earth (Al-TM-RE) alloy system (Yang et al. 2009). This recent work has shed light on the potential glass-forming ability (GFA) of Al-based alloys and has inspired systematic studies on the design of other Al-alloys not containing RE additions. In this chapter, four topics relating to the development of Al-based metallic glasses are discussed: (i) glass formation; (ii) processing methods; (iii) types of Al-based alloys; and (iv) alloy design criteria for improving GFA.

2.2 Overview of Glass Formation in Al-based Alloys

The synthesis of amorphous Al-based alloys alone is a major challenge in material science and physics (He et al. 1988). The main challenge for metallic glass formation is avoiding crystallization during cooling from the melt (Schroers 2010). Crystallization is controlled by two primary factors: the driving force for crystallization and the thermodynamic ability to create critical sized nuclei. The

driving force for crystallization comes from the fact that the Gibbs free energy of the crystalline phase/s is lower than that of the metastable amorphous phase in a supercooled liquid state (Fecht 1995). However, the ability for crystallization decreases as the melt viscosity increases in this supercooled liquid condition, dramatically slowing crystallization kinetics, which enables a metallic glass to form (Busch et al. 2007). Efficiently packed arrangements of atoms (often referred to as clusters) in the liquid result in a high viscosity liquid, which can slow the crystallization process and promote glass formation (Miracle 2004). The chemical fluctuation through long-distance diffusion required for the formation of a crystalline phase also retards the crystallization process, which is also crucial for GFA (Cini et al. 2000).

Despite significant efforts over the past 20 years, bulk glass formation in Al-based systems has proven elusive with no reports of high GFA alloys that generate > 1mm as-cast samples. Fundamentally, Al is different to most other metals, as it resides on the far left of the periodic table (Group 3A) and has three valence electrons with an electronic configuration of $[\text{Ne}]3s^23p^1$ with outer electrons residing in the s and p orbitals. Having a high electron density and high Fermi level (small work-function and high ionization tendency), Al prefers to transfer electrons to transition metals (TMs), such as Ni, Co, Fe, Cr, and Mn, to form covalent bonds and then form intermetallic compounds. Such a strong electronic interaction between Al and TMs is evidenced by the bond shortening in Al-TM compounds and glasses (i.e., Al-TM bonds are significantly shorter than the sum of the corresponding metallic radii), as well as the sp-d hybridized orbital (Fourré et al. 1999, Widom et al. 2000, Cheng et al. 2009).

When Al is alloyed, the non-metallic nature of this element becomes apparent, similar to the other elements in its periodic group, B and Ga (Li et al. 2009). Hence, for most binary alloy systems with Al, few deep eutectic reactions exist, particularly at high solvent concentrations (higher chemical entropy assists with metallic glass formation), where phase equilibria is dominated by high melting point intermetallics. This also strongly hinders the physical ability to undercool Al-based melts relative to cooling rates achievable by conventional copper mould casting methods, hence most Al-based metallic glasses reported are very Al-rich, as will be shown herein.

As mentioned above, a high viscosity alloy melt is important when hindering diffusion and crystallisation kinetics. Here, Al is also slightly disadvantaged with respect to glass formation, where it has been shown that its shear modulus to atomic radius ratio is relatively low, particularly when compared to other base metals with high GFA such as Mg, Zr, La or Ca (Senkov et al. 2005).

2.3 Processing Methods for Al-based Metallic Glasses

Metallic glasses require processing that can suppress crystal nucleation and growth. Several processing techniques are used for the primary and secondary synthesis of Al-based metallic glasses: (1) melt spinning is used to produce thin ribbons with a high cooling rate of 10^4 - 10^6 K/s (Gögebakan et al. 2009); (2) copper mould casting is applied to cast wedge-shaped samples (Chen et al. 2012) and rod-shaped samples (Yang et al. 2009); (3) laser surface melting of either the metal surface or premixed powder on the surface can also form an amorphous layer, and (4) thermoplastic forming, using the high ductility of metallic glass in the temperature interval of supercooled liquid region (SCLR), to generate a final and often complex shape (Schroers 2010).

2.3.1 Melt Spinning

Al-Si metallic glass ribbons were first produced in $\text{Al}_{70}\text{Fe}_{13}\text{Si}_{17}$ alloys by melt spinning (Legresy et al. 1986). The melt spinning technique was performed by arc melting the raw materials in an argon atmosphere in an arc furnace, and then melt spinning the alloys in helium atmosphere in a single roller apparatus with a copper wheel at a circumferential speed of 40 m/s (Inoue et al. 1988b). The size of as-spun ribbons is normally 20 μm in thickness and 1 mm in width with various lengths (Inoue et al. 1988b). Due to its high cooling rate of up to 10^6 K/s (Wang et al. 2004a), it is often used as the first point to distinguish the possibility of glass formation in a new alloy system; later the glass forming range (GFR) of compositions can be used for the inspection of GFA in the development of bulk samples.

2.3.2 Copper Mould Casting

Direct casting is a technique to produce metallic glasses from the liquid. It is an economical and rapid cooling technique for producing near-net shape products; however, several technical issues need to be considered in this process (Schroers 2010), including the following: crystallization is likely to occur due to heterogeneous nucleation; shrinkage in direct die casting prevents heat transfer from the melt to wall; the fast filling procedure limits the complexity of the mould casting; the high threshold temperature in some alloys for direct casting may require a high cost in energy consumption and equipment maintenance.

High pressure die casting is a technique of rapid solidification that can lead to the formation of a metallic glass. The alloys are melted in a sleeve in an argon atmosphere with a high frequency induction coil and cast into the copper mould by moving the top and bottom plungers in an applied hydraulic pressure. It was used in $\text{Al}_{84}\text{Ni}_{10}\text{Ce}_6$ alloys for the formation of BMGs, and an amorphous surface layer 200 μm thick was formed in 5 mm diameter cylindrical samples (Inoue et al. 1994).

In recent developments of Al-based metallic glasses, copper mould casting is widely used to test the GFA of bulk samples. The master alloys are easily produced by arc melting elements of high purity in a Ti-gettered argon atmosphere. The ingots were melted four to six times for chemical homogeneity. There are two main types of casting; injection casting (Chen et al. 2012) and suction casting (Zhang et al. 2012). Depending on the shape of cavity in a copper mould, wedge- or rod-shaped specimens can be obtained by injection casting or suction casting the melt into the copper mould. For example, the rod-shaped samples with diameter of 1 mm were produced by injecting the molten alloy into the copper mould, and the amorphous phase was created in Al-Ni-Y-Co-La rod (Yang et al. 2009). In the current study, the wedge-shaped samples were produced by suction casting the melt into a copper mould with a wedge shaped cavity.

2.3.3 Laser Surface Melting

Laser surface melting is a technique to form an amorphous surface layer. It can be performed by placing a focused laser beam on the metal surface. The re-melting zone is $\sim 120 \mu\text{m}$ (Chen et al. 2011). The low cooling rate of laser surface melting was suitable for BMGs such as Zr-based alloys rather than conventional metallic glasses.

Al-based alloys were found to form only crystalline phases after laser surface melting at high laser scanning speeds(Audebert et al. 2003).

2.3.4 Thermoplastic Forming

To overcome drawbacks in direct casting, several thermoplastic forming techniques have been developed, which makes use of the dramatic softening behaviour above the glass transition temperature in metallic glasses to produce near-net shape products (Schroers 2010); thermoplastic forming techniques included rolling, extrusion, compression molding, top-down nanofabrication or lithography, blow molding, and thermoplastic expansion. Compared with copper mould casting, thermoplastic forming has the advantages of low porosity of 0.004 % and low shrinkage of 0.2 % (Schroers et al. 2007). BMGs are produced by suppressing the nucleation where a cooling rate as low as 1K/s is sufficient for glass formation (Perepezko et al. 2008); thus, the conventional metallic glasses that are sensitive to the temperature for crystallization is not suitable for the superplastic forming methods.

2.4 Types of Al-based Metallic Glasses

Al-based metallic glasses can be categorized into four main types: (1) Al-LTM-RE; (2) Al-ETM-LTM; (3) Al-LTM-AEM, and (4) Al-TM-Metalloid (where TM = transition metals; ETM = early transition metals; LTM = late transition metals; RE = rare earth elements; AEM = alkaline earth metals). Each specific alloy system and the range of metallic glasses reported to date will now be described.

2.4.1 Type A: Al-LTM-RE

Al-LTM-RE is a type of Al-based metallic glass where LTM includes Ni, Fe, Co, and RE elements are lanthanide elements such as La, Ce, Nd, etc. Al-LTM-RE-type metallic glasses have attracted a lot of research interest due to their high GFA and thermal stability such as the largest SCLR ($T_x - T_g$) of about 20K in Al-based metallic glasses (Stojanova et al. 2012), where T_g is the glass transition temperature and T_x is onset crystallization temperature. Among Al-TM-RE alloys, two systems have been studied most intensively: Al-Ni-RE and Al-Fe-RE. In general, Al-Ni-RE alloys showed better mechanical properties, while Al-Fe-Re alloys exhibited higher thermal stability (Audebert et al. 1997).

2.4.1.1 Al-Fe-Gd-(Ni) Alloys

In Al-TM-RE alloys, $\text{Al}_{87}\text{Fe}_{8.7}\text{Ce}_{4.3}$, $\text{Al}_{87}\text{Co}_{8.7}\text{Ce}_{4.3}$, $\text{Al}_{87}\text{Ni}_{8.7}\text{Ce}_{4.3}$, $\text{Al}_{87}\text{Rh}_{8.7}\text{Ce}_{4.3}$, $\text{Al}_{87}\text{Co}_{8.7}\text{Y}_{4.3}$, $\text{Al}_{87}\text{Co}_{8.7}\text{Hf}_{4.3}$, $\text{Al}_{87}\text{Ni}_{8.7}\text{Y}_{4.3}$, and $\text{Al}_{87}\text{Ni}_{8.7}\text{Hf}_{4.3}$ were firstly found to form single-phase metallic glasses in as-spun ribbons via arc melting in an argon atmosphere followed by melt spinning in a partial helium atmosphere; tensile testing using a 30mm gauge revealed the highest tensile strength of 940 MPa in $\text{Al}_{90}\text{Fe}_5\text{Ce}_5$, which was better than that of any commercial Al alloys (He et al. 1988). In Al-Fe Gd alloys (He et al. 1988), the crystallization temperature T_x , defined as the temperature where 30-50% volume transformed to crystalline phases in 5 minutes, was found to be as high as 310 °C in $\text{Al}_{87}\text{Fe}_{8.7}\text{Gd}_{4.3}$; the crystallization path revealed the first exothermal peak was responsible for primary crystallization of the Al phase; the second and third peaks were according to the crystallization of fcc Al, $\text{Al}_{10}\text{Fe}_2\text{Gd}$, and $\text{Al}_2(\text{Fe,Gd})$ phases. The reduced glass transition temperature, which is the ratio of glass transition temperature and melting temperature, was between 0.65 and 0.7, and glass formers were off-eutectic in Al-Fe-Gd alloys. Melt spinning showed that amorphous ribbons can be formed in the Al-rich end of the Al-Fe-Nb system, $\text{Al}_{90}\text{Fe}_7\text{Nb}_3$ and $\text{Al}_{87}\text{Fe}_{10}\text{Nb}_3$, with T_x up to 350 °C.

Later in the quaternary $\text{Al}_{85}\text{Ni}_6\text{Fe}_3\text{Gd}_6$, the tensile strength was further increased up to 1280 MPa with critical thickness of 250 μm in as-spun ribbons (He et al. 1993). DSC results revealed a very low reduced glass transition temperature $T_{rg}=0.44$ and a T_x of 256 °C; isothermal DSC showed a high crystallization activation energy of 4.4eV implying high thermal stability below T_x . The elastic modulus, E , of the ribbons was 75 GPa that was slightly higher than pure Al (70 GPa), which was measured by ultrasound wave velocity V and density ρ , where $E=\rho \times V^2$. Though ribbons had good thermal stability that remained fully amorphous after 100h annealing at 200 °C, embrittlement after low temperature annealing was observed in $\text{Al}_{85}\text{Ni}_6\text{Fe}_3\text{Gd}_6$, which may be due to structural relaxation similar to that in other metallic glasses. Both synchrotron and neutron scattering showed strong short-range order between Al and Fe, which might result in high shear viscosity resisting nucleation and growth of crystal phases.

2.4.1.2 Al-Fe/Ni-Y-Cu Alloys

Studies in Al-Fe-Y showed that substituting Al with Cu could improve thermal stability and mechanical properties. For example, substitution of Al by 1% Cu in

$\text{Al}_{88}\text{Y}_7\text{Fe}_5$ could improve the onset crystallization temperature (Perepezko et al. 2010). A similar effect was also found in Al-Ni-Y alloys that the substitution of Cu for Al increased the thermal stability, but substitution of Cu for Ni decreased the thermal stability and generated nanocrystals in $\text{Al}_{88}\text{Ni}_8\text{Y}_4$ as-spun ribbons (Hong et al. 2001). After annealing, the addition of Cu in Al-Ni-Y ribbons increased the nanocrystal number density and refined its nanocrystal size. Also, atom probe tomography (APT) showed rejection of Cu from the nanocrystals, and redistribution of Cu at the interface of each nanocrystal and the amorphous matrix was believed to slow their growth (Hong et al. 2001).

2.4.1.3 Al-Ni-Sm Alloys

An early study of Al-Sm alloys showed fully amorphous $\text{Al}_{92}\text{Sm}_8$ ribbons were formed by melt spinning at a wheel speed of 24 m/s (Wilde et al. 1999). In ternary Al-Ni-Sm ribbons (Aliaga et al. 2011), amorphous phases were identified in compositions with higher Sm content. The radius ratios of Sm/Al and Ni/Al are 1.2642 and 0.8701, which favoured Sm centred Al-Sm clusters with coordination number (N) = 17 and Ni centred Al-Ni clusters with N=11. Since the cluster of N=11 was unstable and had a similar structure of cluster with N=12, the Ni-centred Al-Ni cluster was supposed to be N=12. Four compositions along $\lambda \approx 1$ showed increased GFA with increased amount of Sm, which might be due to the stabilization of the icosahedral cluster (N=12) by Sm addition. However, thermal stability was decreased with Sm (Fig. 2.1). Reverse Monte Carlo simulation of high-energy X-ray scattering patterns showed the Sm-centred clusters had N=16 in the $\text{Al}_{89}\text{Sm}_{11}$ alloy in both the liquid state and at room temperature (Kalay et al. 2010). The decreased thermal stability was believed to be due to the lower thermal stability of Al-Sm clusters compared with Al-Ni clusters (N=12) (Aliaga et al. 2011).

2.4.1.4 Al-Ni-Gd Alloys

Previous studies on the Al-Ni-Gd system showed that amorphous ribbons can easily be generated by melt spinning in the composition area near $\text{Al}_{87}\text{Ni}_7\text{Gd}_6$. With decreased Al content, the reduced glass transition temperature T_{rg} increased from about 0.40 in $\text{Al}_{87}\text{Ni}_7\text{Gd}_5$ ribbons to 0.49 for $\text{Al}_{82}\text{Ni}_7\text{Gd}_{11}$ ribbons; also, the viscosity of the alloy melts increased with decreasing Al content. However, better thermal stability and improved reduced glass transition temperature in alloys with low Al

content did not exhibit good GFA experimentally, which was believed to be due to the increased solidification temperature range between the initial and final melting reactions. Thus, selection of new components, which can decrease the solidification temperature range without destroying the strong chemical bonding between the main elements of this system, would improve the GFA (Guo et al. 2000).

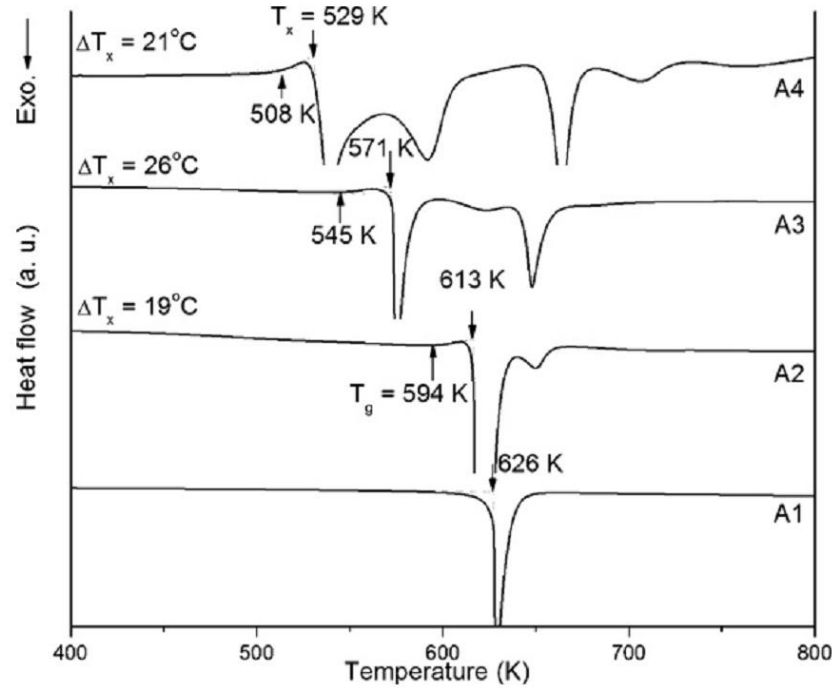


Fig. 2.1 DSC curves of as-quenched ribbons $\text{Al}_{76.5}\text{Ni}_{20.5}\text{Sm}_3$ (A1), $\text{Al}_{80.5}\text{Ni}_{14.5}\text{Sm}_5$ (A2), $\text{Al}_{83.5}\text{Ni}_{10.5}\text{Sm}_{6.5}$ (A3), $\text{Al}_{87.5}\text{Ni}_4\text{Sm}_{8.5}$ (A4) at 40 K/min (Aliaga et al. 2011).

2.4.1.5 Al-Ni-La Alloys

Though enormous efforts were made in early research, Al-LTM-RE metallic glasses with very high GFA were only reported in 2006 for Al-Ni-La alloys, where critical casting thickness was up to 780 μm and a nanocrystalline zone in the range 780 to 950 μm (Sanders et al. 2006). The discovery of potential GFA in Al-Ni-La could be traced back to 1991 when early research on La-based BMGs showed formation of metallic glasses at the Al-rich end with SCLR $\Delta T_x = (T_x - T_g)$ of 20 K by DTA (Inoue et al. 1991). The study on substitution of Ni by Co in Al-Ni-La ribbons found that the onset crystallization temperature and SCLR were both increased, but excessive Co

over 7 at.% decreased its GFA, whereby X-ray diffraction (XRD) revealed crystalline phases (Huang et al. 2008).

2.4.1.6 Al-Ni-Y-(Co)-(La) Alloys

A study on $\text{Al}_{86}\text{Ni}_9\text{Y}_5$ nanopillars showed that their yield strength was size-independent, but the ductility was strongly size-dependent (Kuzmin et al. 2012). Nanopillars of 315nm in diameter had a yield stress of 0.8GPa with 26% strain, but that of 490nm in diameter had a yield stress of 0.8GPa and 7 % strain. The brittle to ductile transition threshold was proposed to be 300nm; below that threshold the deformation mode changed from intermittent shear banding to homogeneous flow. This transition was due to the fact that elastic energy was released to the surface when the volume was smaller than the threshold, which avoided the formation of major shear bands and led to larger strain and higher ductility.

A study on $\text{Al}_{88}\text{Ni}_4\text{Y}_8$ ribbons at 200 °C indicated that the elongation was significantly increased at high temperature with a slight weakening in ultimate tensile strength (Yang et al. 2012). Fracture stress was 816 MPa at 200 °C but 889 MPa at room temperature; elongation was 16.8 % at 200 °C and 1.35 % at room temperature. By inspecting the fracture surface using scanning electron microscopy (SEM), increased elongation at 200 °C could be attributed to the viscous-like flow initiated from both sides of ribbons in the super-cooled liquid region. The strain-hardening behaviour during tensile testing can be attributed to dynamic crystallization during deformation. This explanation was derived from the smaller area of the first DSC peak in deformed ribbons, which indicated that less crystallization occurred after deformation by tensile testing at 200 °C. Dynamic crystallization during tensile testing at 200 °C was also confirmed by crystallinity comparison from a XRD pattern and average particle size comparison counted from transmission electron microscopy (TEM) micrographs. The heterogeneous nucleation in Al-Ni-Co-Y ribbons was inspected by the addition of grain refiner of Al_3Ti and TiB_2 by which the $\alpha\text{-Al}$ phase was formed around TiB_2 particles in as-spun $\text{Al}_{85}\text{Y}_8\text{Ni}_5\text{Co}_2$ ribbons (Schumacher et al. 1994a, Schumacher et al. 1994b, Schumacher et al. 1997).

A kinetic study on primary crystallization in quaternary $\text{Al}_{85}\text{Ni}_5\text{Co}_2\text{Y}_8$ (Wang et al. 2004b) showed the crystallization occurs in the following sequence: (1) growth of

quenched-in nuclei, (2) nucleation with high density in amorphous matrix, and then (3) growth of both quenched-in nuclei and those formed in annealing. The quenched-in nuclei of ~ 2 nm was identified by HRTEM to be fcc-Al in as-cast ribbons, and the XRD results after annealing at corresponding the DSC peak temperature revealed that the first exothermic peak was due to the crystallization of fcc-Al, the second peak due to crystallization of AlNiY, and the other two peaks due to coarsening and the presence of Al₃Ni, Al₃Y and Al₉Co₂ (Fig 2.2). A comparison of DSC and TEM data showed that T_g was 250 °C where the α -Al nuclei were around 5-10 nm with a number density of $10^{24}/\text{m}^3$; T_x was 267 °C where average particle size was increased to 20 nm. It implied that separation of nucleation and growth of fcc-Al after annealing occurred in the vicinity of T_g . Electrical resistance measurements (ERM) were shown to more easily detect the nucleation of fcc-Al nanocrystals than DSC, since the size and volume fraction of nanocrystals were so small that DSC could hardly detect the enthalpy release at the initial stage around T_g . However, ERM was sensitive to the formation of interfaces, which were so large that they dominated the nucleation process and acted as defects for electron distribution. The effect of RE replacing Al in Al-Ni-Y was inspected by addition of Ce (Salehi et al. 2013). The as-spun ribbons became amorphous by the addition of 2 at.% Ce or Y in Al₈₆Ni₆Y₈; their thermal stability was also increased with this addition. The glass transition temperature was increased from 180 °C in Al₈₆Ni₆Y₈ to 287 °C in Al₈₄Ni₆Y₆Ce₄; the crystallization temperature was also increased by about 115 K, indicating the RE element effect in the Al-Ni-Y system.

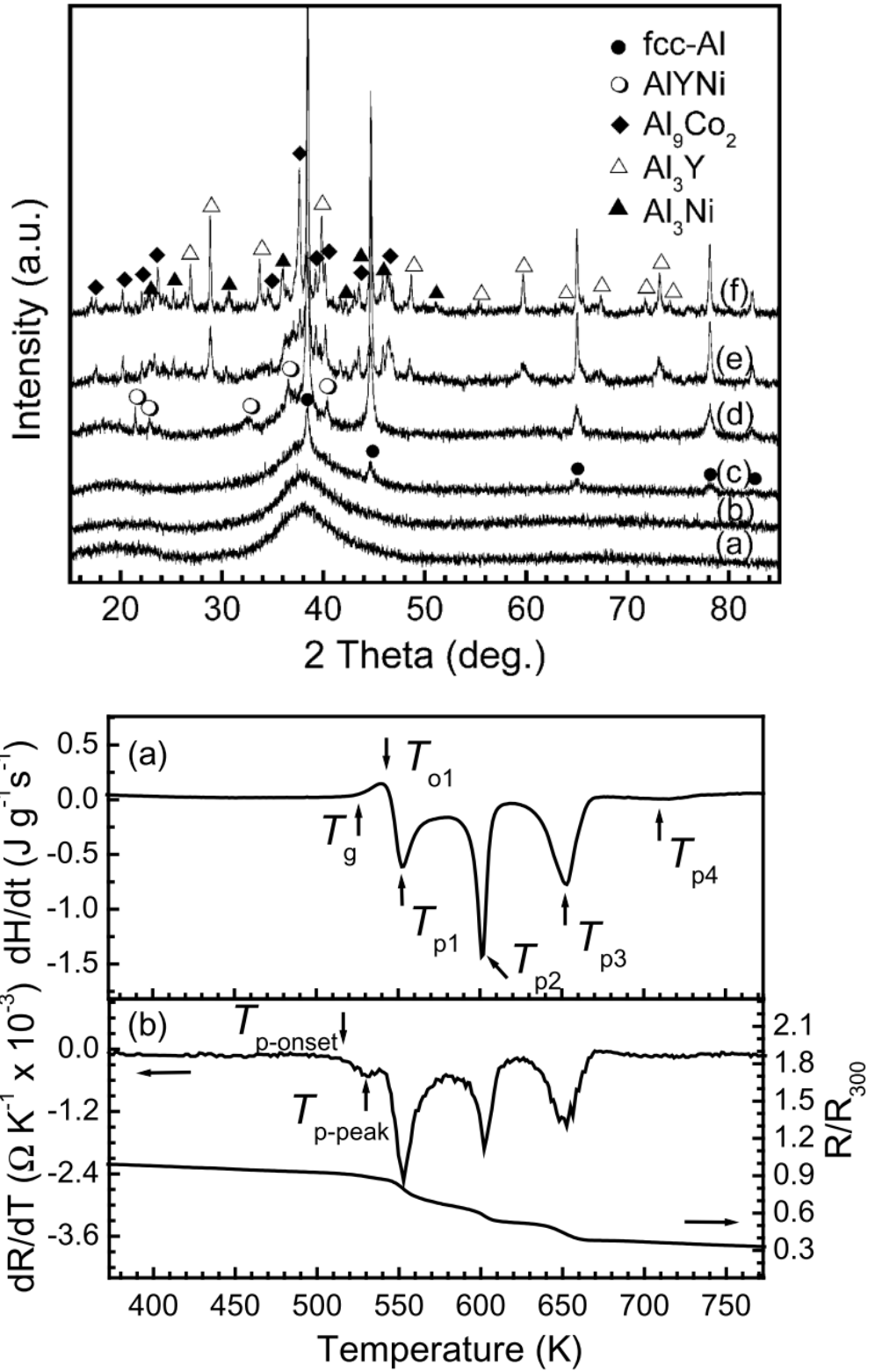


Fig. 2.2 XRD patterns (figure above) of $\text{Al}_{85}\text{Ni}_5\text{Co}_2\text{Y}_8$ glass: (a) as-cast, and heat with 10K/min to (b) 250 °C, (c) 275 °C, (d) 330 °C, (e) 382 °C, (f) 441 °C, associated with DSC scan (figure below a) and resistometry scan (b)(Wang et al. 2004b).

Following the study of Al-Ni-Y-Co alloys, the first Al-based BMG rods with diameters of 1mm were produced by arc melting and copper mould casting in

$\text{Al}_{86}\text{Ni}_7\text{Y}_5\text{Co}_1\text{La}_1$ by substituting Y with La and Ni with Co (Yang et al. 2009). A study of the crystallization behaviour of $\text{Al}_{86}\text{Ni}_6\text{Y}_{4.5}\text{Co}_2\text{La}_{1.5}$ powders (Li et al. 2011) showed its activation energy at onset crystallization temperature T_x to be 418 kJ/mol via the classic Kissinger plot, which was higher than that of $\text{Al}_{85}\text{Ni}_5\text{Y}_6\text{Co}_2\text{Fe}_2$ with 321 kJ/mol; this implied better thermal stability in $\text{Al}_{86}\text{Ni}_6\text{Y}_{4.5}\text{Co}_2\text{La}_{1.5}$. Using an isothermal DSC, the critical cooling rate for $\text{Al}_{86}\text{Ni}_6\text{Y}_{4.5}\text{Co}_2\text{La}_{1.5}$ was determined to be 1000 K/s, which was lower than that of $\text{Al}_{85}\text{Ni}_5\text{Y}_6\text{Co}_2\text{Fe}_2$ with 1500 K/s.

2.4.2 Type B: Al-LTM-ETM

The early development of metal-metal type Al-based metallic glasses also combined late transition metal (LTM) with early transition metal (ETM) elements. Significant discoveries were reported in Al-Cu-V, Al-Cu-Zr, Al-Cu-Hf alloy systems in the form of amorphous ribbons (Tsai et al. 1988b). The morphologies of melt-spun ribbons of about 20 μm in thickness in Al-ETM-LTM alloys are summarized in the Table 2.1.

Table 2.1: The effect of M element on the glass formation of Al -LTM alloys (M=Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W; LTM=Fe, Co, Ni, Cu) (Tsai et al. 1988).

M	Ti	Zr	Hf	V	Nb	Ta	Cr	Mo	W
$\text{Al}_{70}\text{Fe}_{20}\text{M}_{10}$	●	○	○	●	●	●	●	●	●
$\text{Al}_{70}\text{Co}_{20}\text{M}_{10}$	○	○	○	●	●	●	●	●	●
$\text{Al}_{70}\text{Ni}_{20}\text{M}_{10}$	○	○	○	○	○	●	●	○	●
$\text{Al}_{70}\text{Cu}_{20}\text{M}_{10}$	●	○	○	○	●	●	●	○	●

○ : Amorphous, ● : Amorphous+Crystalline , ● : Crystalline

Table 2.1 shows the effectiveness of ETM elements for glass formation in Al-ETM-LTM alloys. The addition of early transition metals in Al-LTM alloys was thought to increase the attractive interactions between constituent elements and raised the viscosity of the supercooled liquid. Further, the coexistence of Al, ETM, and LTM elements was found to decrease the melting temperature of these Al-ETM-LTM alloys, thereby further enhancing their ability to form a glassy structure on cooling from the melt (Tsai et al. 1988b).

2.4.3 Type C: Al-LTM-AEM

2.4.3.1 Al-LTM-Ca Alloys

Metallic glass formation in the form of 0.02 x 1 mm melt spun ribbons has been reported in binary Al-Ca alloys and the Al-[Mg, Fe, Co, Ni, Zn]-Ca system (Inoue et al. 1994) over narrow composition ranges generally containing 5 at.% LTM and 10 at.% Ca. Also, the partial substitution of RE for Ca has been found to form an amorphous phase along with a respectable increase in the critical casting thickness compared to ternary Al-Ni-Ca alloys (Chen et al. 2012). The microstructure by SEM and TEM showed $\text{Al}_{88}\text{Ni}_5\text{Ca}_7\text{Yb}_1$ to have the highest critical thickness of 370 μm followed by $\text{Al}_{88}\text{Ni}_5\text{Ca}_7\text{La}_1$, $\text{Al}_{88}\text{Ni}_5\text{Ca}_7\text{Ce}_1$, $\text{Al}_{88}\text{Ni}_5\text{Ca}_7\text{Y}_1$ with 310 μm , 290 μm , and 260 μm , respectively (Fig 2.3). XRD and DSC results showed the addition of Yb not only impeded the nucleation of fcc-Al phases but also stabilized the liquid phase by reducing the liquidus temperature T_L . As the atomic size followed the sequence of $\text{Ca} (1.97\text{\AA}) > \text{Yb} (1.93\text{\AA}) > \text{La} (1.83\text{\AA}) > \text{Ce} (1.82\text{\AA}) > \text{Y} (1.80\text{\AA})$, it was believed that the highest critical thickness in $\text{Al}_{88}\text{Ni}_5\text{Ca}_7\text{Yb}_1$ is due to the fact that the smallest atomic difference between Ca and Yb maintained the original dense packing structure.

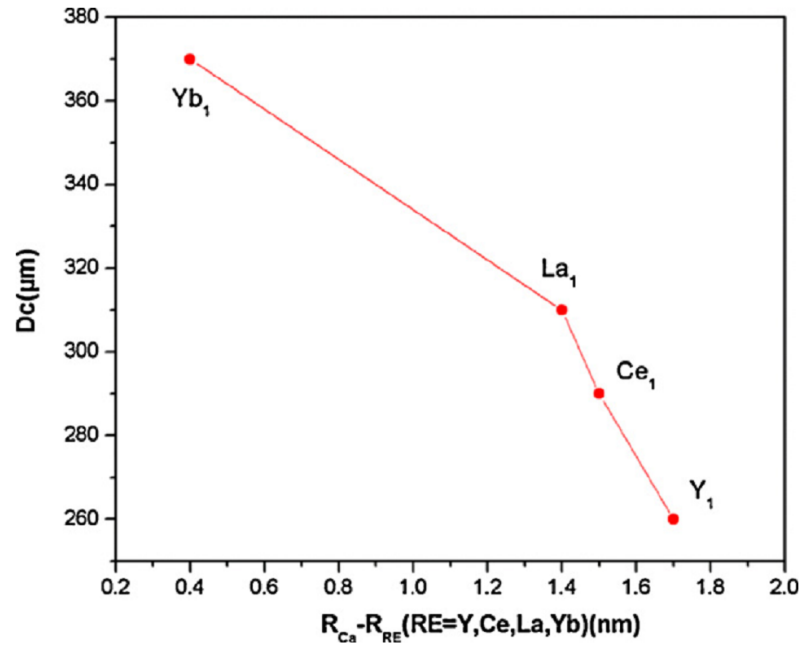


Fig. 2.3 Relationship between critical thickness D_c and atomic size difference to Ca ($R_{\text{Ca}} - R_{\text{RE}}$) (Chen et al. 2012).

2.4.3.2 Al-Cu-Mg-Ni Alloys

Amorphous ribbons were generated by melt spinning in eutectic $\text{Al}_{75}\text{Cu}_{17}\text{Mg}_8$ with 2-8 at.% Ni, but these ribbons were found to be crystallised with Gd (Guo et al. 2001). The negative heat of mixing and atomic size difference in Al-Gd were both larger than that of Al-Ni; however, the non-amorphous results contradicted the conventional criteria. This indicated that the large atomic size of Gd was not critical to glass formation. Meanwhile, increasing the amount of nickel enhanced the amorphous background shoulder at 44° at the expense of it at 38° in XRD, which was believed to be due to the increased strong interaction of Al-Ni bond and the decreased interaction of Al-Al bond. The d-orbital of TM was strongly hybridized with the s-p orbital of Al, which led to the contraction of Al-TM bond similar to covalent bonding. Hence, the addition of Ni may stabilize six to ten Al atoms around the nickel atom and reduce the mobility of Al atoms for better GFA in Al-Cu-Mg system (Guo et al. 2001). The micro alloying effect of Ni in Al-Cu-Mg ribbons also showed improved pitting resistance in both the amorphous phase and the devitrified phase (Aburada et al. 2008).

2.4.4 Type D: Al-TM-Metalloid

Al-TM-Metalloid metallic glasses have also attracted significant amount of research interest. The first Al-TM-metalloid metallic glasses were discovered in the 1980s, where the Al-TM-Si and Al-TM-Ge ribbons were explored for their GFRs (Inoue et al. 1987, Inoue et al. 1988). Over the last three decades, studies of the Al-TM-Metalloid system focused mainly on Al-Ni-Si and Al-Mn-Si, which are described in the following sections.

2.4.4.1 Al-Ni-Si Alloys

The GFR of Al-Ni-Si ribbons by melt spinning was reported by Legresy et al. (1988) for alloys containing 65~70% Al, 13~17% Ni, 15~20% Si (at.%). In a study of crystallization in these Al-Ni-Si ribbons, three types of crystallization were observed for various compositions by in-situ annealing under TEM, which included polymorphic, eutectic, and primary crystallization (Legresy et al. 1988). In polymorphic crystallization, stable phases were transformed from a hexagonal phase nucleated in an amorphous matrix. In eutectic crystallization, hexagonal phases with fine Al particles were formed in amorphous matrix, which acted as heterogeneous

nucleation sites in subsequent micro-crystallization. In primary crystallization, a complex mixture of metastable phases was formed after the formation of the hexagonal phase.

A study on Al-TM-Si and Al-TM-Ge (Inoue et al. 1988a) showed the widest glass formation ranges in Al-Co-Si and Al-Fe-Ge alloys. The composition range became narrow in the order of $\text{Co} > \text{Fe} > \text{Mn} > \text{Ni} > \text{Cr}$ in Al-TM-Si and $\text{Fe} > \text{Co} > \text{Mn} > \text{Cr} > \text{V} > \text{Ni}$ in Al-TM-Ge. Since the Al-Si and Al-Ge interactions were repulsive, glass formation was believed to be due to the attractive interaction of TM-Al and TM-Si (Ge). Both the hardness and crystallization temperature T_x were enhanced dramatically with increasing TM content, but they were less dependent with the amount of Si or Ge, which indicated that hardness and crystallization temperature were dominated by the attractive interaction of TM-Al and TM-Si(Ge). Electrical resistivity at room temperature was raised with the amount of TM and Si or Ge, and it was maximized in $\text{Al}_{65}\text{Mn}_{10}\text{Si}_{25}$ and $\text{Al}_{60}\text{Mn}_{10}\text{Ge}_{30}$ alloys. Electrical resistivity was closely related to phase separation of short range order in amorphous ribbons, which was raised when the split of first halo peaks in XRD and the electron diffraction patterns became clearer.

A recent study has shown an individual element effect on the GFA in Al-Ni-Si alloys. Previous studies in Al-Ni-based ribbons found that the addition of Si decreased the intensity of pre-peaks in XRD and the crystallization temperature T_x , indicating less medium range order (MRO) and, thus, promoting the primary crystallization of fcc Al. Meanwhile, Co increased the intensity of the pre-peaks and the crystallization temperature T_x , implying enhanced MRO and thus stabilizing the amorphous structure by suppressing the primary crystallization with eutectic crystallization(Wang 2011). Besides this ternary alloy, binary Ni-Si alloys were also simulated to inspect the reaction between Ni and Si. A molecular dynamics simulation on $\text{Ni}_{95}\text{Si}_5$ and $\text{Ni}_{90}\text{Si}_{10}$ indicated that the growth rate of Ni-Si alloys was majorly dependent on the diffusion rate of liquid atoms across the liquid-solid interface in the simulated undercool range; and the addition of Si into Ni-Si alloys transferred the diffusionless growth of Ni to diffusion-limited growth of Ni-Si alloys at high undercooling, and thus increased the activation energy and significantly decreased the growth rate of crystalline(Lu 2011).

In Al-LTM-Metalloid alloys, GFA was found to increase by the addition of RE elements. These elements not only have a strong negative heat of mixing with both Al and LTM, but can also form RE-centred clusters with $N=17$. For example, $\text{Al}_{86}\text{Si}_{0.5}\text{Ni}_{4.06}\text{Co}_{2.94}\text{Y}_6\text{Sc}_{0.5}$ rods with addition of Sc had peaks with lower intensity in XRD than that without Sc. Though a few peaks present were identified to be fcc-Al crystals (Zhuo et al. 2009), DSC revealed that the enthalpy released from the as-cast rod was 4.34 kJ/mol and that of amorphous ribbons was 4.59 kJ/mol, which implied the volume fraction of the amorphous phase was up to 94.6%. Both HRTEM and bright field TEM images with SAED confirmed that micro-sized fcc-Al phases were located in the centre of the as-cast rod (Zhuo et al. 2009). Improved GFA was also found in $\text{Al}_{82}\text{Ni}_8\text{Si}_3\text{Ce}_7$ and $\text{Al}_{82}\text{Ni}_8\text{Si}_3\text{Mm}_7$ ribbons (Fig 2.4); solute-lean $\text{Al}_{89}\text{Ni}_8\text{Si}_3$ ribbons is fully crystallised, but amorphous ribbons can be formed when the RE addition was above 5 at.%(Song et al. 2007). DSC revealed a SCLR ($T_x - T_g$) of 10 °C and reduced the glass transition temperature T_g of 0.5 to 0.6. Also, the crystallization temperature T_x was raised with an increasing amount of RE replacing Al. When the melt spinning wheel speed decreased from 36.5 m/s to 27.5 m/s, $\text{Al}_{84}\text{Ni}_8\text{Si}_3\text{Ce}_5$ crystallised whereas $\text{Al}_{84}\text{Ni}_8\text{Si}_3\text{Mm}_5$ was amorphous, thereby indicating that Mm can increase the GFA of Al-Ni-Si alloys.

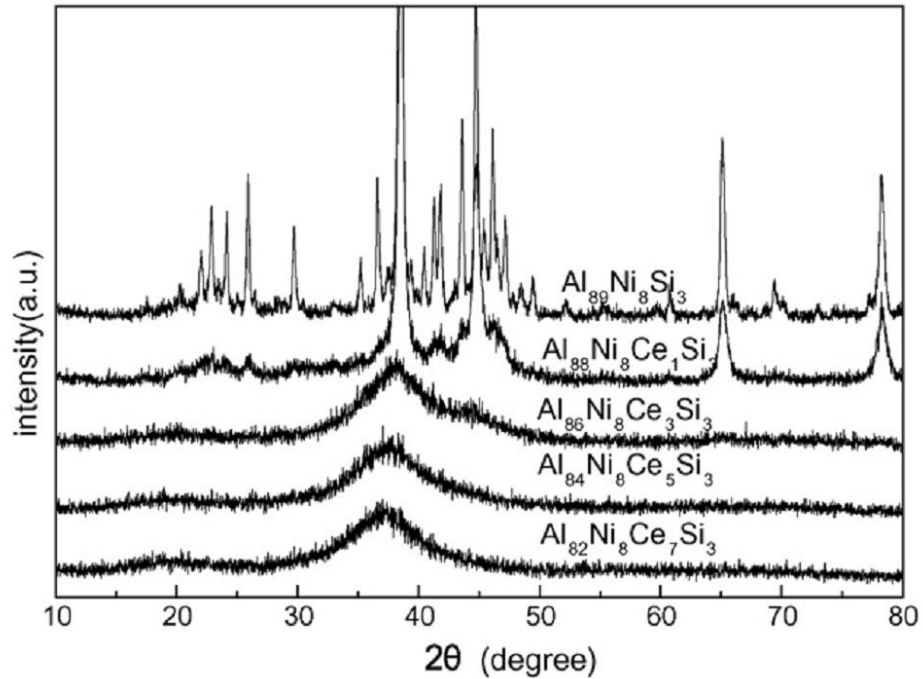


Fig. 2.4 XRD patterns of as-spun $\text{Al}_{82-x}\text{Ni}_8\text{Mm}_x\text{Si}_3$ ($x=0,1,3,5,7$) ribbons (Song et al. 2007).

2.4.4.2 Al-Mn-Si/Ge Alloys

The interest in research on Al-Mn-Si-(Ge) began due to their magnetic properties. Susceptibility measurements and neutron scattering on liquid $\text{Al}_{1-x-y}\text{Pd}_x\text{Mn}_y$ ($x \sim 0.2$, $y = 0.017 \sim 0.072$) (Hippert et al. 1996) and liquid $\text{Al}_{0.8}\text{Mn}_{0.2}$ (Maret et al. 1991) indicated that a fraction of Mn atoms carry a large magnetic moment, while the remaining Mn sites are non-magnetic. By increasing Mn in Al-Mn and Al-Mn-Si icosahedral alloys, the magnetic moment was increased to a maximum of $1.5 \pm 0.5 \mu_B$; in amorphous Al-Mn-Si ribbons, it showed spin-glass behaviour, which can be magnetized under an applied field when Si is less than 6 at.% (Hauser et al. 1986). Spin-glass behaviour was also observed in $\text{Al}_{65}\text{Mn}_{20}\text{Ge}_{15}$ icosahedral ribbons below 8K (McHenry et al. 1990). Higher Curie temperatures were found in amorphous Al-Mn-Si alloys with high Si content. O'Handley et al. (Dunlap et al. 1989) revealed a Curie temperature of 115K in $\text{Al}_{55}\text{Mn}_{20}\text{Si}_{25}$ amorphous ribbons with applied field 50 Oe and 100 Oe. Hauser et al. (1986) proposed that Heusler-like ordering in amorphous Al-Mn-Si was responsible for this ferromagnetism. The spin-glass behaviour can be considered as a potential precursor to collective magnetism in these alloys (McHenry et al. 1990).

The features of those magnetic properties were small magnetization with a relatively high Curie temperature (Hafner et al. 1998). Mossbauer spectroscopy showed two types of transition metals including magnetic and nonmagnetic sites (Stadnik et al. 1991), and only a small amount of Mn sites carry relatively large magnetic moments (Hafner et al. 1998). Magnetic moments of $0.45 \mu_B$ for Cr and $2.10 \mu_B$ for Mn was observed in $\text{Al}_{65}\text{Mn}_{(20-x)}\text{Cr}_x\text{Ge}_{15}$, where a magnetic moment of Mn in this alloy is the largest magnetic moment observed in Al-Mn-Metalloid quasicrystalline alloys (McHenry et al. 1990).

The formation of quasi-crystalline structures by annealing of the amorphous phase indicated the similarity of short-range atomic configurations between quasicrystalline and amorphous. The single quasicrystalline phases could be produced by annealing for 90min at 648K in $\text{Al}_{50}\text{Mn}_{20}\text{Si}_{30}$ or 45min at 623K in $\text{Al}_{55}\text{Mn}_{20}\text{Si}_{25}$ (Dunlap et al. 1989).

Recent research on the Al-Mn-Si ternary phase diagram revealed the liquid projection figure with more precise liquidus lines and eutectic points (Krendelsberger et al. 2002). The GFR of the Al-Mn-Si alloys produced by Inoue et al. (1988) were

located near the eutectic points in the liquidus projection diagram (Krendelsberger et al. 2002), which agreed with the driving force criteria.

2.5 Design Criteria for Al-based Metallic Glasses

Since the synthesis of Al-based metallic glasses is a major challenge (He et al. 1988), it is important to select a suitable design method for the development of Al-Si-based alloys. In the past three decades, many efforts have been made to generate models and criteria to predict the GFA of a given alloying system, which includes Inoue's selection criteria, cluster line criteria, inverse Monte Carlo method, topological instability criteria, cluster-plus-glue atom model, efficiently packed clusters, and driving force criteria etc. These models will be described in the following sections for comparison and selection.

2.5.1 Inoue Selection Criteria

After many experiments, Inoue suggested three empirical rules for alloys with high GFA (Inoue et al. 1993, Inoue 1997, Inoue et al. 1998, Inoue 2000): (1) multicomponent systems with more than three elements; (2) there is a significant difference in atomic size ratios above about 12% among the three main constituent elements, and (3) there is a negative heat of mixing among the three main constituent elements. It is believed that the high GFA present in Ln-, Mg-, Zr-based glasses were attributed to the difficulty of nucleation and growth of a crystalline phase caused by efficiently packed clusters in a SCLR from the large atomic size mismatch and negative heat of mixing (Inoue 1995). As it has been successfully applied in several alloy systems, the Inoue selection criteria were used in this thesis in the selection of constitutive elements for Al-Si-based alloys.

range of simple and complex alloys, including Zr-, Ca-, Mg-, and Fe-based metallic glasses.

Table 2.2: Coordination number N of the ideal radius ratio R^* for efficiently packed clusters (Miracle et al. 2006).

N	$R^*(N)$	N	$R^*(N)$
3	0.154701	14	1.04733
4	0.224745	15	1.11632
5	0.361654	16	1.18318
6	0.414214	17	1.24810
7	0.518145	18	1.31123
8	0.616517	19	1.37271
9	0.709914	20	1.43267
10	0.798907	21	1.49119
11	0.884003	22	1.54840
12	0.902113	23	1.60436
13	0.976006	24	1.65915

With a specific solute-to-solvent ratio, metallic glass composition would fall into the same category of coordination number, which validated their internal relationship to dense packing structure. Concentrations predicted for Al-based metallic glasses include <17-12> for Al-(Ce,Y,La)-(Fe,Co,Cu,Ni), <16-12> for Al-Hf-(Fe,Co,Cu,Ni), and <15-12> for Al-Zr-(Fe,Co,Cu,Ni) (Miracle 2004). The local packing was efficient around both the solute and solvent atom species to achieve an efficient overall packing efficiency termed ‘global packing efficiency’ (Miracle 2004). By considering the contact number of various balls according to their radius ratio (Miracle et al. 2003), the relationship between coordination number of the first shell and the radius ratio was shown in Table 2.2. Miracle's model was selected in the current thesis for the design of efficiently packed clusters.

Since the chemical basis that a particular solute may improve the stability of metallic glasses was not established, topologically equivalent but chemically distinct solutes can have different effects on the stability of amorphous structures. As a quantitative description of the chemical interaction is necessary to explain how the topologically equivalent but chemically distinct solutes may enhance or inhibit glass stability, the present model was not fully predictive. To compensate the insufficient part of

Miracle's model, multiple criteria were used in this thesis, which will be introduced in the next sections.

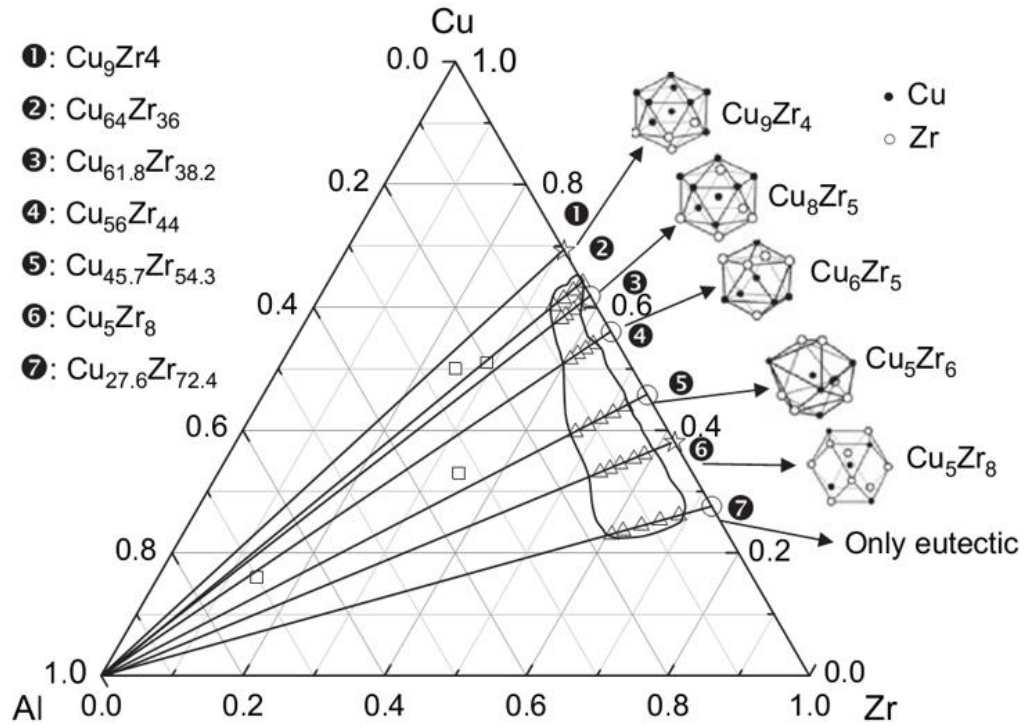


Fig. 2.6 Composition charts of the Cu-Zr-Al ternary system (Wang et al. 2007).

2.5.3 Cluster Line Criterion

As a single model is insufficient to predict GFR of all alloys, it became a popular practice to apply multiple rules from different criteria. For example, the cluster line criterion is proposed for predicting GFR of Cu-Zr-Al alloys (Wang et al. 2007), which three rules have been used for the selection of a favourite cluster line: (1) topologically dense packing with Miracle's model where the radius ratio between the centre atom and the first-shell atoms was very close to the ideal ratio of an effectively packed cluster (Miracle et al. 2003) such as 0.4% for Cu₈Zr₅; (2) strong chemical short-range order where a large amount of dissimilar pairs were present between the centre atom and first-shell atoms and a less amount of dissimilar pairs among first-shell atoms, and (3) short composition distance to deep eutectics, for example, Cu₆₄Zr₃₆ BMG of $\varnothing$ 2mm rods (Xu et al. 2004) was close to the binary eutectic point of Cu_{61.8}Zr_{38.6}. Based on these rules, cluster lines for favoured glass-forming compositions were proposed, and the Cu- and Zr-based BMG rods of 3 mm in diameter were formed along cluster lines (open triangles in Fig. 2.6).

2.5.4 Driving Force Criterion

The short composition distance to deep eutectics mentioned in the cluster line criterion is a thermodynamic factor that affects the GFA, which could be explained by the driving force criterion. The driving force criterion is a principle for predicting the composition of high GFA by thermodynamically calculating the driving force of crystalline phases in the undercooled liquid state. It assumed the crystalline phases with the highest driving force are most likely to form first, then the formation of glass can be promoted when the nucleation and growth of crystal phases are retarded, and the composition with highest GFA can be the one with the lowest driving force (Kim et al. 2005).

The molar Gibbs free energy of a solution phase can be calculated by an ordinary substitutional solution model (Equation 2.1), where x_i denotes the mole fraction of element i , G_i is the Gibbs free energy, and $L_{i,j}$ is the interaction energy of elements i and j . The Gibbs free energy of formation of the compound can then be expressed in Equation 2.2 (Kim et al. 2004). The driving force criterion well predicted the GFA in Mg-Cu-Y (Kim et al. 2005), Cu-Ti-Zr (Kim et al. 2004) and Cu-Zr-Al (Bo et al. 2010) systems; the fact implied that the compositions with high GFA is closely related with a relatively low driving force in an undercooled liquid state. The driving force criteria were used in the current study for the assistance of identifying the potential GFR of Al-Si based alloys.

$$\begin{aligned} G_m = & x_{Cu} {}^0G_{Cu} + x_{Ti} {}^0G_{Ti} + x_{Zr} {}^0G_{Zr} + RT(x_{Cu} \ln x_{Cu} \\ & + x_{Ti} \ln x_{Ti} + x_{Zr} \ln x_{Zr}) + x_{Cu}x_{Ti}L_{Cu,Ti} \\ & + x_{Cu}x_{Zr}L_{Cu,Zr} + x_{Ti}x_{Zr}L_{Ti,Zr} + x_{Cu}x_{Ti}x_{Zr}L_{Cu,Ti,Zr} \end{aligned}$$

Equation 2.1 Molar Gibbs energy of a phase calculated by an ordinary substitutional solution model (Kim et al. 2004)

$${}^0G_{Cu_2TiZr} = 2{}^0G_{Cu}^{fcc} + {}^0G_{Ti}^{hcp} + {}^0G_{Zr}^{hcp} + \Delta G_f^{Cu_2TiZr}$$

Equation 2.2 Gibbs energy of formation of a phase (Kim et al. 2004)

2.5.5 Inverse Monte Carlo Method

Compared with the structure factor derived from extended X-ray absorption fine structure (EXAFS) data in a synchrotron, the effective pair potential between Al and a solute atom are calculated using ‘VASP’ software based on the density functional theory (Fig 2.8) (Sheng et al. 2007). The atomic configuration of Al-based metallic glasses were found to have solute-centred, quasi-equivalent clusters surrounded by solvent Al atoms (Sheng et al. 2008), which were dense and randomly connected with tendency of an icosahedral arrangement in MRO. Though polyhedra of other coordinate numbers existed, Ni-centred clusters were found to be the polyhedral of CN=9, while La-centred clusters were polyhedral of CN=17. No predetermined subunit was observed in the simulated configuration, which may be due to the bond shortening. Bond shortening, where the bond length is shorter than the sum of the Al and solute radius, is also observed in other Al-TM metallic glasses. Bond shortening was postulated to be due to sp-d electron hybridization and other electron interactions, but detailed investigation of electron origin remain open.

The polyhedral with different coordination numbers would have different topology, and intermixes of these polyhedral are believed to be the reason for increased GFR in multicomponent Al-based alloys (Fig 2.7). For example, with preferred clusters of $\text{Al}_{9.4}\text{Ni}$ and $\text{Al}_{17.5}\text{La}$ in the ternary phase diagram, $\text{Al}_{86}\text{Ni}_9\text{La}_5$ metallic glasses were produced with critical thicknesses over 700 μm (Sanders et al. 2006); Al-based amorphous rods with critical thicknesses over 1 mm were also designed with this method by using $\text{Al}_{9.4}\text{Ni}$ and $\text{Al}_{16.9}\text{Y}$ clusters (Yang et al. 2009). This model predicted the best glass formers in a series of Al-Ni-RE alloys, such as $\text{Al}_{85.8}\text{Ni}_{9.1}\text{Y}_{5.1}$, $\text{Al}_{85.9}\text{Ni}_{9.1}\text{La}_5$, $\text{Al}_{85.7}\text{Ni}_{9.1}\text{Gd}_{5.2}$ and $\text{Al}_{85.8}\text{Ni}_{9.1}\text{Ce}_{5.1}$ alloys; however, it is not universally agreed with experimentally determined best glass formers, such as Al-Fe-Ce and Al-Co-Y (Yang et al. 2010). Reverse Monte Carlo simulations produced structures that are consistent to the measured radial distribution functions, but they are not sufficient to show the real structure because the consistency can be achieved by a number of non-equivalent structures (Miracle 2004). Therefore, this method was not selected for the cluster design in this thesis.

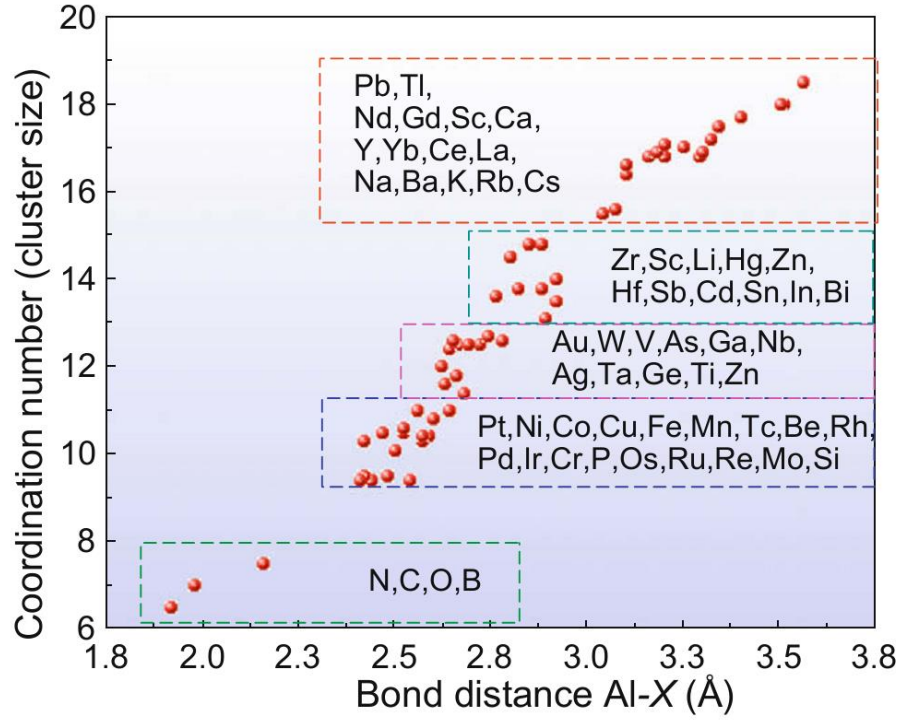


Fig. 2.7 Coordination number as a function of bond distance, where X is the solute atom. Combination of different size clusters may help form better Al-based metallic glasses (Sheng et al. 2008).

2.5.6 Topological Instability Criteria

The concept of topological instability was first proposed to reveal the relationship between the minimum solute concentration and atomic volume mismatch (Egami et al. 1984); it also predicted the binary Al-based metallic glasses well. By observing the minimum concentration to form glass and the atomic mismatch between a solute and matrix, it was found that these two factors were inversely related, as shown below (Egami et al. 1984):

$$\lambda_0 = C_B^{\min} \times \left| \frac{V_b - V_a}{V_a} \right| \approx 0.1$$

where $C_B^{\min}$ was the minimum solute concentration of glass formation, and V_a and V_b were volume of matrix and solutes.

Elements (as a solute) in Al-based glasses

3 Li 2.76 (13.6)	4 Be 2.42 (10.3)											5 B 2.16 (7.5)	6 C 1.98 (7.0)	7 N 1.92 (6.5)	8 O 2.16 (7.5)	9 F	10 Ne
11 Na 3.32 (17.2)	12 Mg 2.88 (13.8)											13 Al 2.74 (12.7)	14 Si 2.56 (11.0)	15 P 2.47 (10.5)	16 S 2.35 (12.8)	17 Cl	18 Ar
19 K 3.51 (18.0)	20 Ca 3.30 (16.9)	21 Sc 2.89 (13.1)	22 Ti 2.78 (12.6)	23 V 2.66 (11.8)	24 Cr 2.52 (10.5)	25 Mn 2.50 (10.1)	26 Fe 2.42 (9.5)	27 Co 2.41 (9.4)	28 Ni 2.44 (9.4)	29 Cu 2.48 (9.5)	30 Zn 2.65 (12.6)	31 Ga 2.64 (12.4)	32 Ge 2.69 (12.5)	33 As 2.62 (12.0)	34 Se 2.62 (13.5)	35 Br	36 Kr
37 Rb 3.50 (18.0)	38 Sr 3.29 (16.8)	39 Y 3.18 (16.9)	40 Zr 2.92 (13.5)	41 Nb 2.71 (12.5)	42 Mo 2.64 (11.0)	43 Tc 2.57 (10.3)	44 Ru 2.60 (10.8)	45 Rh 2.59 (10.4)	46 Pd 2.59 (10.4)	47 Ag 2.67 (12.5)	48 Cd 2.85 (14.8)	49 In 3.04 (15.5)	50 Sn 2.88 (14.8)	51 Sb 2.8 (14.5)	52 Te	53 I	54 Xe
55 Cs 3.56 (18.5)	56 Ba 3.40 (17.7)		72 Hf 2.92 (14.0)	73 Ta 2.72 (12.5)	74 W 2.68 (11.4)	75 Re 2.60 (10.8)	76 Os 2.52 (10.6)	77 Ir 2.57 (10.4)	78 Pt 2.54 (9.4)	79 Au 2.63 (11.6)	80 Hg 2.82 (13.8)	81 Tl 3.10 (16.4)	82 Pb 3.10 (16.4)	83 Bi 3.07 (15.6)	84 Po	85 At	86 Rn
			57 La 3.34 (17.5)	58 Ce 3.25 (17.0)	59 Pr	60 Nd 3.20 (16.8)	61 Pm	62 Sm	63 Eu	64 Gd 3.16 (16.8)	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb 3.20 (17.1)	71 Lu 3.10 (16.6)

Fig. 2.8 Bond distance of Al-solute clusters with preferred average coordination number (Sheng et al. 2008).

According to this criterion, alloys were defined to fall within three categories: (1) the glassy alloys with $\lambda > 0.1$, which exhibited a supercooled region upon heating; (2) the nanocrystalline alloys with $\lambda < 0.1$, which had nanocrystallization during heating; and (3) the nano-glassy alloys with $\lambda \approx 1$, which had nanocrystallization in a supercooled region. The best glass-forming compositions in Al-LTM-RE were found to be off-eutectic and nano-glassy type with $\lambda \approx 1$.

The Al-Ni-Sm alloys were investigated by this method along $\lambda=1$ (Fig 2.9)(Aliaga et al. 2011). Along this instability criteria line, a glass transition temperature was observed with higher Sm content indicating better glass formation with the cluster with N=17. Also, crystallization temperature was increased with higher Ni content, indicating a better thermal stability, which might be due to the more stable icosahedron cluster of Al-Ni with N=12 compared with that of 17 in Al-Sm clusters.

This method could identify the minimum concentration of solute atoms in alloys to form amorphous phases; however, it does not provide the information of phase regions where the optimized glass-forming candidates are located. Since the main

purpose of the thesis is to explore the GFA of potential glass-forming alloys; this criterion was not selected in the design of Al-Si-based alloys.

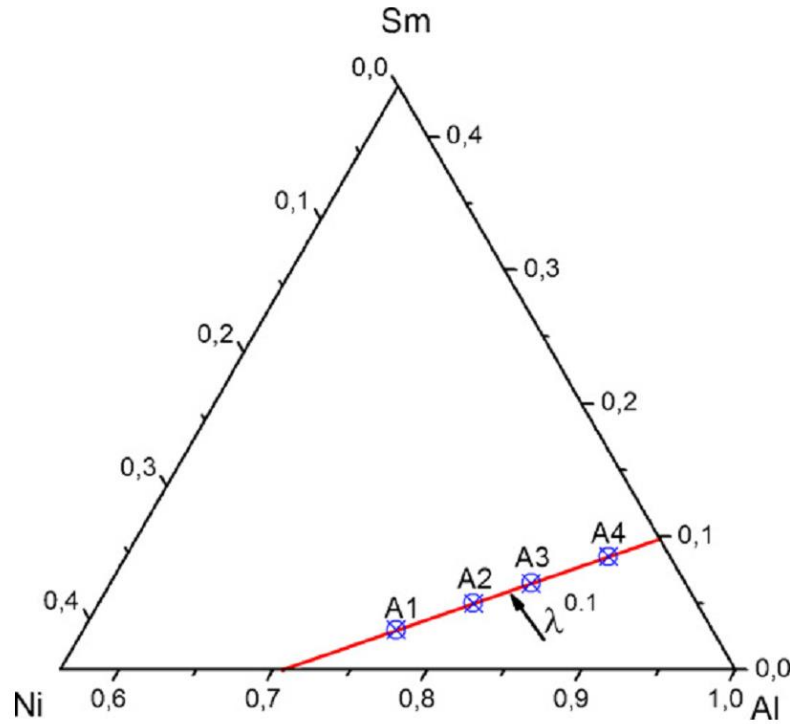


Fig. 2.9 Composition selected along the transversal line $\lambda=1$ in a Al-Ni-Sm glass formation triangle (Aliaga et al. 2011).

2.5.7 Cluster plus glue atom model assisted with electron per atom ratio

The electron per atom ratio was found to be important for determining glass formers with, locally, the highest GFA (Han et al. 2011). The e/a ratio was defined as the integration of the constitutional contribution of the e/a value. By the phase stability criteria and a cluster-resonance model, the e/a ratio can be calculated by atomic density ρ_a and the first-shell radius r_1 as $e/a = (1.25^3 \pi / 3) * (1 / \rho_a * r_1^3)$. Atomic density ρ_a can be obtained by measuring the alloy density ρ , and r_1 can be evaluated from devitrification phase in XRD. By considering each cluster as a large sphere, the atomic number Z of an ideal metallic glass cluster can be calculated as $e/a = 23.614 / Z$. With the atomic number Z of ideal metallic glasses, the formula for the locally highest glass-forming composition in a cluster-plus-glue atom model can be calculated. This principle is validated in $[\text{Cu}_8\text{Zr}_5]\text{Al}$, $[\text{Ni}_3\text{Zr}_9](\text{NiAl}_2)$, and $[\text{Ni}_7\text{Nb}_5\text{Zr}]\text{Ni}_3$ (Han et al. 2011). In this model, the density needs to be measured after casting; and the atomic number of ideal metallic glasses provided many

possible combinations of atomic structures and different compositions. Therefore, this criterion was deemed unsuitable in the prediction of glass forming candidates in the current thesis.

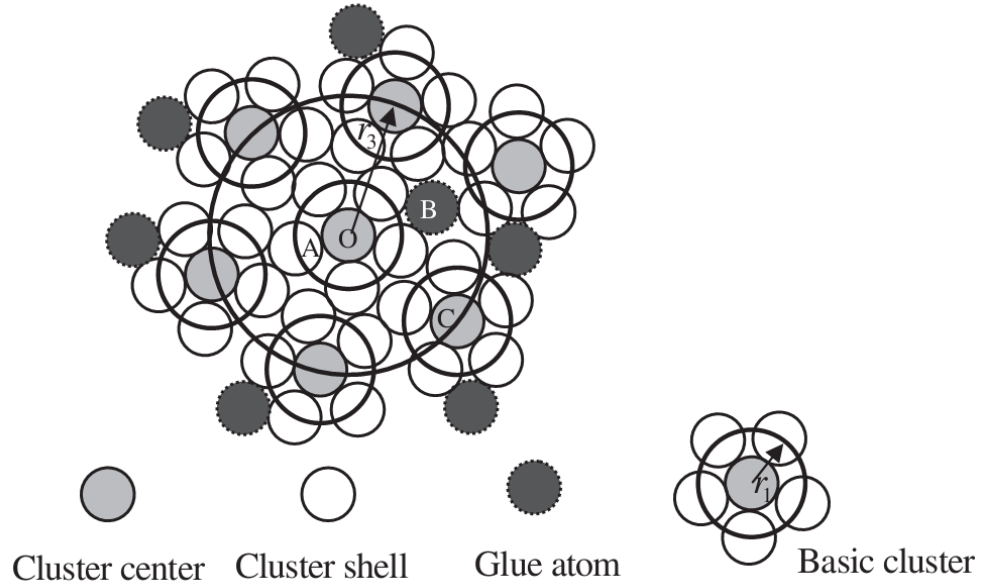


Fig. 2.10 Two-dimensional presentation of a cluster-resonance model (Han et al. 2011).

2.6 Significance, Innovation, and Structure of Thesis

The chapter 2 provided a review of literature about the development of Al-based alloys. It was shown that four main types of Al-based metallic glasses have been investigated since the 1980s: (1) Al-TM-RE; (2) Al-ETM-LTM; (3) Al-LTM-AEM, and (4) Al-TM-Metalloid. The major challenge with all these alloy types is to devise compositions that do not crystallize easily during casting, i.e. to improve their glass-forming ability (GFA). Many efforts have been made to improve the GFA of Al-TM-RE alloys.

2.6.1 Significance and Innovation

After extensive studies of Al-Ni-RE and Al-Fe-RE based alloys, the first bulk metallic glasses (BMGs) were generated in the complex Al-Ni-Co-Y-La system by copper mould casting that produced ~1 mm diameter glassy rods. This raised an important question about the GFA of Al-based alloys without RE elements. In Al-ETM-LTM alloys, a few amorphous ribbons were formed. In Al-LTM-AEM alloys, no amorphous phase was formed in Al-Ni-Ca wedges without Yb; Al-Cu-Mg

ribbons without Ni were also crystallised. It indicated the poor GFA in Al-LTM-AEM. In the Al-TM-Metalloid system, a series of alloys, including Al-Mn-Si, Al-Cr-Si, Al-Fe-Si, Al-Ni-Si, Al-Co-Si, were found to form amorphous ribbons, but none of these alloys have been investigated by slow-cooling methods such as gravity casting. Therefore, in this thesis, a systematic study was carried out on Al-Si-based alloys to understand their GFA by copper mould casting. As this is the first time the Al-metalloid alloys were synthesized by slow-cooling method, the innovations of design principles were applied to maximize the chance of creation of metallic glasses without rare earth elements.

2.6.2 Structure of Thesis

The applied contemporary design principles, latest synthesis methods, characterizing, thermal analysis, chemical analysis and mechanical testing of the Al-Si-based alloys are described in Chapter 3. The effect of early transition metals, such as Mn, Mo and Cr, on GFR and GFA of the alloys is given in Chapter 4. The effect of late transition metals, such as Co and Fe, on the GFR and GFA of the alloys is given in Chapter 5. Finally, the GFR and GFA of Al-Ni-Si ternary alloys and Al-Ni-Si-Co quaternary alloys is given in Chapter 6. The GFR and simulation methods used in the thesis are discussed in detail in Chapter 7. Finally, the major conclusions are given in Chapter 8 with Appendix A supplying information of the efficiently packed cluster model and sample method of calculation.

Chapter 3

Experimental Procedure

3.1. Introduction

In this thesis, several Al-TM-Metalloid alloy systems are examined for potential bulk-metallic glass formation, namely Al-Mn-Si, Al-Mn-Ge, Al-Cr-Si, Al-Mo-Si, Al-Fe-Si, Al-Ni-Si, Al-Co-Si, and Al-Ni-Co-Si alloys. Specific composition design techniques were utilised to choose alloy compositions with the highest propensity for glass formation, as outlined in Section 3.2. Casting, sample preparation, microstructural characterisation, and composition analysis are outlined in details in this chapter.

3.2 Alloy Design Principles

Synthesis of Al-based metallic glasses is a major challenge due to the very high cooling rates from the melt required to suppress crystallization (He et al. 1988, Uzun et al. 2004, Kiliçaslan et al. 2013). After a review of the empirical, physical property, thermodynamic, topological, and computer-based models in the current literature, a systematic approach was created for the development of Al-TM-Si alloys in this thesis. It includes the heat-of-mixing rule for the selection of elements, the driving force criterion for the phase region inspection, and Miracle's model of efficiently packed clusters for optimizing compositions with the highest likeliness of bulk metallic glass formation.

3.2.1 Heat of Mixing Criterion

Due to the repulsive interactions between Al and Si, the binary alloys formed neither solid solutions nor metallic glass ribbons upon melt spinning (Uzun et al. 2004). The study of ternary Al-TM-Si metallic glass ribbons indicates that the formation of an

amorphous phase was a result of the attractive interactions between TM-Si and TM-Al (Inoue et al. 1988). The heat of mixing is a good indicator of the interaction between elements, and a large negative heat of mixing implies strong attractive interactions. The heat of mixing is calculated from the enthalpies of mixing the binary liquid in an A-B system at equi-atomic compositions (Takeuchi et al. 2005). The heat of mixing for various transition metals is listed in Table 3.1. The elements with large heat of mixing were selected for the development of Al-Si-based alloys in this work and are highlighted in Table 3.1.

Table 3.1: The heat of mixing between certain transition metals and either Al or Si (Takeuchi et al. 2005).

		24	25	26	27	28	29	30	42
		Cr	Mn	Fe	Co	Ni	Cu	Zn	Mo
13	Al	-10	-19	-11	-19	-22	-1	1	-5
14	Si	-37	-45	-35	-38	-40	-19	-18	-35

3.2.2 Driving Force Criterion

The driving force criterion is a principle that assumes the crystalline phases with the highest driving forces are most likely to form first; then the formation of glass can be promoted when the nucleation and crystal growth of these phases is suppressed. Essentially, the composition with the highest GFA is the one with the lowest driving force for crystallization (Kim et al. 2005). When the degree of undercooling is small, the compositional dependence of the liquidus temperature is close to that of the driving forces of the crystalline phases (Kim et al. 2004). Undercooling is a phenomenon of decreasing the solidification temperature of a liquid below its thermodynamic melting point; the degree of undercooling is the amount, in degrees Kelvin, between the onset of solidification and melting point. For low-cooling-rate casting methods such as copper mould suction casting, the degree of undercooling is relatively small, and the compositional dependence of the liquidus temperature can be used as a guide to predict the compositional dependence of the driving forces of crystalline phases. The phase regions with lower liquidus temperatures such as eutectic points and liquidus lines in liquidus projection diagrams were prioritized for inspection.

3.2.3 Composition Design

Previous research showed that a 12% difference in atomic size was significant for metallic glass formation (Inoue 2000). Other research revealed that the critical solute concentration to form a metallic glass was inversely related to the radius ratio R of the solute and solvent atoms because the amorphous state was stabilised as the solid solution of the corresponding composition was topologically unstable (Egami et al. 1984). A quantitative model for this relationship was built on three dimensions; i.e., Miracle's model introduced the contacting surface, q , between the centre atom and the first shell atoms and calculated the critical radius ratio, R^* , of the solute and solvent for efficiently packed clusters in the specific coordination number, N (Miracle et al. 2003). The radius ratio value of R is calculated by the average radius ratio of atoms in the first shell.

$$R = \frac{R_{center}}{R_{shell}} = \frac{R_{center}}{\sum R_i \times at. \%_i}$$

Equation 3.1 The Radius ratio between centre atom and atoms in the first shell.

The critical radius ratio, R^* , of the solute and solvent for efficiently packed clusters in the specific coordination number, N , is calculated by following equations.

$$N^T = \begin{cases} \frac{4\pi}{6 \arccos \{ \sin(\pi/3) [1 - 1/(R+1)^2]^{1/2} \} - \pi} & \text{for } 0.225 \leq R < 0.414, \\ \frac{4\pi}{8 \arccos \{ \sin(\pi/4) [1 - 1/(R+1)^2]^{1/2} \} - 2\pi} & \text{for } 0.414 \leq R < 0.902, \\ \frac{4\pi}{10 \arccos \{ \sin(\pi/5) [1 - 1/(R+1)^2]^{1/2} \} - 3\pi} & \text{for } 0.902 \leq R. \end{cases}$$

Equation 3.2 The critical radius ratio based on each coordination number of clusters.

The critical radius ratio of clusters in each coordination number was tabulated according to the previous equations.

Table 3.2: Critical radius ratio R^* and the corresponding coordination number N (Miracle et al. 2003).

N	R_N^*	N	R_N^*
3	0.155 ^a	14	1.047
4	0.225	15	1.116
5	0.362	16	1.183
6	0.414	17	1.248
7	0.518	18	1.311
8	0.617	19	1.373
9	0.710	20	1.433
10	0.799	21	1.491
11	0.884	22	1.548
12	0.902	23	1.604
13	0.976	24	1.659

For example, $\text{Al}_{72.72}\text{Cr}_{18.18}\text{Si}_{9.09}$ in Table 3.3 is derived from the Si centred cluster with a coordination number of 10 ($\text{CN} = 10$), which includes 2 chromium atoms and 8 aluminium atoms in the first shell. The corresponding radius ratio can be calculated based on this cluster structure. The Si centred $\text{Al}_8\text{Cr}_2\text{Si}_1$ clusters corresponding to $\text{Al}_{72.72}\text{Cr}_{18.18}\text{Si}_{9.09}$ would have a critical radius ratio R^* of 0.799, and the difference to the critical radius ratio can be evaluated as follows. The full explanation is detailed in APPENDIX A.

$$R_{\text{shell}} = \frac{0.143 \times 8 + 0.1249 \times 2}{10} = 0.1412 \text{ nm}$$

Equation 3.3 The average radius in the first shell.

$$R = \frac{R_{\text{center}}}{R_{\text{shell}}} = \frac{0.1153}{0.1412} = 0.827$$

Equation 3.4 The radius ratio between centre atom and atoms in the first shell.

$$\Delta = \left(\frac{R}{R^*} - 1 \right) \times 100\% = \left(\frac{0.827}{0.799} - 1 \right) \times 100\% = 3.53\%$$

Equation 3.5 The deviation from ideal packing or packing efficiency of the cluster.

Table 3.3: The calculated radius ratio and difference to the critical radius ratio in efficiently packed Al-Cr-Si clusters.

Clusters	R	R*	Δ (%)	N
Al _{72.72} Cr _{18.18} Si _{9.09}	0.827	0.799	3.53	10
Al _{63.63} Cr _{18.18} Si _{18.18}	0.844	0.799	5.63	10
	1.068	1.116	-4.26	15
Al _{61.54} Cr _{7.69} Si _{30.76}	0.934	0.902	3.52	12
	1.079	1.116	-3.34	15
Al _{61.54} Cr _{15.38} Si _{23.08}	0.928	0.902	2.91	12
Al _{54.54} Cr _{9.09} Si _{36.36}	0.868	0.799	8.60	10

3.3 Alloy Synthesis

The raw materials used in this thesis along with their form, purity and suppliers are listed in the Table 3.4. High purity elements were used where possible to limit the effects impurities may have on glass-forming ability.

Table 3.4: Raw materials used for producing the Al-Si-based alloys.

Materials	Form	Purity wt.%	Source
Aluminium	Shot	99.99	Aldrich Chemical Company
Silicon	Lumps	99.99	Alfa Aesar
Chromium	Crystallite	99.996	Aldrich Chemical Company
Nickel	Foil	99.98	Sigma-Aldrich Co.
Manganese	Electrolytic Chips	99.8	Sigma-Aldrich Co.
Molybdenum	Rod	99.95	Aldrich Chemical Company
Iron	Electrolytic Chips	99.9	Sigma-Aldrich Co.
Cobalt	Cylinders	99.98	Materion Co.
Germanium	Lumps	99.99	Alfa Aesar

3.3.1 Initial Induction Furnace Melting

An in-house induction furnace was used to melt the aluminium shot into rods for easy handling. Three parameters were important for casting: charge temperature; injection pressure, and the fluid velocity at the mould gate. These three factors can determine the length, porosity, and crystal phases present in the casting (Laws et al. 2008).

The aluminium shot was loaded into graphite crucibles that were coated with boron nitride for refractory isolation to prevent composition contamination from the crucible walls. The chamber was purged twice with high-pressure argon for argon circulation. An 85% current was used for heating and mixing the raw materials. The

temperature control unit was set to 750 °C, i.e., well above the melting temperature in order to melt potentially refractory intermetallic compounds and remove any impurities. After reaching 750 °C, the raw materials were stirred at two different times with a tungsten rod for ensuring good mixing and homogenisation. The tungsten rod became hot after making twenty to thirty circular stirring motions each time; then, the hot rod was immersed in a water bucket for cooling. The crucible was clamped with tongs, and the molten aluminium was poured into a copper mould, thereby casting the aluminium rod via gravity casting.

3.3.2 Arc Melting of the Alloys

Master alloys and cast wedges were prepared with an Edmund-Buehler Compact Arc Melter MAM-1. Raw materials used to cast a master alloy of about 1 ml in volume were measured on a digital mass balance. All rods of metals were cut with a diamond saw, and the surface oxide was polished off with grade 1200 silicon carbide paper; sheets of metals were cut with a foot stamp metal sheet cutting machine and trimmed with an offset snip. A silicon lump was broken up and the small pieces weighed. The raw materials were loaded and stacked in a densely-packed manner on the water-cooled copper hearth, along with a titanium oxygen getter. The chamber was purged with high purity argon to prevent oxidation during melting. A vacuum was created in the chamber with a rotary pump, and the pressure was maintained below 2.0×10^{-1} mbar. The chamber was filled with high purity argon gas to 1 bar. Purging was repeated to further reduce the presence of leftover air. A high vacuum level below 9.8×10^{-5} mbar was obtained in the chamber with a turbo pump. The chamber was then sealed and filled with ultra-high purity argon to 1 bar. The titanium getter was melted prior to alloying to remove (scavenge) any remaining oxygen in the chamber after vacuum purging providing a highly inert melting atmosphere.

During melting, the potentiometer was set at 3. An electric arc was ignited by controlling the electrode briefly to touch the plate, which discharges static electrons. The three factors of arc current, distance to the raw materials, and melting time were adjusted to optimise melting. After the pieces of raw material were fused into one master alloy, the latter was turned over and re-melted. This was repeated six times to thoroughly homogenise the alloy. During casting, a special copper hearth was used for casting the alloys, which could incorporate customised copper moulds for vacuum casting. The wedge-shaped cavity in the two copper moulds had a length of

30mm; one had a width of 3mm, and the other had a width of 1.5mm. Therefore, the angle for the 10:1 mould and the 20:1 mould was 5.71 ° and 2.8 °, respectively. The base of the special copper hearth was sealed with a stainless steel cap, which was connected to the vacuum reservoir by a steel pipe. The purging process was similar to that for melting but with an additional step to create a vacuum in the reservoir. Wedges were obtained via casting the master alloy piece in the copper mould through the vacuum force from the reservoir.

3.4 Metallographic Preparation

Due to the complex geometry and the small size of the cast wedges, the specimens were cold mounted in a 26 mm diameter cup with a mixture of epoxy resin and hardener for easy handling during metallographic preparation and for proper sample holding in various characterisation techniques. Hot mounting was avoided as these rapidly cooled alloys are far from equilibrium and sensitive to temperature. Mounted samples were cut with a table saw to ensure the height was less than 8.5 mm to accommodate the sample cradle in the X-ray diffraction (XRD) facility. The samples were ground to produce parallel and flat surfaces. SiC papers were used in the order of 180, 320, 800, and 1200 grades; each sample was held still to produce parallel grinding marks on surface, then the sample was rotated perpendicular to the previous direction and held still to produce parallel grinding marks. It was repeated several times in order to produce a flat surface. Ultrasonic cleaning with soapy water was used to remove the grinding residues, and an air gun was used to dry the samples. After grinding with the 800 and 1200 grade SiC papers, optical microscopy was used to inspect the sample surface that the grinding marks were parallel. Then the samples were polished with three separate rotating pads, i.e., containing 3 and 1 micron diamond suspensions in kerosene and 0.1 micron diamond paste dissolved in polishing oil. Before each change of the polishing pad, the polishing oil that was left on the samples was removed by ultrasonic cleaning with soapy water, and the sample was dried with an air gun; moreover, the polishing marks were checked to be parallel on the surface with an optical microscope.

3.5 Structural Characterisation

3.5.1 Mono-Capillary X-Ray Diffraction

A Panalytical X'Pert Materials Research Diffractometer (MRD) was used for the analysis of any crystalline phases and the degree of crystallinity of the cast wedges. The wedges were mounted in epoxy resin and polished parallel on both surfaces. The surface finish of each sample was 0.25 μm for the XRD measurements. In the parameter settings, the current and voltage were 40mA and 45kV. The Cu0.2 mm/Ni0.02 mm attenuator and divergent slit of $1/16^\circ$ were used. A Pixcel detector was used; and a receiving slit with an active length of 0.385 mm was used. A 2 θ scan, Z-axis scan, Omega scan, and another Z-axis scan were performed for new sample alignment prior to the generation of the final 2 θ X-ray diffraction spectrum presented in results. A 2 θ scan was used to adjust the detector parallel to the sample surface. The scan range was 0.6° ; the step size was 0.01° and the time per step was 0.5 seconds. A Z-axis scan was used to align the detector at the height of the middle line in the x-ray beam path. The scan height range was 2 mm; the step size was 0.02 mm, and the time per step was 0.5 seconds. An Omega scan was used to align the top surface of the sample parallel to the beam. The scan range was 1° ; the step size was 0.02° ; and the time per step was 0.5 seconds. Because the mono-capillary x-ray guide can generate an X-ray beam with a diameter of 0.5 mm, a camera was mounted to select a specific spot on the cross-section of the wedges. Movement of the sample stage was controlled by the x and y values in mm; a photo of the area of interest was captured for reference. For the actual XRD measurement, the Cu/Ni attenuator was replaced by a Ni filter to generate Cu K α radiation with a wavelength of 1.5418Å. The scanning range was 20 to 80° ; the step size was 0.039° ; and the time per step was 4 seconds. X'Pert HighScore Plus software was used for the identification of peaks in the XRD patterns. The peaks were searched by a significance of 2, a minimum tip width of 0.01° ; and a maximum tip width of 1° . The background of unity was determined by a granularity of 10 and a bending factor of 0. The potential crystalline phases were selected according to their score of matching with pre-determined peaks of crystal phases in the database.

3.5.2 Scanning Electron Microscopy

A Hitachi S3400 scanning electron microscope fitted with secondary and backscatter electron detectors enabled both the topographic and compositional surface imaging

of the cast wedges. This SEM can be used in high-vacuum mode for imaging from 20 times to 20,000 times magnification. The working distance and voltage were set at 10 mm and 15 kV, respectively; the probe current was adjusted to 50% at low magnification and 30% at high magnification to avoid sample heating and image shifting from electron deposition.

Energy dispersive spectroscopy (EDS) was used for the semi-quantitative analysis of the elements in each casting. For good signal counts, the voltage was in the range of 15 to 20kV and probe current was between 40% and 60%. The following four functions were used in the study: full area spectrum, point scan, line scan, and mapping. The full area spectrum scans the whole area to detect potential elements in the cast wedges; this can sometimes identify energy peaks from oxygen and coating elements. The point scan was used to obtain the composition of a specific point normally located in the centre of a secondary phase and featureless matrix. The line scan was performed to observe any composition changes along a line that often crossed the area of a featureless region and crystallised regions near the edge of the wedge tips. The mapping function was usually utilised for element distribution around the secondary phases and grain boundaries. However, an error margin of up to 5% in each element limits the EDS to providing only an estimate of the elemental distribution in each phase. More precise quantitative analysis was performed using an inductively coupled plasma mass spectrometer (ICP-MS) and an electron probe micro analyser (EPMA).

The nano-characterization of selected alloys was performed using the FEI Nova NanoSEM 230 FESEM. It is an ultra-high resolution field-emission scanning electron microscope. The working distance is set as 5.1mm and the voltage is 5kV.

3.5.3 Transmission Electron Microscopy

A Nova Nanolab 200 DualbeamTM Focused Ion Beam (FIB) with both an electron gun and an ion gun was used for milling. The small beam size and imaging function made the focused ion beam ideal for preparing cross-sections of site-specific specimens for transmission electron microscopy (TEM). By using the dual beam focused ion beam, the image was obtained from the electron beam while the sputtering was achieved by the ion beam, which minimised observed sputtering damage. The images in the region of interest were focused and captured under 100

times magnification in the window of the electron beam image. The working distance Z was decreased from 8 mm to 5 mm after focusing under 1000 times magnification and linking in each time. The tilting angle T increased from 5' to 30' to 52' after centring the same small feature in the window each time. Platinum deposition with an ion beam of 2 to 6 pA/ μm^2 was used to protect the top surface of the specimen. Milling was carried out with an ion beam of 5 to 7 nA followed by cleaning with an ion beam of 0.1 to 1 nA. The lift-out process was performed using a solid glass rod with a sharp tip of 20 to 30 μm in the arm of the micromanipulator under a light optical microscope. The electron transparent membrane was lifted out by the electrostatic forces and placed in a mesh grid for the TEM analysis.

A Philips CM200 FEG TEM was used to inspect the Al-Ni-Si foils prepared by FIB milling. The TEM offered detailed structural analysis with spatial resolution of a few nanometres, and its selected area electron diffraction (SAED) provided interesting crystal lattice information (Vernon-Parry et al. 2001). The process included a status check, filament setup, specimen loading, alignment of condenser aperture, alignment of pivot point, alignment of objective aperture, height adjustment, image focusing, and capturing. The TEM micrographs were captured under a voltage of 200 kV for the foils from the centre and edge of the same wedge tip.

3.6 Composition Analysis

3.6.1 Laser Ablation Inductively Coupled Plasma Mass Spectrometry

Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) was used for composition analysis of the matrix in the cast wedges. In LA-ICP-MS, evaporation was accomplished with a focused laser beam in argon gas at zero pressure that then transported the ablated materials to an ICP-MS. In ICP-MS, the ablated materials were ionized, and these positively charged ions were analysed by mass spectrometry (Becker 2002). The experimental data of relative sensitive coefficients were compared to that of standard reference samples for quantitative analysis. LA-ICP-MS was selected for this study rather than standard ICP-MS because the former can directly analyse the composition from the surface area of a solid sample that is 10 μm to 300 μm in diameter (Walaszek et al. 2013) with no solution preparation and low contamination risk, which is very critical for highly pure samples. However, in LA-ICP-MS, the precision of trace element determination

is 2 to 10%, which is not as good as the 1 to 5% in ICP-MS; moreover, LA-ICP-MS is also subject to errors due to the inhomogeneity of samples in direct sampling. Since the featureless region at the wedge tip was a very small area in each of the mounted samples, the upper part of the wedge away from the tip was removed from the resin for composition analysis for this experimental procedure.

3.6.2 Electron Probe Microanalysis

A JEOL JXA-8500F Hyperprobe was also used for the composition determination of the cast wedges. Electron probe microanalysis (EPMA) uses an x-ray emission from an electron beam bombardment on elements to identify the element on the surface of a specimen and estimate its quantity accurately (Boyde et al. 1961). The concentration of a given element in a sample is roughly calculated by the k-ratio or k-value, which is compared to the intensity of the x-ray emitted from the sample and to that from a reference with a known concentration (Feller-Kniepmeier et al. 1961). As the x-ray emission wavelength varied in different electron transitions, such as $K\alpha$ and $L\alpha$ for each element, the Al, Ni, and Si elements and their emission wavelengths/energies to be targeted in the matrix were checked before measurement. Potential problems with overlapping peaks were avoided by selecting another peak, such as $L\alpha$ instead of $K\alpha$, for the element of interest. Because the error margin in the measurement of light elements is quite high, i.e., up to 10%, the oxygen content was measured by stoichiometry rather than by direct spectrometric analysis.

The wedges for EPMA were polished to a mirror finish. Light pressure was used in the polishing process, and a very clean nylon pad was used along with silica powders of 0.04 μ m in diameter and distilled water. The upper and lower surfaces of the sample were polished to a parallel and flat finish in order to ensure that the polished sample surface was perpendicular to the electron beam. Indeed, one degree of deviation from the perpendicular position would result in approximately 1% measurement error. Before carbon coating, all samples were baked overnight in a vacuum oven to prevent outgassing in the carbon coating chamber. Because metallic glasses are temperature-sensitive and cannot be baked, samples were outgassed in a vacuum chamber for 48 hours before carbon coating. A sample holder with 9 holes that are 26mm in diameter was used to accommodate the resin-mounted specimens. Due to the multiple holes in the sample holder, the sample was normally marked for

easy reference. To avoid contamination from a marker pen, sample positions in the sample holder were recorded on paper.

3.7 Thermal Analysis

A Netzsch 404C differential scanning calorimeter (DSC) was used for the thermal analysis of the wedge tips. The temperature difference between the sample and the reference were compared using the DSC curve where a present peak was related to the structure transition in the sample. The energy required to initiate the transition was indicated by the peak temperature, and the energy involved in the transition was calculated by the peak area (van Dooren et al. 1984). The peak temperature related to crystallisation in the metallic glasses was raised by increasing the heating rate from 5K/min to 20K/min (Roy et al. 2011). Wedge tips of about 8 to 10 mg were measured on an analytical balance with an accuracy of 0.01 mg. An aluminium oxide pan was used for testing temperature above 1000 °C. Both the sample pan and the reference pan were placed in the heater, and the temperature difference was recorded as a function of time. The result was analysed with the Proteus Analysis program. The DSC peak, the DSC onset, and the glass transition were evaluated by setting the evaluation limits on the heating and cooling curves.

3.8 Microhardness Testing

A Struers Duramin-A300 microhardness tester was used to inspect the Vickers hardness in the Al-Ni-Si wedge tips via various indentation loads with a dwell time of 15 seconds. The microhardness test was used for samples on the small scale; the load was as low as 10g, and the indented area was observed and evaluated with a high resolution microscope (Chen et al. 2006). The sample surface was polished with a 0.5 µm diamond paste in polishing oil in order to ensure the accuracy of the hardness results. Three points were tested under each load. The Vickers hardness value was based on the equation $H_v = 1854.4P/(d^2)$ where P is the applied load in mN and d is the diagonal length of the indentation in µm. The procedure included program setting, sample loading, focusing, indentation, and evaluation. A single indentation method was used for the individual tests on the small area of the wedge tip. Loads of 100g, 200g, 500g, and 1000g were applied for the indentation under the 1200 times magnification lens. An additional evaluation was used for validation and precise measurement after each test. The crosshair was positioned in the centre of the

indentation, and parallel lines were used to define the corners of the real size of the indentation marks. Hardness values under various loads and associated optical micrographs of the indentation marks were exported and compared in the same chart for analysis.

Chapter 4

Glass Formation in Al-Early Transition Metal-Metalloid Alloys

4.1 Introduction

Early melt spinning studies showed that it is possible to generate amorphous ribbons of Al-based alloys containing metalloids and early transition metals (ETM) such as Al-Mn-Si, Al-Cr-Si, and Al-Mo-Si (Inoue et al. 1988, Kimura et al. 1988, Tsai et al. 1989). However, critical thickness measurements were not reported for revealing the actual glass-forming ability (GFA) of such alloys by methods such as copper mould wedge casting. This chapter describes the GFA and structural evolution of a series of Al-Mn-Si, Al-Cr-Si, and Al-Mo-Si alloys produced by this casting technique.

4.2 Al-Mn-Si-Ge Alloy System

4.2.1 Introduction to Al-Mn-Si Alloys

Previously, the Al-Mn-Si alloy system drew considerable research attention due to the magnetic properties of amorphous ribbons at low temperatures. Spin-glass behaviour was observed in $\text{Al}_{65}\text{Mn}_{20}\text{Ge}_{15}$ icosahedral ribbons below 8K (McHenry et al. 1990). Furthermore, higher Curie temperatures were found in amorphous Al-Mn-Si alloys with high Si content, which were 115K and 112K, respectively, in $\text{Al}_{55}\text{Mn}_{20}\text{Si}_{25}$ and $\text{Al}_{50}\text{Mn}_{20}\text{Si}_{30}$ amorphous ribbons with applied fields of 50 Oe and 100 Oe (Dunlap et al. 1989). The magnetic properties of these Al alloys were ascribed to the magnetic moment of Mn in the amorphous ribbons (Maret et al. 1991). Although spin-glass behaviour was considered to be a potential precursor to collective magnetism in these alloys (McHenry et al. 1990), no critical casting thickness measurements were reported in these alloys for revealing their GFA.

4.2.2 Composition Design and X-Ray Diffraction of the Al-Mn-Si Alloys

$\text{Al}_{50}\text{Si}_{30}\text{Mn}_{20}$ and $\text{Al}_{50}\text{Ge}_{30}\text{Mn}_{20}$ melt-spun ribbons were previously found to be fully amorphous by X-ray diffraction (XRD) (Inoue et al. 1988, Inoue et al. 1988). Hence, a series of Al-Mn-Si-Ge cone-shape rod samples were prepared by arc melting and casting into a copper mould, in order to investigate the GFA of the base $\text{Al}_{50}\text{Mn}_{20}\text{Si}_{30}$ alloy with various amounts of Ge. The compositions investigated were two ternary base alloys and a series of quaternary alloys. The atomic packing efficiency was calculated based on the efficiently packed clusters and presented as the percentage of the deviation with respect to the radius ratio of ideally packed clusters. The key values are provided in Table 4.1. The $\text{Al}_{50}\text{Si}_{30}\text{Mn}_{20}$ alloy is marked in the ternary phase diagram of Fig. 4.1.

Table 4.1: Packing efficiency, based on the deviation from the ideal radius ratio, is calculated for each element-centred cluster (see APPENDIX A).

Cone-shaped	Deviation from ideal radius ratio			
	Al (N=15)	Si (N=10)	Ge (N=10)	Mn (N=13)
Samples	$\Delta E\%$	$\Delta E\%$	$\Delta E\%$	$\Delta E\%$
$\text{Al}_{50}\text{Si}_{30}\text{Mn}_{20}$	-2.1	2.6		5.5
$\text{Al}_{50}\text{Ge}_{30}\text{Mn}_{20}$	-3.3		6.5	4.3
$\text{Al}_{50}\text{Si}_{25}\text{Ge}_5\text{Mn}_{20}$	-2.3	2.4	3.3	5.3
$\text{Al}_{50}\text{Si}_{20}\text{Ge}_{10}\text{Mn}_{20}$	-2.5	2.2	3.9	5.1
$\text{Al}_{50}\text{Si}_{15}\text{Ge}_{15}\text{Mn}_{20}$	-2.7	2.0	4.6	4.9
$\text{Al}_{50}\text{Si}_{10}\text{Ge}_{20}\text{Mn}_{20}$	-2.9	1.8	5.2	4.7
$\text{Al}_{50}\text{Si}_5\text{Ge}_{25}\text{Mn}_{20}$	-3.1	1.6	5.9	4.5

Cross sections were cut at approximately 2mm from the tip of the cone-shaped casting for each alloy and mounted in epoxy resin for analysis by XRD. The XRD patterns in Fig. 4.2 show that crystalline phases are present in the cross sections of all alloys. The peak positions with various amounts of Ge showed that the crystalline phases changed markedly when the Ge content was increased from 5 to 25 at.%. The phases identified in the $\text{Al}_{50}\text{Mn}_{20}\text{Si}_{25}\text{Ge}_5$ alloy were $\text{Al}_9\text{Mn}_3\text{Si}$ and Mn_5Ge_2 , and the phases identified in the $\text{Al}_{50}\text{Mn}_{20}\text{Si}_5\text{Ge}_{25}$ alloy were AlMnGe , Ge , and $\text{Al}_{4.01}\text{MnSi}_{0.74}$. Increasing the amount of Ge increased the diversity of crystal phases in the alloys. These XRD patterns were obtained in the centre of the cross sections and the crystalline peaks present in all compositions indicated that all of these seven compositions inspected are not fully amorphous.

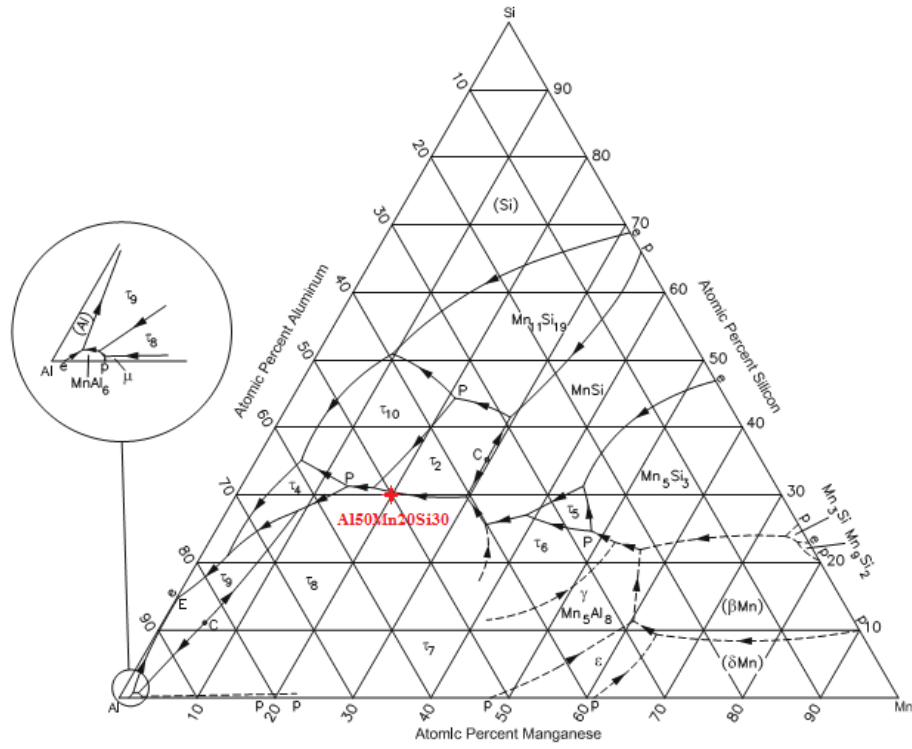


Fig. 4.1 The $\text{Al}_{50}\text{Mn}_{20}\text{Si}_{30}$ ternary alloy on the liquidus projection.

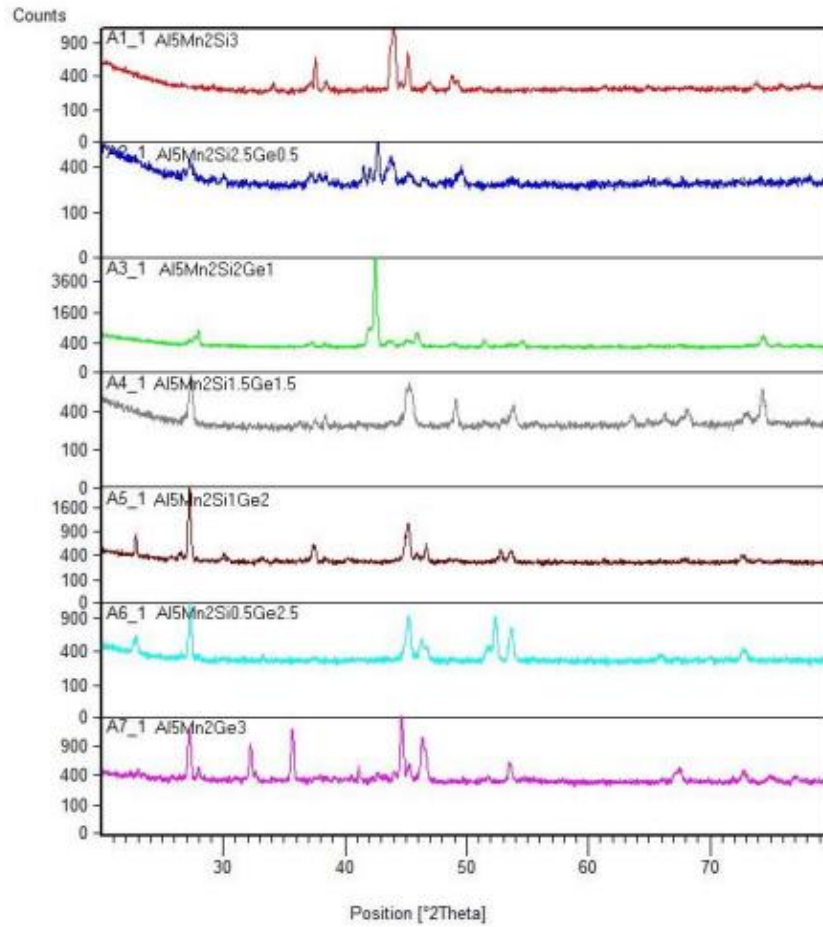


Fig. 4.2 XRD spectra of $\text{Al}_{50}\text{Mn}_{20}\text{Si}_{30}$ and $\text{Al}_{50}\text{Mn}_{20}\text{Ge}_{30}$ ternary alloys and Al-Mn-Si-Ge quaternary alloys with increasing amounts of Ge replacing Si.

4.2.3 Scanning Electron Microscopy of the Al-Mn-Si Alloys

In order to determine the GFA of the alloys based on their critical casting thickness, the microstructures were analysed using scanning electron microscopy (SEM). An SEM micrograph of the $\text{Al}_{50}\text{Mn}_{20}\text{Si}_{30}$ alloy is shown in Fig. 4.3a. One can see a featureless zone at the very edge of the as-cast cross section, but this region is notably absent in the $\text{Al}_{50}\text{Mn}_{20}\text{Ge}_{30}$ alloy (Fig. 4.3c). This finding implies that the GFA of the $\text{Al}_{50}\text{Mn}_{20}\text{Si}_{30}$ alloy is higher than that of the $\text{Al}_{50}\text{Mn}_{20}\text{Ge}_{30}$ alloy for equivalent casting conditions. Based on the XRD data, three phases shown in the SEM micrographs of the $\text{Al}_{50}\text{Mn}_{20}\text{Si}_{30}$ alloy were identified as $\text{Al}_{79.5}\text{Mn}_{20.5}$, $\text{Al}_5\text{Mn}_2\text{Si}_5$, and MnSi. According to the quantity of heavy elements in each phase, the dark grey, light grey, and white regions in the $\text{Al}_{50}\text{Mn}_{20}\text{Si}_{30}$ matrix were $\text{Al}_{79.5}\text{Mn}_{20.5}$, $\text{Al}_5\text{Mn}_2\text{Si}_5$, and MnSi, respectively. The width of the featureless zone at the edge of the $\text{Al}_{50}\text{Mn}_{20}\text{Si}_{30}$ alloy indicates that it is a marginal glass former with a limited GFA for forming amorphous ribbons. For the $\text{Al}_{50}\text{Mn}_{20}\text{Ge}_{30}$ alloy, four phases appear in the SEM micrographs (Fig. 4.3c-d), which were identified to be AlMnGe, Mn, $\text{Al}_{78}\text{Mn}_{22}$, and $\text{Al}_{86}\text{Mn}_{14}$ by XRD, in the order of brightest to darkest.

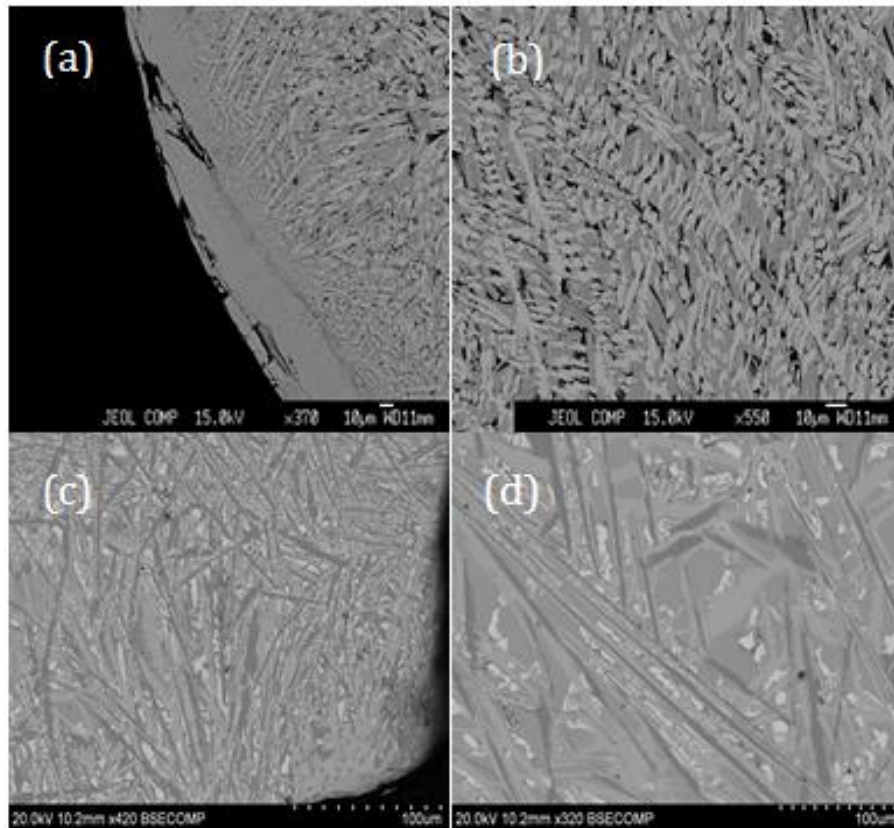


Fig. 4.3 SEM micrographs of the as-cast $\text{Al}_{50}\text{Mn}_{20}\text{Si}_{30}$ alloy at (a) the edge and (b) the core, and as-cast $\text{Al}_{50}\text{Mn}_{20}\text{Ge}_{30}$ alloy at (c) the edge and (d) the core.

4.2.4 Electron Probe Microanalysis of the Al-Mn-Si Alloys

The featureless zones (Fig. 4.3a) were further investigated by electron probe microanalysis (EPMA), as described in Section 3.6.2. The secondary electron SEM images of the $\text{Al}_{50}\text{Mn}_{20}\text{Si}_{30}$ alloys are shown in Fig. 4.4. High-purity standards of Al, Mn, and Si were used for the quantitative analysis of the compositional makeup of the various phases. Nine points were measured in the centre of each phase, as well as the featureless zone of the top and bottom flashing line. (A flashing line is essentially where some metal has flowed outwards from the main casting into the thin section where the two copper mould faces join in a split-type mould). The results are listed in Table 4.2. Based on these measurements, no significant variation was found in composition between the two flashing line regions. However, the crystalline phases with dark and bright contrast were Mn-rich compared with the featureless zone at the top and bottom flashing lines. The composition at the flashing line region was similar to $\text{Al}_{50}\text{Mn}_{20}\text{Si}_{30}$ (Point 3-9 in Fig. 4.4), which indicates the composition at the flashing-line region after casting is consistent with the calculated composition of the charge prior to casting. The selected compositions were calculated to be most densely packed for high GFA, but the appearance of the two Mn-rich crystalline phases, $\text{Al}_{51}\text{Mn}_{26}\text{Si}_{23}$ and $\text{Al}_{50}\text{Mn}_{25}\text{Si}_{25}$ (Point 1 and Point 2 in Fig. 4.4), at the core of the rod and around the featureless zone indicated that the diffusion of Mn is a limiting factor to form an amorphous zone in the $\text{Al}_{50}\text{Mn}_{20}\text{Si}_{30}$ alloy.

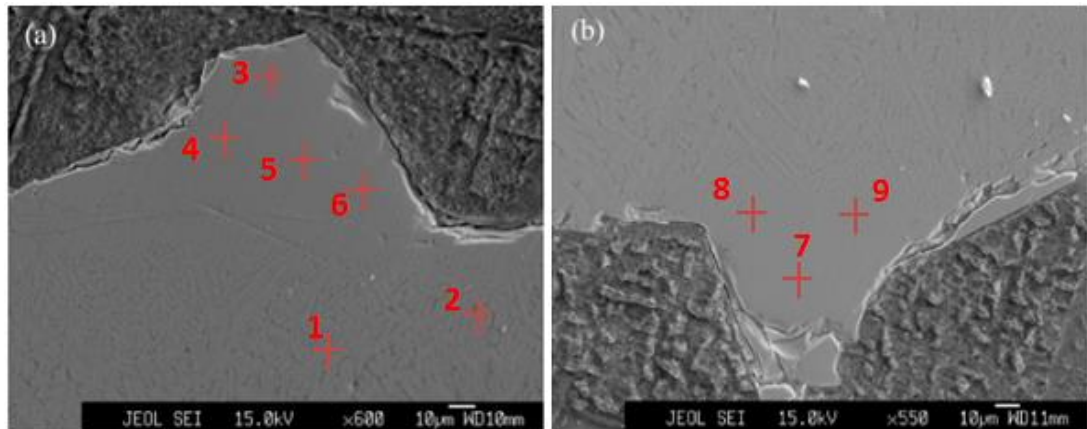


Fig. 4.4 Secondary electron images of the $\text{Al}_{50}\text{Mn}_{20}\text{Si}_{30}$ cone-shaped rod for the (a) top flashing line and (b) the bottom flashing line.

Table 4.2: Average composition (at.%) of the phases identified in $\text{Al}_{50}\text{Mn}_{20}\text{Si}_{30}$.

No.	Al	Mn	Si	Total	Comments
1	50.97	26.01	23.01	100	A1sample-white
2	50.06	24.69	25.25	100	A1sample-dark
3	49.73	21.12	29.16	100	A1sample-edge
4	47.80	21.26	30.94	100	A1sample-flash2
5	48.55	21.14	30.31	100	A1sample-flash3
6	49.59	20.51	29.90	100	A1sample-flash4
7	52.16	20.31	27.53	100	A1sample-bottomflash
8	49.46	21.29	29.25	100	A1sample-bottomflash2
9	51.31	21.12	27.57	100	A1sample-bottomflash3

4.2.5 Differential Scanning Calorimetry of the Al-Mn-Si Alloys

The thermal stability of the of $\text{Al}_{50}\text{Mn}_{20}\text{Si}_{30}$ (cone tip) was investigated with differential scanning calorimetry (DSC) up to 1000 °C(1273 K) using a heating rate of 15 K/min, as shown in Fig. 4.5. The heating and cooling curves are marked in red and blue, respectively, in Fig. 4.5. Two prominent endothermic peaks are evident at 771 °C and 814 °C during heating, likely corresponding to the nearby peritectic reactions shown in Fig.4.1, followed by the melting of multiple phases up to the liquidus at 900 °C (Krendelsberger et al. 2002). Major exothermic peaks appear at 870 °C, 779 °C, 771 °C, 703 °C, 626 °C, and 563 °C during cooling at much lower temperatures than the onset of melting during heating. The exothermic peaks shown in the cooling curve may be due to the different phases precipitating during solidification, following a very different crystallisation path to that of the rapidly cooled sample. Minimal exothermic events due to crystallisation were observed during heating, implying that the featureless zones at the flashing lines of the cast sample were either too small in volume fraction or not amorphous.

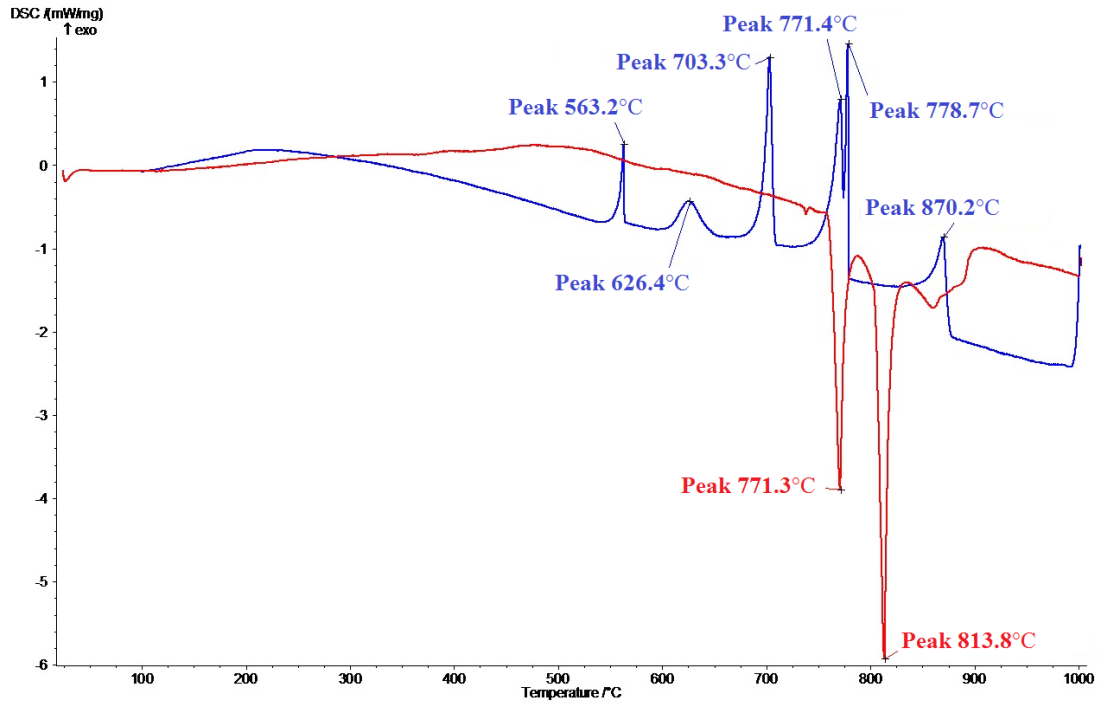


Fig. 4.5 DSC analysis of residue taken from the tip of an $\text{Al}_{50}\text{Mn}_{20}\text{Si}_{30}$ cone-shaped sample; the maximum heating temperature is 1000 °C with a heating rate of 15K per minute.

4.3. Al-Mo-Si Alloy System

4.3.1 Composition Design in the Al-Mo-Si Alloys

A previous study on Al-Si-X alloys showed that fully amorphous Al-Mo-Si melt-spun ribbons can be generated (Inoue et al. 1988). However, there have been no reports of critical thickness measurements of Al-Mo-Si alloys produced by copper mould casting. In order to determine the optimized composition with the highest GFA in Al-Mo-Si ternary alloys, a topological model of efficiently packed clusters was used. Using this model, two types of clusters were found to be efficiently packed: one is a Si-centred cluster with a coordination number (N) of 10 and the other type is an Al-centred cluster with $N = 15$. In order to narrow down the phase region of interest, the driving force criteria was used such that the compositions with lower liquidus temperature would own lower driving forces for crystallisation. Applying the topologically efficiently packed cluster model in the phase region selected by the driving force criteria, five potential glass-forming Al-Mo-Si compositions were selected: $\text{Al}_{63.63}\text{Mo}_{27.27}\text{Si}_{9.09}$, $\text{Al}_{54.54}\text{Mo}_{27.27}\text{Si}_{18.18}$, $\text{Al}_{54.54}\text{Mo}_{36.36}\text{Si}_{9.09}$, $\text{Al}_{50}\text{Mo}_{31.25}\text{Si}_{18.75}$, and $\text{Al}_{43.75}\text{Mo}_{31.25}\text{Si}_{25.00}$ (Table 4.3). The calculated compositions

are marked on the Al-Mo-Si phase diagram (Fig. 4.6) for easy reference, and these five compositions containing efficiently packed clusters are located along the liquidus lines.

Table 4.3: Investigated Al-Mo-Si compositions (at.%) based on Miracle's atomic packing model: R is the radius ratio between the centre atom and first shell atoms, R* is the critical radius ratio, Δ is the difference from the critical radius ratio, N is the coordination number, P is the point number indicated in the phase diagram, and Note is the designation.

	R	R*	Δ (%)	N	P	Note
$\text{Al}_{63.63}\text{Mo}_{27.27}\text{Si}_{9.09}$	0.818	0.799	2.36	10	1	M1
$\text{Al}_{54.54}\text{Mo}_{27.27}\text{Si}_{18.18}$	0.834	0.799	4.41	10	2	M2
$\text{Al}_{54.54}\text{Mo}_{36.36}\text{Si}_{9.09}$	0.821	0.799	2.85	10	3	M3
$\text{Al}_{50}\text{Mo}_{31.25}\text{Si}_{18.75}$	1.058	1.116	-5.23	15	4	M4
$\text{Al}_{43.75}\text{Mo}_{31.25}\text{Si}_{25.00}$	1.072	1.116	-3.92	15	5	M5

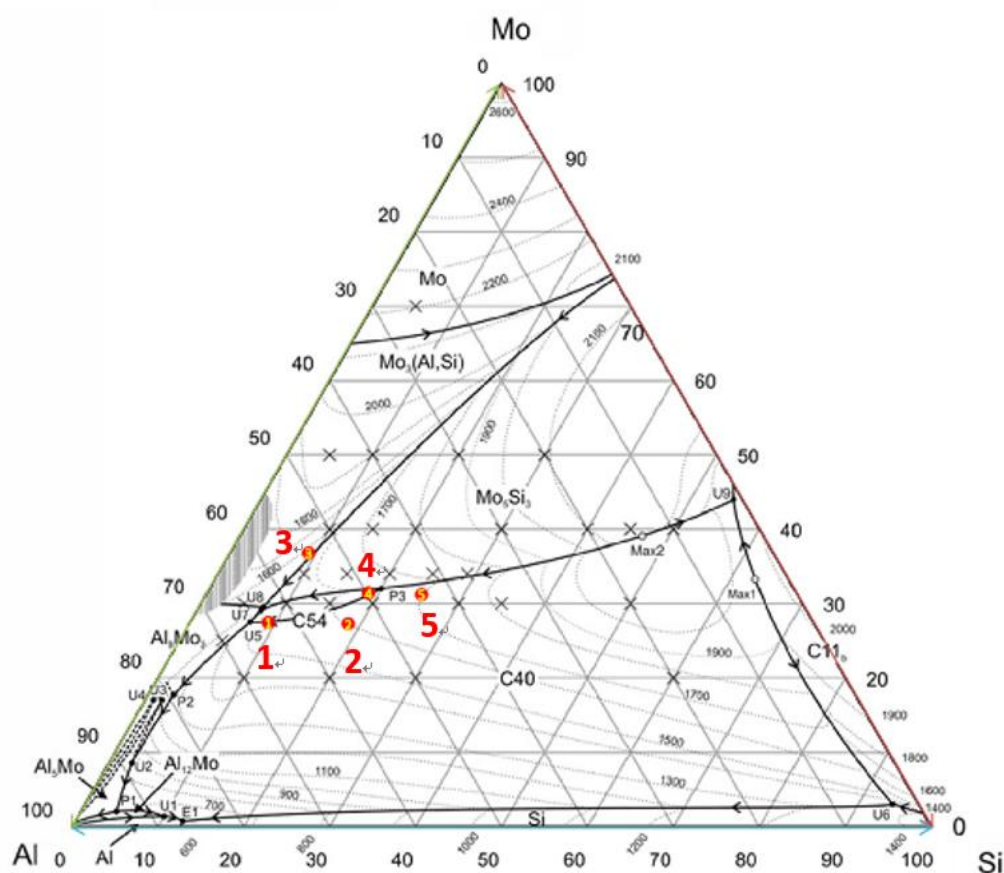


Fig. 4.6 The locations of the five calculated compositions in the Al-Mo-Si ternary phase diagram.

4.3.2 Copper Mould Casting of the Al-Mo-Si Alloys

Al-Mo-Si as-cast wedges are very difficult to generate by suction casting (Section 3.3.2) due to high viscosity and the considerably high melting point of these alloys arising from the addition of Mo. In the $\text{Al}_{63.63}\text{Mo}_{27.27}\text{Si}_{9.09}$ alloy, only half of the melted ingot was cast into the cavity of the 20:1 copper mould with 60% current (Fig. 4.7a); only one third of the ingot was cast into the cavity of the 10:1 copper mould with up to 70% current (Fig. 4.7b). The melt could not be completely sucked through the copper mould, except for $\text{Al}_{54.54}\text{Mo}_{36.36}\text{Si}_{9.09}$ which had completely infiltrated the copper vacuum reservoir plate (bottom of Fig. 4.7e). For each alloy given in Table 4.3, the microstructure at the wedge tip was investigated using SEM.

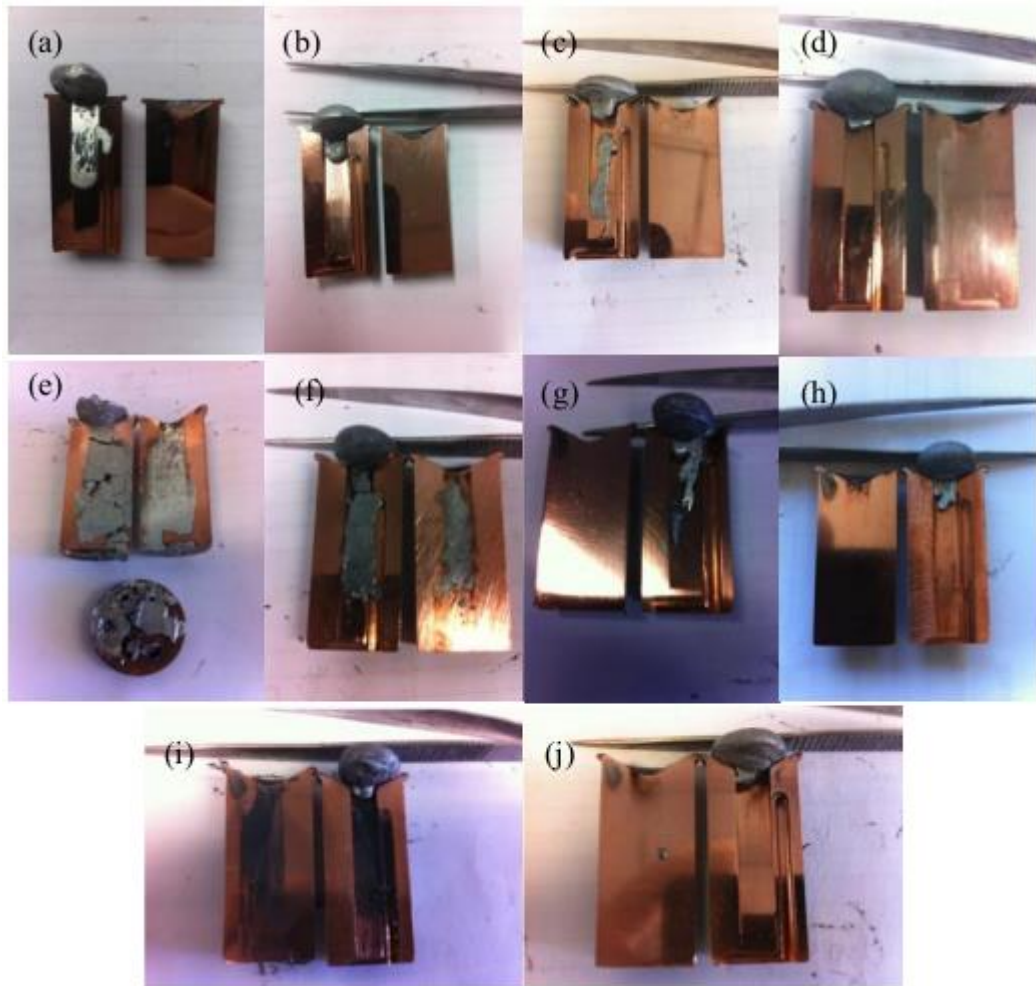


Fig. 4.7 Al-Mo-Si wedges cast by 10:1 moulds with compositions of (a) M1, (c) M2, (e) M3, (g) M4, (i) M5, and by 20:1 moulds with compositions of (b) M1, (d) M2, (f) M3, (h) M4, (j) M5.

4.3.3 Scanning Electron Microscopy of the Al-Mo-Si Alloys

Due to the low GFA of the Al-Mn-Si-Ge alloys, cold-mounted wedges of the alloys were investigated using SEM to determine the existence of a featureless zone at the wedge tip.

4.3.3.1 $\text{Al}_{54.54}\text{Mo}_{27.27}\text{Si}_{18.18}$ alloy

This alloy, generated in the 10:1 copper mould shown in Fig. 4.8, has a featureless zone 60 μm in width at its wedge tip (Fig. 4.8a), followed by the formation of secondary phases that are gradually replaced by a fine crystalline region with dendrites (Fig. 4.8b). These observations indicate that this alloy has a low GFA.

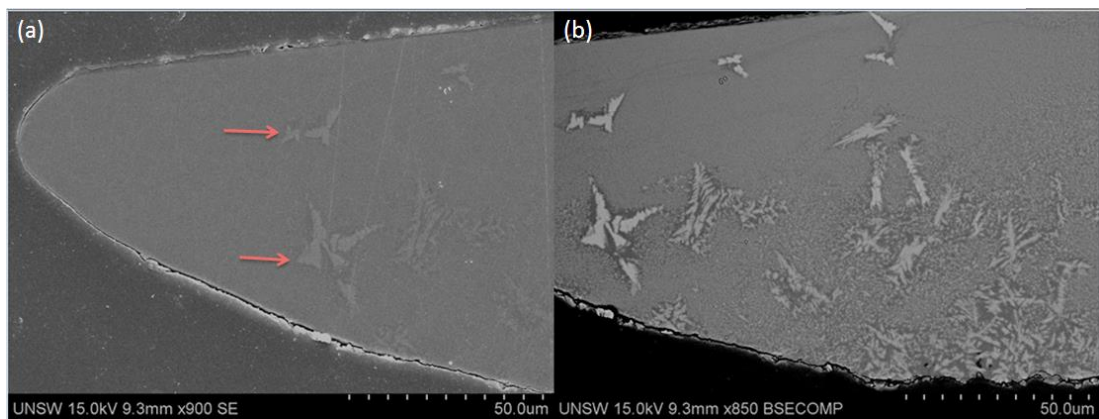


Fig. 4.8 The wedge tip of the $\text{Al}_{54.54}\text{Mo}_{27.27}\text{Si}_{18.18}$ alloy generated by the 10:1 mould.

4.3.3.2 $\text{Al}_{54.54}\text{Mo}_{36.36}\text{Si}_{9.09}$ alloy

Both wedge tips using the 10:1 and 20:1 moulds exhibited dendrites (Fig. 4.9), thereby indicating no amorphous zone for this composition. The low GFA may be due to the relatively low viscosity of the melt. In order to fully melt the pure molybdenum ingot at 2623 $^{\circ}\text{C}$, excessive heat was used that prolonged the time of arc docking on the pack of raw materials. Compared with other compositions (Fig. 4.7 e-f), the melt was easily sucked into the copper mould. The low viscosity of the melt may be insufficient to arrest crystallisation, therefore leading to the formation of dendrites in the wedge tips.

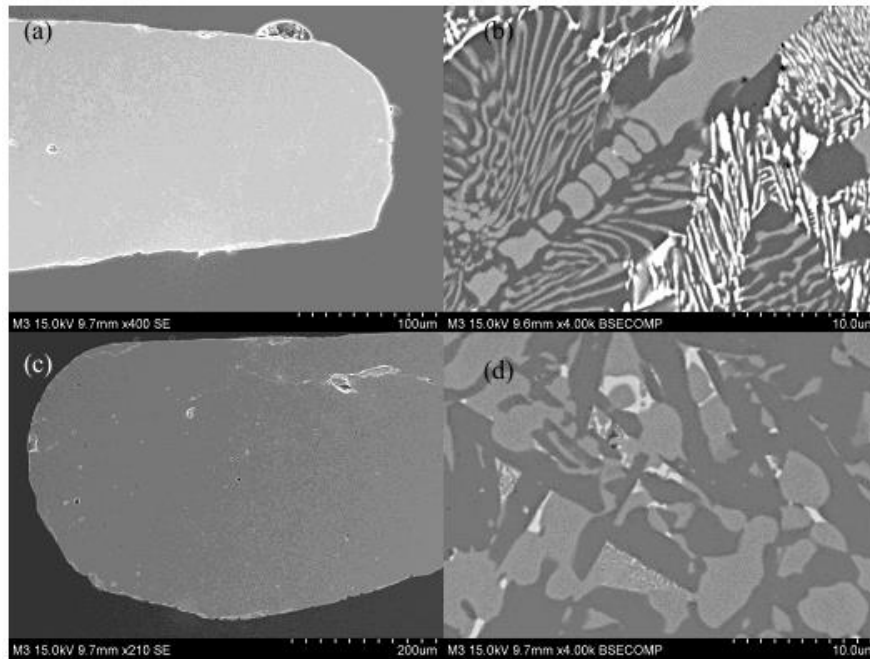


Fig. 4.9 The wedge tip of the $\text{Al}_{54.54}\text{Mo}_{36.36}\text{Si}_{9.09}$ alloy generated by the 10:1 mould (ab) and the 20:1 mould (c-d).

4.3.3.3 $\text{Al}_{50}\text{Mo}_{31.25}\text{Si}_{18.75}$ alloy

For this alloy, the 20:1 mould casting generated a featureless wedge tip. Fine crystals with flake-shaped morphologies started to appear at $44\mu\text{m}$ in wedge width (Fig. 4.10a) and the number density of these crystalline phases in the matrix gradually increased at $93\mu\text{m}$ width (Fig. 4.10b). This observation indicates that the GFA of this alloy composition is low and probably only suitable for generating amorphous melt-spun ribbons.

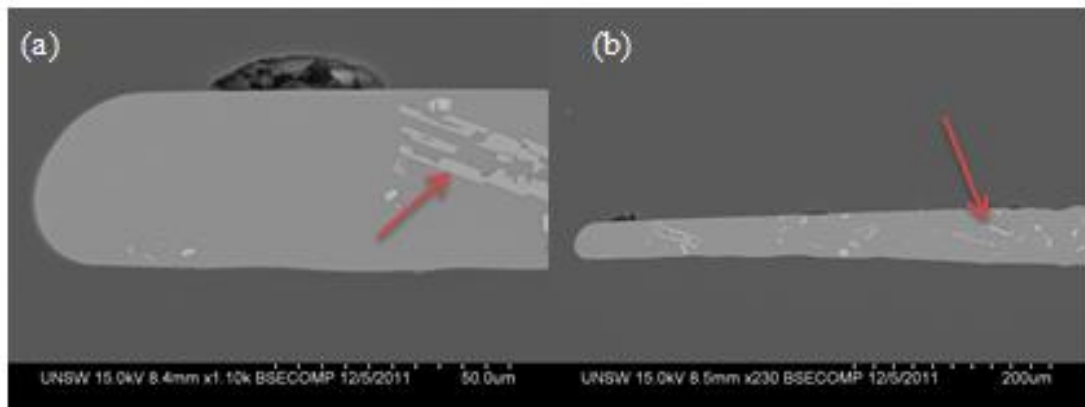


Fig. 4.10 The wedge tip of the $\text{Al}_{50}\text{Mo}_{31.25}\text{Si}_{18.75}$ alloy generated by the 20:1 mould.

4.3.3.4 $\text{Al}_{43.75}\text{Mo}_{31.25}\text{Si}_{25}$ alloy

As shown in Fig. 4.7i-j, there were difficulties in producing this alloy by suction casting and only droplets were produced in the cavity of the 20:1 copper mould. The micrographs of these droplets (Fig. 4.11a-b) demonstrated that they are fully crystallised without featureless zones in their matrix measuring approximately 0.5-2mm in width.

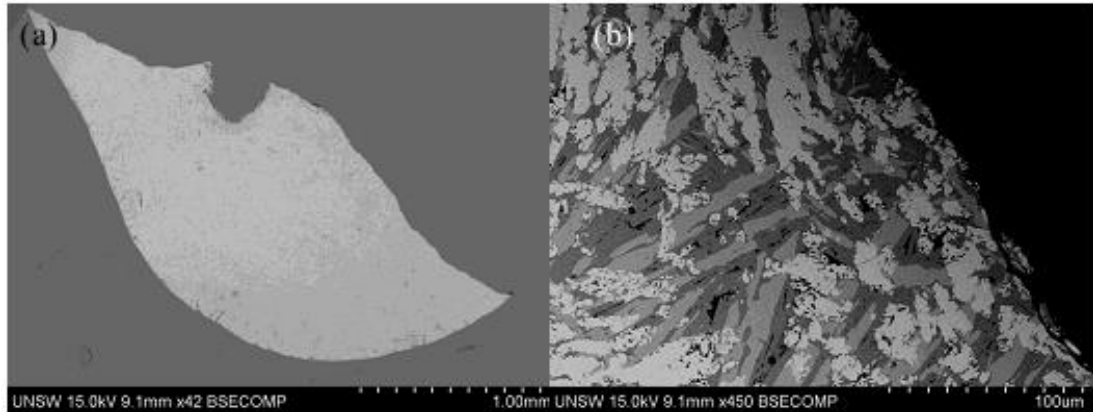


Fig. 4.11 The morphology of the $\text{Al}_{43.75}\text{Mo}_{31.25}\text{Si}_{25}$ alloy generated by the 10:1 mould (a-b).

Based on these casting experiments and the subsequent SEM analyses (Figs 4.8-4.11), it is clear that the addition of refractory Mo increases the viscosity of the melt, thereby causing difficulties when casting the alloys into the copper mould. The GFA of each alloy, based on the different structural zones present in the cast wedges, are summarised in Fig. 4.12. The GFA is low in these Al-Mo-Si alloys. The $\text{Al}_{54.54}\text{Mo}_{36.36}\text{Si}_{9.09}$ and $\text{Al}_{43.75}\text{Mo}_{31.25}\text{Si}_{25}$ wedges were fully crystallised at their tips. The featureless zones were only 44µm in width in the $\text{Al}_{50}\text{Mo}_{31.25}\text{Si}_{18.75}$ alloy and were followed by the appearance of rod-shape secondary phases. A featureless zone 60µm in width was present in the wedge tip of the $\text{Al}_{54.54}\text{Mo}_{27.27}\text{Si}_{18.18}$ alloy.

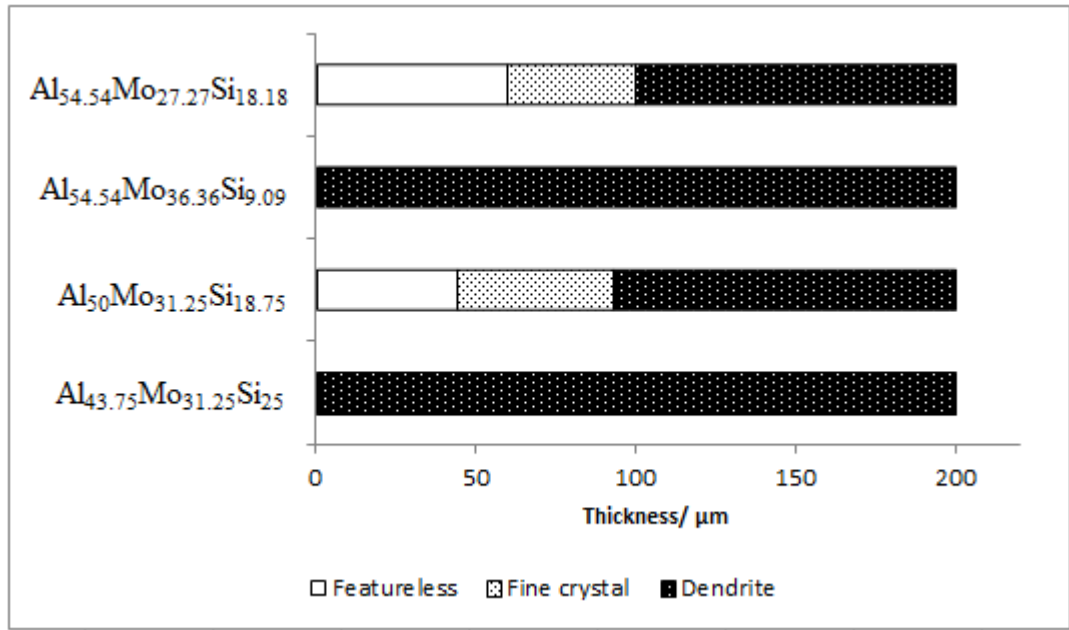


Fig. 4.12 Thickness of the different zones in the Al-Mo-Si alloys.

4.4. Al-Cr-Si Alloy System

4.4.1 Composition Design in the Al-Cr-Si Alloys

Similar to the Al-Mo-Si alloys, the Al-Cr-Si alloys can also form fully amorphous ribbons by melt spinning. The amorphous ribbons can be generated over a compositional range of 5–18 at.% Cr and 22–38 at.% Si (Inoue et al. 1988). However, no critical thickness measurements have been reported for this class of alloy. In the current study, five compositions based on efficiently packed clusters were formulated. These calculations showed that the packing efficiency in the Al-Cr-Si alloys was high in Si-centred clusters with $N = 10$, Cr-centred clusters with $N = 12$, and Al-centred clusters with $N = 15$. The packing efficiencies of these compositions are listed in Table 4.4. The compositions of $\text{Al}_{63.63}\text{Cr}_{18.18}\text{Si}_{18.18}$ and $\text{Al}_{61.54}\text{Cr}_{7.69}\text{Si}_{30.76}$ contained two types of efficiently packed clusters, and the packing efficiency according to the different centre atoms in both compositions are also provided in Table 4.4. These calculated compositions are furthermore marked on the liquidus projection of the Al-Cr-Si alloy in Fig. 4.13.

Table 4.4: Investigated Al-Cr-Si compositions (at.%) based on Miracle's atomic packing model: R is the radius ratio between the centre atom and first shell atoms, R* is the critical radius ratio, Δ is the deviation from the critical radius ratio, N is the coordination number, C is the centre atom of an efficiently packed cluster, P is the point number marked in the phase diagram, and Note is the designation.

Clusters	R	R*	Δ (%)	N	C	P	Note
Al _{72.72} Cr _{18.18} Si _{9.09}	0.827	0.799	3.53	10	Si	1	Cr1
Al _{63.63} Cr _{18.18} Si _{18.18}	0.844	0.799	5.63	10	Si	2	Cr2
	1.068	1.116	-4.26	15	Al	2	Cr2
Al _{61.54} Cr _{7.69} Si _{30.76}	0.934	0.902	3.52	12	Cr	3	Cr3
	1.079	1.116	-3.34	15	Al	3	Cr3
Al _{61.54} Cr _{15.38} Si _{23.08}	0.928	0.902	2.91	12	Cr	4	Cr4
Al _{54.54} Cr _{9.09} Si _{36.36}	0.868	0.799	8.60	10	Si	5	Cr5

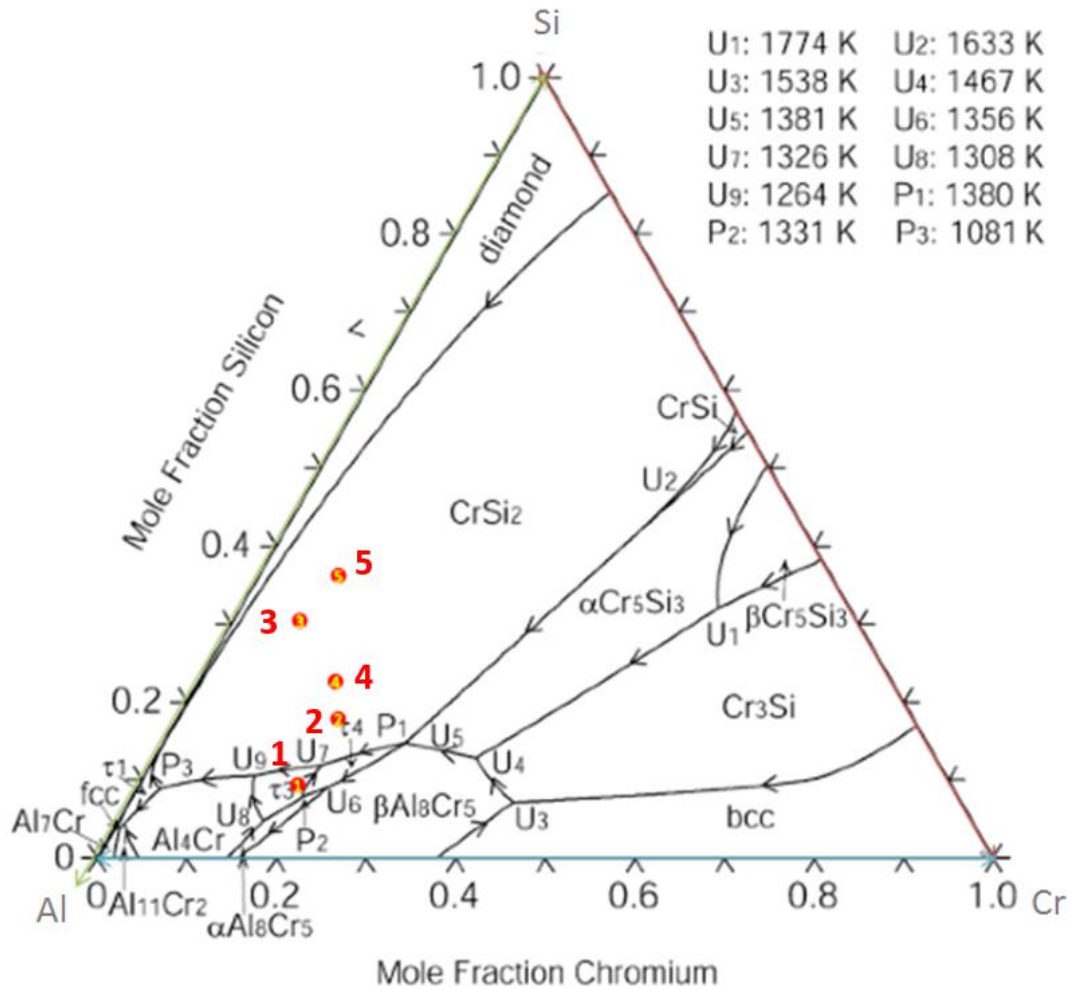


Fig. 4.13 The five compositions located on the liquidus projection of the Al-Cr-Si ternary phase diagram (Liang et al. 2009).

4.4.2 Copper Mould Casting of the Al-Cr-Si Alloys

The Al-Cr-Si alloys listed in Table 4.4 were cast into either 20:1 or 10:1 copper moulds under various casting conditions (see chapter 3). Wedges generated for each casting condition are shown in Fig. 4.14. The $\text{Al}_{72.72}\text{Cr}_{18.18}\text{Si}_{9.09}$ alloy (Fig. 4.14a–b) was cast under the condition of 30% current and 50% open valve for enough viscosity and suction force. In the 20:1 copper mould, which has smaller cross section, the melt was sucked perfectly through the cavity for $\text{Al}_{63.63}\text{Cr}_{18.18}\text{Si}_{18.18}$ (Fig. 4.14a). However, when cast using 10:1 copper mould, casting material was observed in the vacuum reservoir plate (bottom of Fig. 4.14b), indicating that the 10:1 copper mould allowed excessive suction force for this particular composition. Other Al-Cr-Si alloys were cast using less than 40% open valve to avoid overflows. The images taken after each casting reveal a well-managed melt flow into the mould cavity and a well-shaped wedge (Fig. 4.14).



Fig. 4.14 The Al-Cr-Si wedges produced using 20:1 moulds with compositions of (a) Cr1, (c) Cr2, (e) Cr3, (g) Cr4, (i) Cr5, and 10:1 moulds with compositions of (b) Cr1, (d) Cr2, (f) Cr3, (h) Cr4, (j) Cr5.

4.4.3 Scanning Electron Microscopy of the Al-Cr-Si Alloys

Similar to the Al-Mo-Si alloys, the featureless zone at the tip of the as-cast Al-Cr-Si wedges was very small. This region was investigated using SEM with the goal of determining the extent of the featureless zone.

4.4.3.1 $\text{Al}_{72.72}\text{Cr}_{18.18}\text{Si}_{9.09}$ alloy

The cast tips of this alloy produced in the 20:1 and 10:1 moulds were both approximately 200 μm in width. The wedge of the 20:1 mould showed isotropic crystal dendrite flowers at its tip (Fig. 4.15a–b); the wedge of the 10:1 mould showed an anisotropic dendritic structure (Fig. 4.15c–d). These results can be attributed to a higher cooling rate in the 20:1 copper mould with a smaller cross-sectional area. Unfortunately, none of the cast wedges in this alloy had a featureless tip.

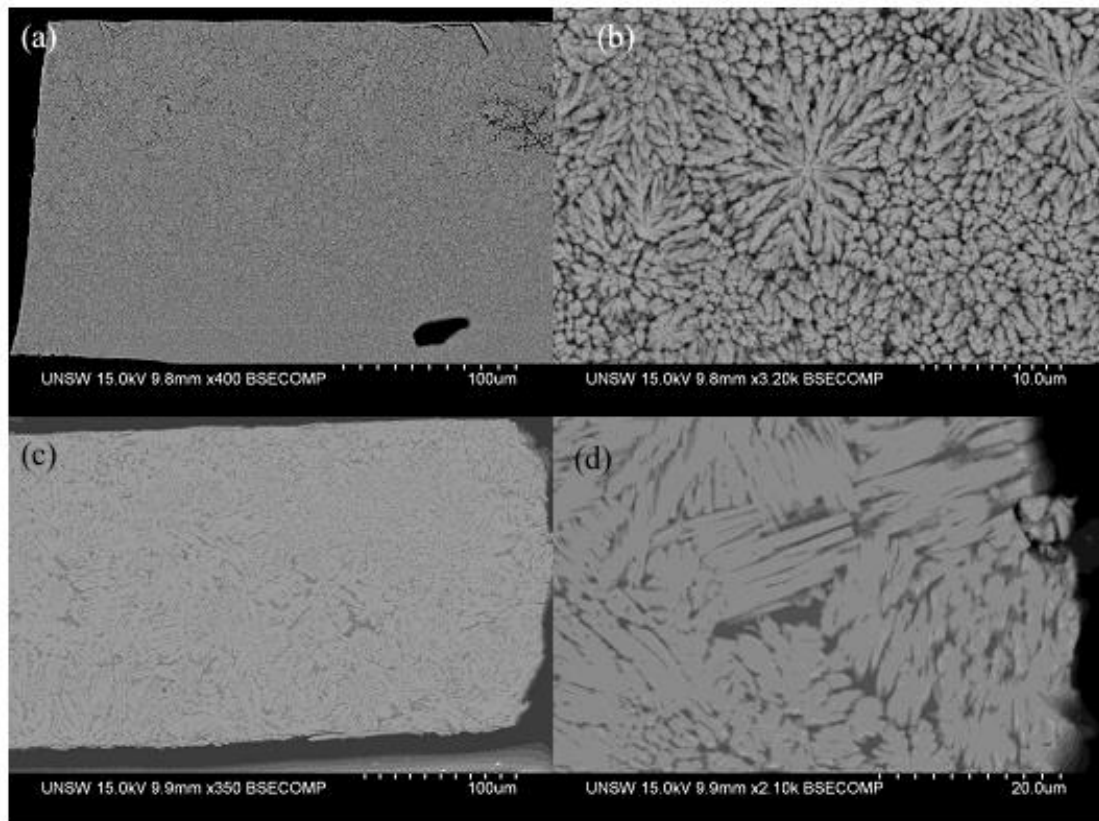


Fig. 4.15 Microstructure of $\text{Al}_{72.72}\text{Cr}_{18.18}\text{Si}_{9.09}$ tips in the 20:1 mould (a–b) and the 10:1 mould (c–d).

4.4.3.2 Al_{63.63}Cr_{18.18}Si_{18.18} alloy

The tips of this alloy showed improved GFA, as demonstrated in the series of micrographs in Fig. 4.16. A narrow featureless zone was generated at the edge of the tip (Fig. 4.16a) and extended 40 µm in width (Fig. 4.16b–c) where fine crystal appeared in the centre in the 20:1 wedge. However, this zone was replaced by a dendritic structure for thicknesses greater than 55 µm. The wedge of the 10:1 mould features a tip approximately 185 µm in width (Fig. 4.16d). As a result, there is no featureless zone in this tip with a large cross-sectional area. The microstructural differences of this alloy produced in the different copper moulds showed that the featureless zone was highly dependent on the cooling rate and could only be formed in copper moulds with small cross-sectional areas and high thermal conduction.

4.4.3.3 Al_{61.54}Cr_{7.69}Si_{30.76} alloy

The tips of this alloy (Fig. 4.17) showed improved GFA compared with previous alloys. The wedge cast by the 20:1 mould exhibited a featureless zone up to 150 µm in width (Fig. 4.17a-c), where the isolated crystal nuclei started to appear from the centre of the matrix (Fig. 4.17c). As the GFA increased in this composition, the wedge of the 10:1 mould with a tip 80 µm in width also exhibited a featureless zone up to 40 µm wide at the edge. Compared to crystallisation at 40 µm in the Al_{63.63}Cr_{18.18}Si_{18.18} alloy, the 150 µm wide featureless tip of the Al_{61.54}Cr_{7.69}Si_{30.76} alloy indicates a slightly higher GFA.

4.4.3.4 Al_{61.54}Cr_{15.38}Si_{23.08} alloy

This alloy generated a fully crystallised tip in both the 20:1 and 10:1 moulds (Fig. 4.18), which implies that the GFA is negligible for this composition.

4.4.3.5 Al_{54.54}Cr_{9.09}Si_{36.36} alloy

For this alloy, the wedge of the 20:1 mould showed a mostly featureless tip 100 µm in width (Fig. 4.19a), with crystalline regions appearing in the centre. The same composition cast into the 10:1 mould showed full crystallisation 80 µm from the tip (Fig. 4.19c), again indicating a low GFA for this composition.

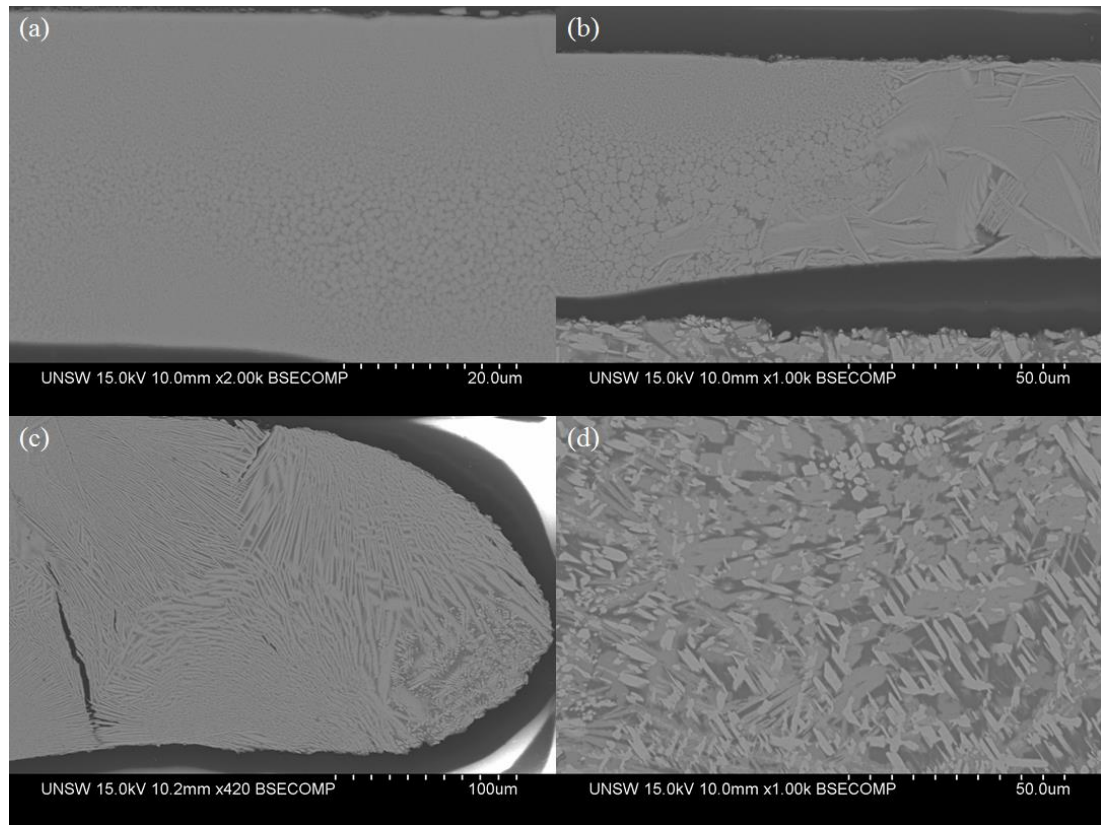


Fig. 4.16 The 20:1 wedge at (a) 40 μm and (b) 55 μm, and (c–d) the 10:1 wedge of $\text{Al}_{63.63}\text{Cr}_{18.18}\text{Si}_{18.18}$ alloys.

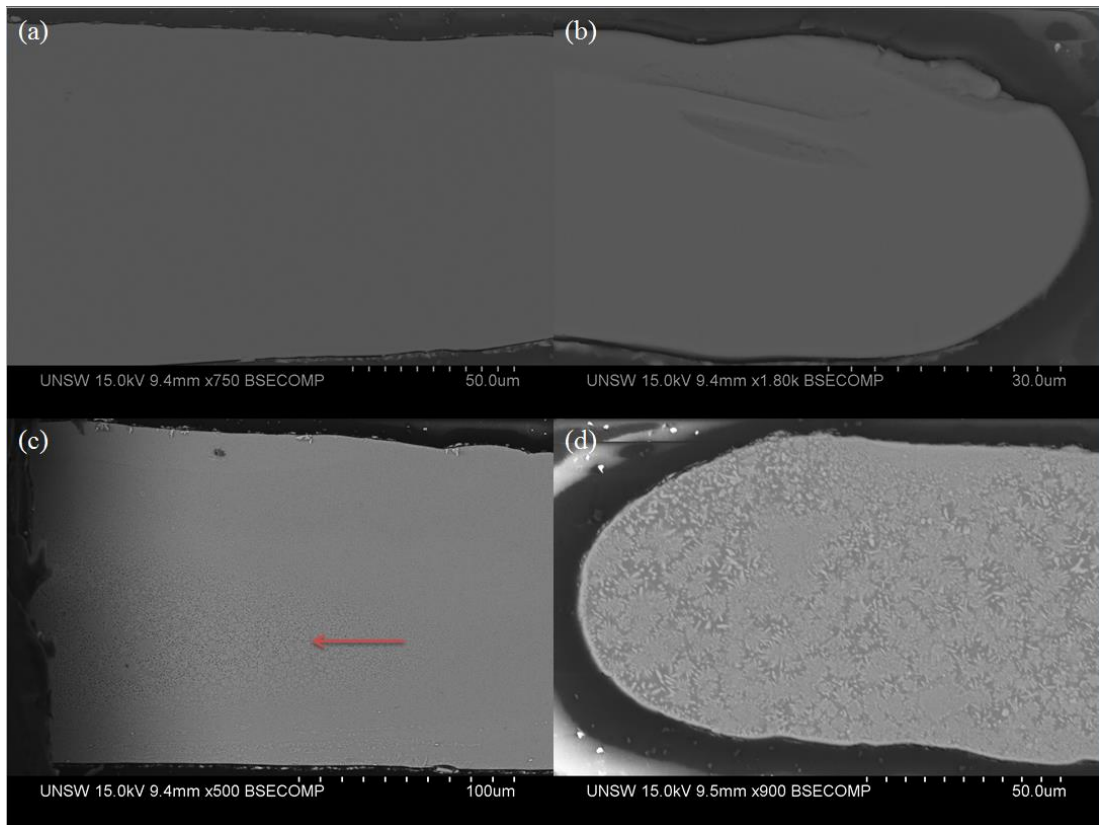


Fig. 4.17 The 20:1 wedge at (a) 40 μm (b) 100 μm (c) 150 μm, and (d) the 10:1 wedge of $\text{Al}_{61.54}\text{Cr}_{7.69}\text{Si}_{30.76}$ alloys.

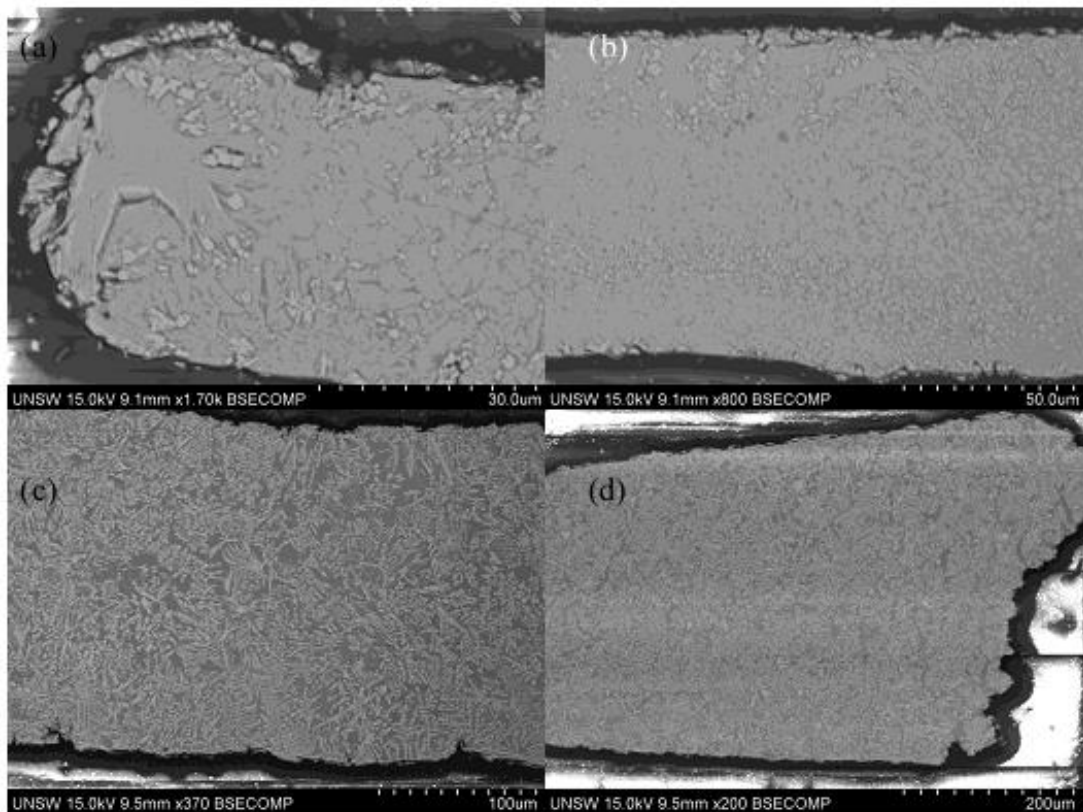


Fig. 4.18 $\text{Al}_{61.54}\text{Cr}_{15.38}\text{Si}_{23.08}$ tips in the 20:1 mould (a–b) and the 10:1 mould (c–d).

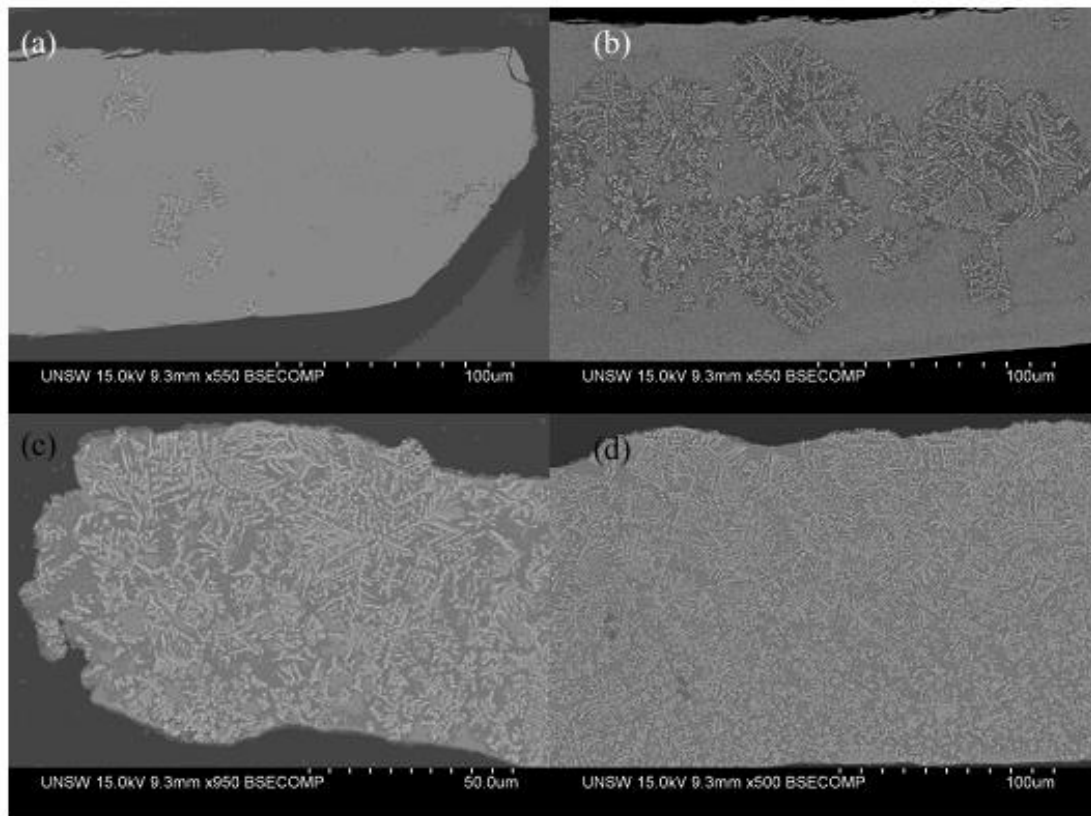


Fig. 4.19 $\text{Al}_{54.54}\text{Cr}_{9.09}\text{Si}_{36.36}$ tips in the 20:1 mould (a–b) and the 10:1 mould (c–d).

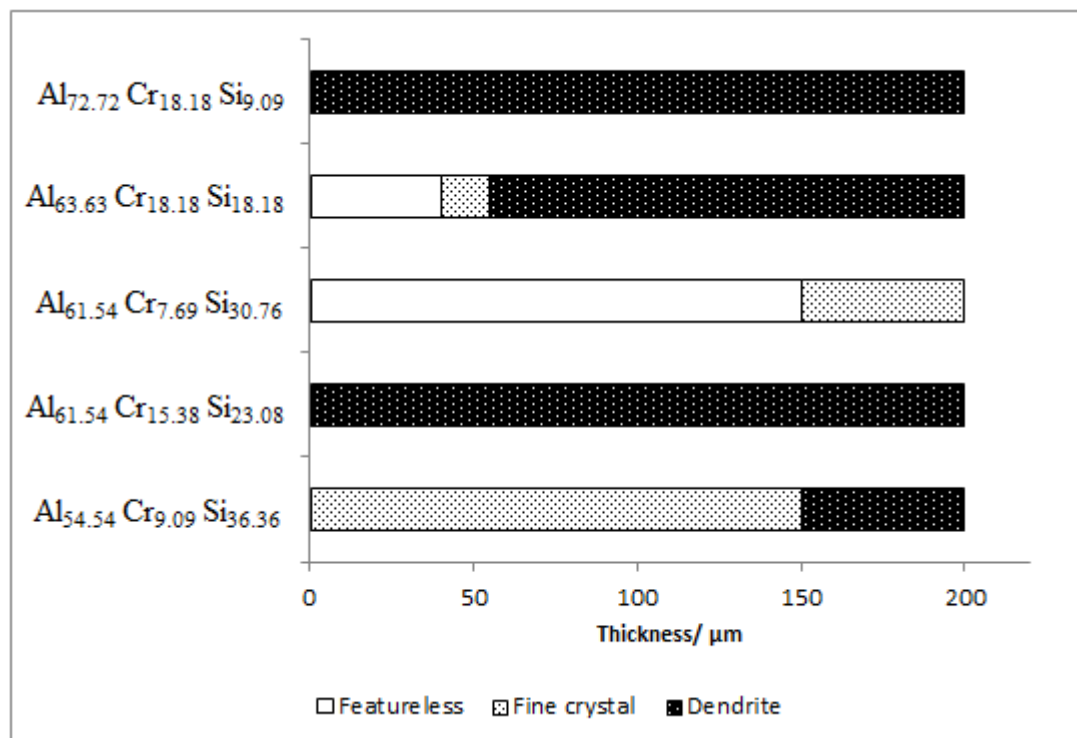


Fig. 4.20 Thickness of the different structures in the Al-Cr-Si alloys.

The GFA of each of the Al-Cr-Si alloys, based on the different structural zones present in the cast wedges, are summarised in Fig. 4.20. Based on the SEM images, a featureless zone of 150µm and 40µm in width were formed at the wedge tip of $\text{Al}_{61.54}\text{Cr}_{7.69}\text{Si}_{30.76}$ and $\text{Al}_{63.63}\text{Cr}_{18.18}\text{Si}_{18.18}$ alloys generated from the 20:1 mould (Fig. 4.17a–c and Fig. 4.16a–b). Fine crystalline appeared in $\text{Al}_{54.54}\text{Cr}_{9.09}\text{Si}_{36.36}$ wedge tips of 100µm and dendrites were initiated at 150µm (Fig. 4.19a–b). Therefore, the GFA of these alloys is higher than that of the Al-Mo-Si alloys, which had featureless zones only 60µm in wedge width.

Chapter 5

Glass Formation in Al-Fe-Si and Al-Co-Si Alloys

5.1 Introduction

In addition to the propensity for metallic glass formation in the **Al-ETM-Si/Ge** ternary and quaternary alloy systems (ETM = Mn, Cr, Mo) (see Chapter 4), fully amorphous melt-spun ribbons of thicknesses up to 20 μm have been reported in both the **Al-LTM-Si** system (LTM = Fe, Co, Ni) (Inoue et al. 1988). As stated in chapter 4, critical casting thickness data (relating to the alloy's glass-forming ability) remains largely unreported for these alloys using such techniques as copper mould wedge casting. In this chapter, the GFA of a series of **Al-Fe-Si** and **Al-Co-Si** ternary alloys was investigated via the design of potential glass forming compositions followed by wedge casting and structural analysis of the cast alloys.

5.2 Al-Fe-Si Alloy System

5.2.1 Composition Design of the Al-Fe-Si Alloys

Previous melt spinning studies on the Al-LTM-Si system showed that fully amorphous ribbons can be produced in certain Al-Fe-Si compositions, which had the second largest composition range of glass formation for Al-Si alloys containing transition metals (Inoue et al. 1988). However, no critical thickness data for relating composition to GFA using copper mould wedge casting has been reported for this system. Using the efficiently packed cluster model (Miracle et al. 2003, Miracle 2004), potential Al-Fe-Si compositions were computed based on the highest packing efficiency in the first coordination shell (Table 5.1). It was found that the highest packing efficiency occurred for Si-centred clusters with a coordination number (N)

of 10, Fe-centred clusters with N of 12, and Al-centred clusters with N of 15. Based on these calculations, five Al-Fe-Si compositions were selected for further investigation by copper mould casting (Fig. 5.1); these candidate alloys were also selected as they fall on liquidus lines in the ternary phase diagram. Among the compositions identified, $\text{Al}_{63.63}\text{Fe}_{18.18}\text{Si}_{18.18}$ (F1) was found to have two types of clusters with N of 10 and 15, respectively. Two wedges per composition were cast into the 10:1 and 20:1 copper moulds for investigating both the critical casting thickness and the variation in structure as a function of cooling rate.

Table 5.1: Investigated Al-Fe-Si compositions (at.%) based on Miracle's atomic packing model: R is the radius ratio between the centre atom and first shell atoms, R* is the critical radius ratio, Δ is the difference to critical radius ratio, N is coordination number, and Note is the designation.

	R	R*	Δ (%)	N	Note
$\text{Al}_{63.63}\text{Fe}_{18.18}\text{Si}_{18.18}$	0.845	0.799	5.75	10	F1
	1.070	1.116	-4.15	15	F1
$\text{Al}_{62.5}\text{Fe}_{12.5}\text{Si}_{25}$	1.074	1.116	-3.73	15	F2
$\text{Al}_{53.85}\text{Fe}_{23.08}\text{Si}_{23.08}$	0.934	0.902	3.52	12	F3
$\text{Al}_{50}\text{Fe}_{31.75}\text{Si}_{18.75}$	1.090	1.116	-2.31	15	F4
$\text{Al}_{50}\text{Fe}_{25}\text{Si}_{25}$	1.095	1.116	-1.87	15	F5

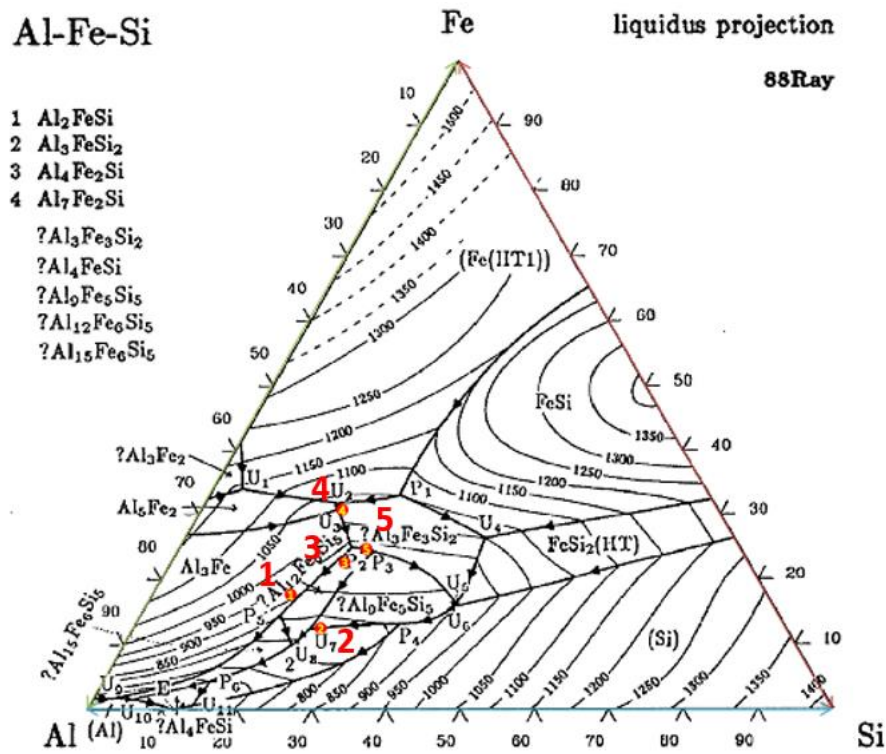


Fig. 5.1 Location of the five candidate alloys on the Al-Fe-Si phase diagram.

5.2.2 Copper Mould Casting of the Al-Fe-Si Alloys

After several melting and casting trials in the arc melter, the casting parameters were optimized to be 40-50% current with fully opened vacuum valve for generating a sharp wedge tip and maximized cooling rate. The casting results of the Al-Fe-Si alloys are given in Fig. 5.2; these castings were better than the Al-Mo-Si wedges described in Chapter 4 due to the lower viscosity of the melt and the application of a higher suction force.

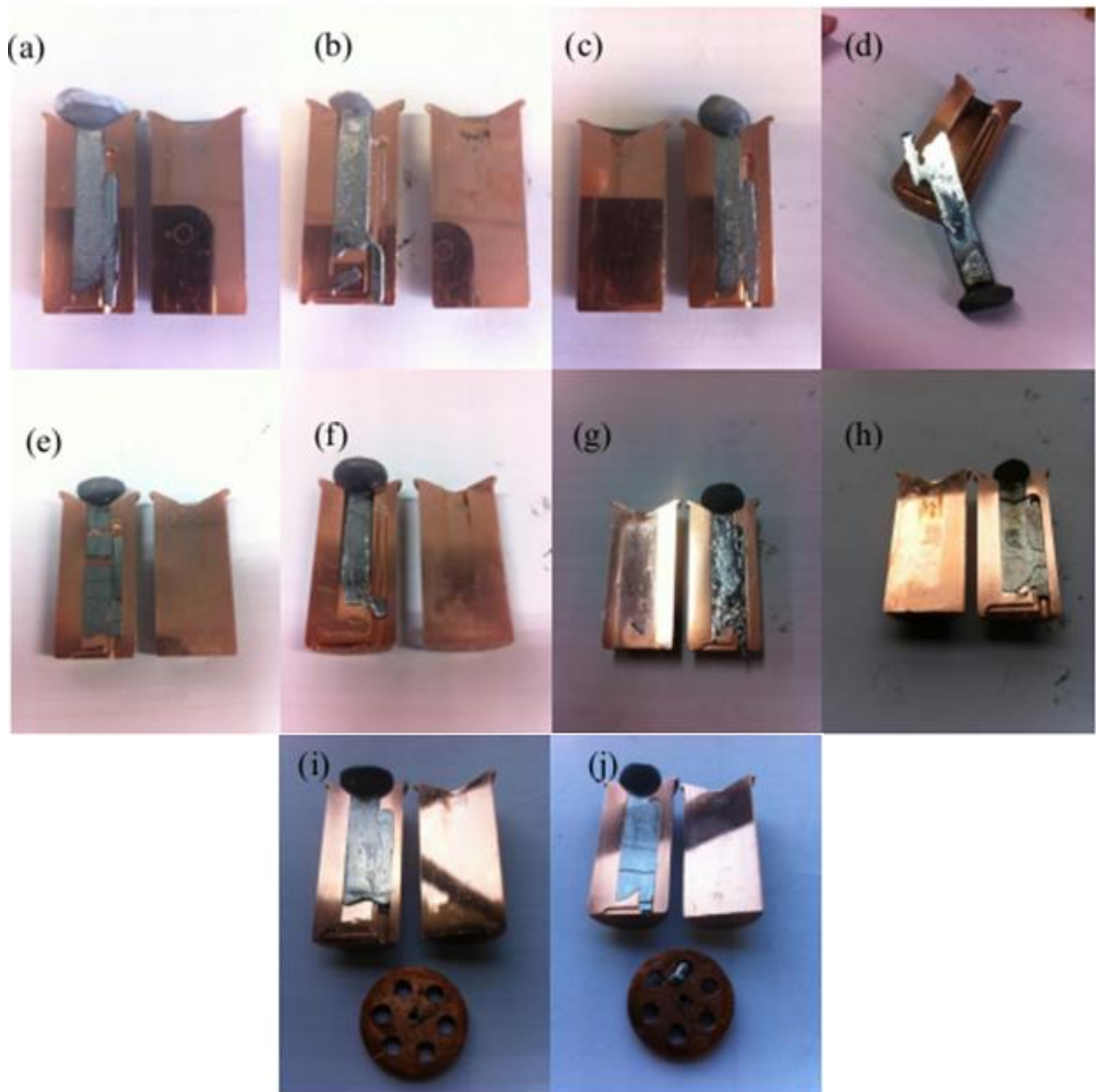


Fig. 5.2 The Al-Fe-Si wedges cast into a 10:1 copper mould with compositions of (a) F1, (c) F2, (e) F3, (g) F4, (i) F5, and a 20:1 copper mould with compositions of (b) F1, (d) F2, (f) F3, (h) F4, (j) F5.

5.2.3 Scanning Electron Microscopy of the Al-Fe-Si Alloys

5.2.3.1 $\text{Al}_{63.63}\text{Fe}_{18.18}\text{Si}_{18.18}$ alloy

For the $\text{Al}_{63.63}\text{Fe}_{18.18}\text{Si}_{18.18}$ alloy (F1) cast into the 20:1 mould (Fig. 5.3a-b), although a featureless zone of 20 μm was generated in the edge of the wedge tip, fine crystals were present in the central region of the tip 78 μm wide and extended to 150 μm in width. After casting into the 10:1 mould (Fig. 5.3c-d), the evolution of elongated dendritic structures were evident throughout the entire tip which indicates that this alloy composition has a very low GFA.

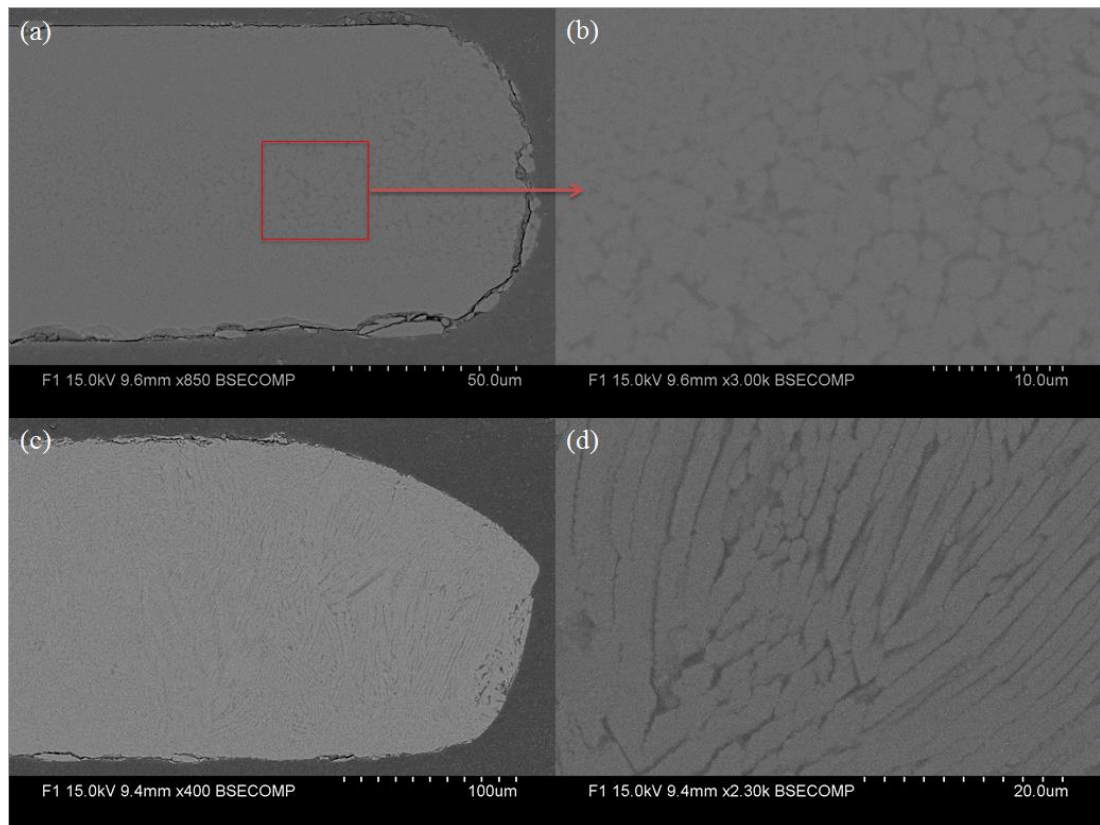


Fig. 5.3 Wedge tips of $\text{Al}_{63.63}\text{Fe}_{18.18}\text{Si}_{18.18}$ alloy (F1) after casting into the (a-b) 20:1 mould and (c-d) 10:1 mould, respectively.

5.2.3.2 $\text{Al}_{62.5}\text{Fe}_{12.5}\text{Si}_{25}$ and $\text{Al}_{53.85}\text{Fe}_{23.08}\text{Si}_{23.08}$ alloys

For the $\text{Al}_{62.5}\text{Fe}_{12.5}\text{Si}_{25}$ alloy (F2), Fig. 5.4 shows parallel dendrites at both tips of wedges by 20:1 and 10:1 moulds, thereby indicating that this alloy also has a low GFA. The wedge tip of $\text{Al}_{53.85}\text{Fe}_{23.08}\text{Si}_{23.08}$ alloy (F3) after casting into the 20:1 mould had a width of 360 μm (Fig. 5.5a-b), whereas the 10:1 mould generated a width of 500 μm (Fig. 5.5c-d). Rod-like crystals were observed at both tips, implying that the GFA of this alloy is also quite low.

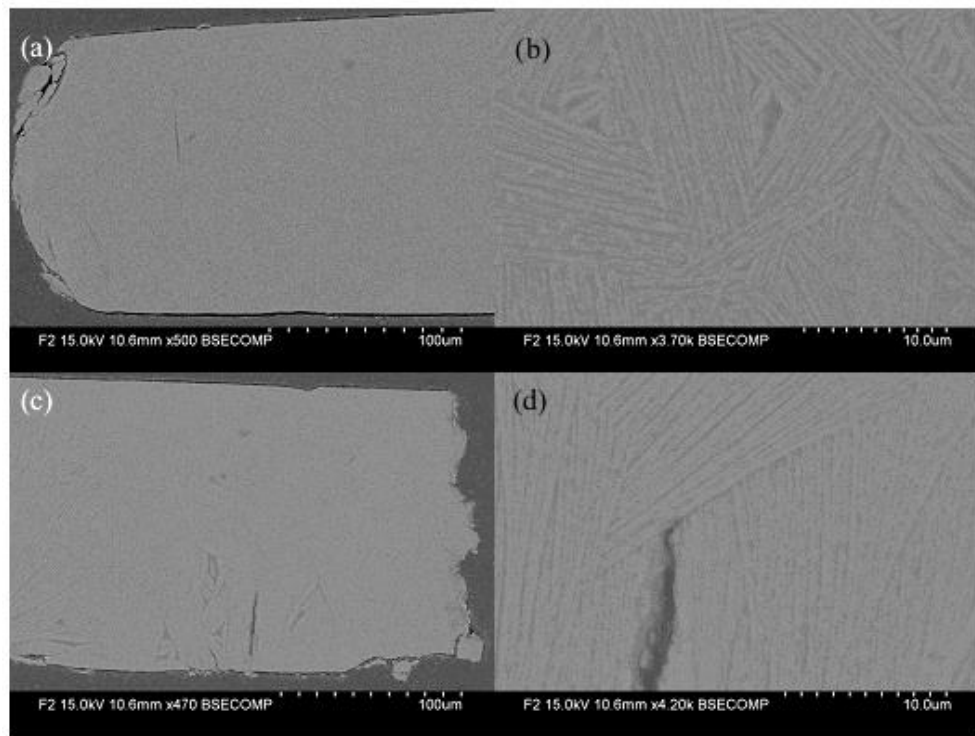


Fig. 5.4 Wedge tips of the $\text{Al}_{62.5}\text{Fe}_{12.5}\text{Si}_{25}$ alloy (F2) after casting into the 20:1 (a-b) and 10:1 (c-d) mould, respectively.

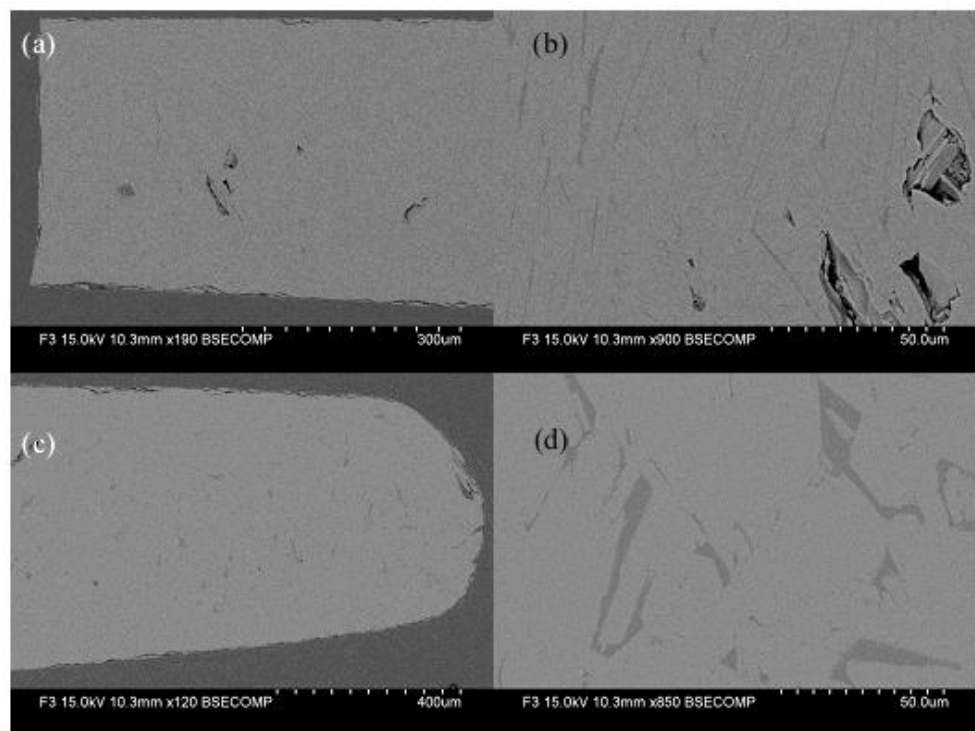


Fig. 5.5 Wedge tips of $\text{Al}_{53.85}\text{Fe}_{23.08}\text{Si}_{23.08}$ alloy (F3) after casting into the 20:1 (a-b) and 10:1 (c-d) mould, respectively.

5.2.3.3 Al₅₀Fe_{31.75}Si_{18.75} and Al₅₀Fe₂₅Si₂₅ alloys

For the Al₅₀Fe_{31.75}Si_{18.75} alloy (F4), the width of the wedge tip was 275 μm (Fig. 5.6a-b) and 680 μm (Fig. 5.6c-d) for the 20:1 and 10:1 mould, respectively. Secondary phases and dendrites were present in both wedges, which confirmed negligible GFA in the Al₅₀Fe_{31.75}Si_{18.75} alloy. The wedge tip of the Al₅₀Fe₂₅Si₂₅ alloy (F5) after casting into the by 20:1 and 10:1 copper mould had width of 160 μm and 480 μm , respectively (Fig. 5.7). Rod shaped dendrites were present at both wedge tips indicating it is unable to form amorphous phase in the Al₅₀Fe₂₅Si₂₅ alloy by copper mould casting.

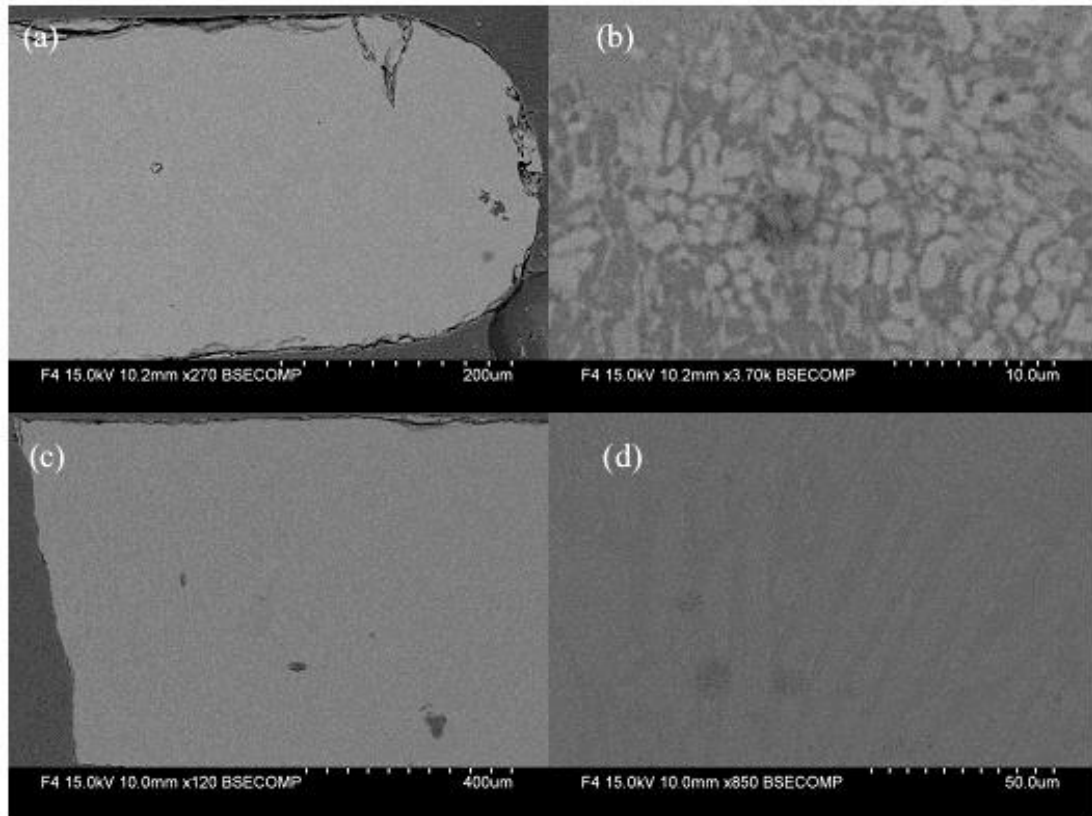


Fig. 5.6 Wedge tips of Al₅₀Fe_{31.75}Si_{18.75} alloy (F4) after casting into the 20:1 (a-b) and 10:1 (c-d) mould, respectively.

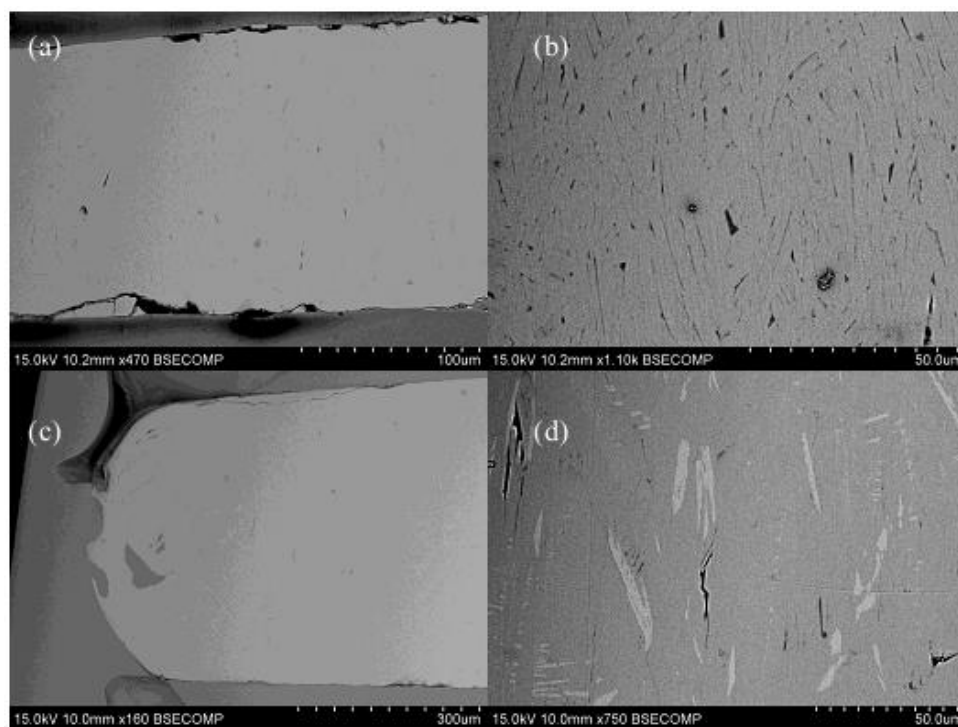


Fig. 5.7 Wedge tips of $\text{Al}_{50}\text{Fe}_{25}\text{Si}_{25}$ alloy (F5) after casting into the 20:1 (a-b) and 10:1 (c-d) mould, respectively.

Fig. 5.8 summarises the phases generated in the five Al-Fe-Si alloys as a function of wedge thickness. No alloys generated a fully amorphous zone at the wedge tip, with a featureless zone only present at the edge for the $\text{Al}_{63.63}\text{Fe}_{18.18}\text{Si}_{18.18}$ alloy tip after casting into the 20:1 mould. However, fine crystals were present in the centre area of the wedge at $78\mu\text{m}$ in width with these crystals being replaced by dendrites at a width of $150\mu\text{m}$. Overall, the GFA of the Al-Fe-Si alloys are inferior to that of Al-Cr-Si alloys (Chapter 4).

5.2.4 X-Ray Diffraction of the Al-Fe-Si Alloys

The crystalline phases generated in the Al-Fe-Si alloys, as observed by SEM (Figs 5.3-5.7), were investigated further by XRD. Comparing these diffraction spectra (Fig. 5.9), the largest difference was between $\text{Al}_{63.63}\text{Fe}_{18.18}\text{Si}_{18.18}$ (F1), $\text{Al}_{53.85}\text{Fe}_{23.08}\text{Si}_{23.08}$ (F3), and $\text{Al}_{50}\text{Fe}_{25}\text{Si}_{25}$ (F5). Using HighScore Plus (section 3.5.1), the rod-shaped dendrites in $\text{Al}_{63.63}\text{Fe}_{18.18}\text{Si}_{18.18}$ (F1) were likely to be AlFe and Fe_5Si_3 , as shown in the indexed XRD pattern in Fig. 5.10. The two crystalline phases observed in the $\text{Al}_{53.85}\text{Fe}_{23.08}\text{Si}_{23.08}$ (F3) alloy (Fig. 5.5) were rod-shape $\text{Al}_8\text{Fe}_2\text{Si}$ (bright) and Si

(dark), as shown in Fig. 5.11. The three phases in the $\text{Al}_{50}\text{Fe}_{25}\text{Si}_{25}$ alloy (F5) correspond to Fe (bright), $\text{Al}_{82}\text{Fe}_{18}$ (grey) and Si (dark) phase, as shown in Fig. 5.12.

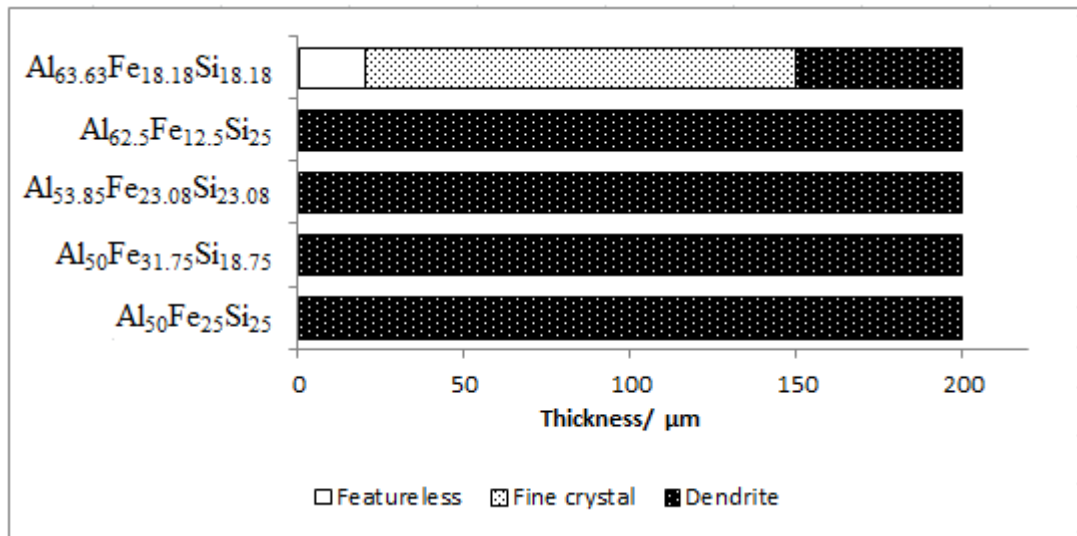


Fig. 5.8 The structures generated in the in Al-Fe-Si alloys as a function of wedge width.

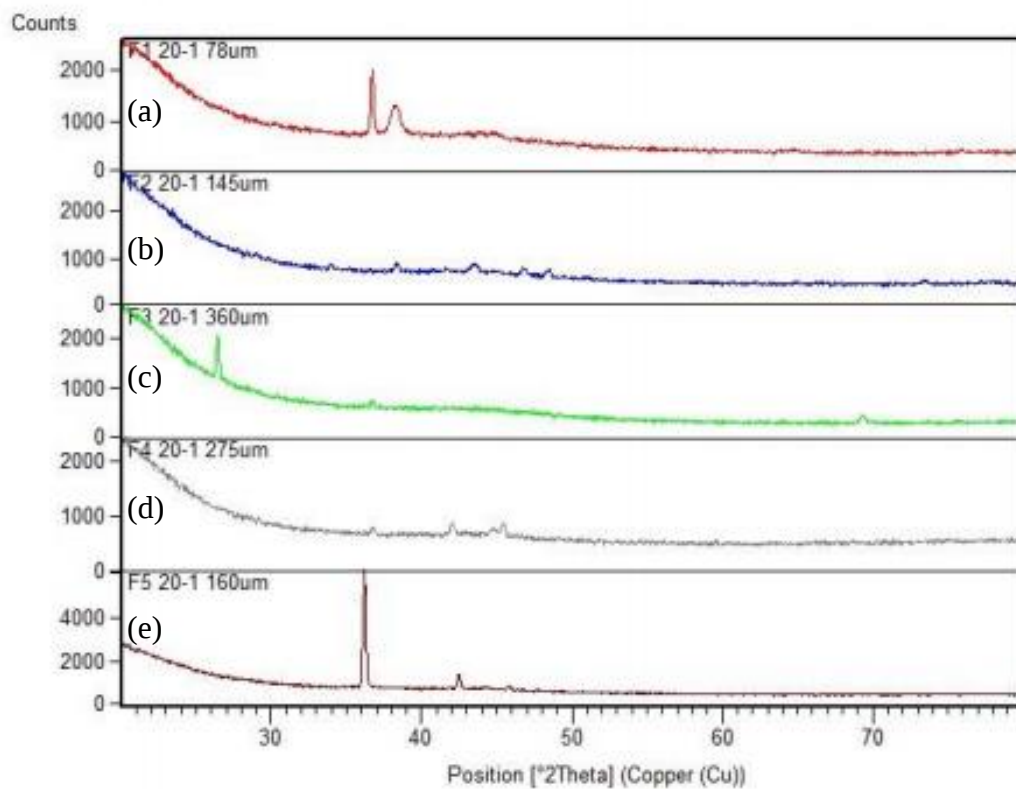


Fig. 5.9 XRD patterns at the tips of Al-Fe-Si wedges for compositions of (a) $\text{Al}_{63.63}\text{Fe}_{18.18}\text{Si}_{18.18}$ (b) $\text{Al}_{62.5}\text{Fe}_{12.5}\text{Si}_{25}$ (c) $\text{Al}_{53.85}\text{Fe}_{23.08}\text{Si}_{23.08}$ (d) $\text{Al}_{50}\text{Fe}_{31.75}\text{Si}_{18.75}$ (e) $\text{Al}_{50}\text{Fe}_{25}\text{Si}_{25}$.

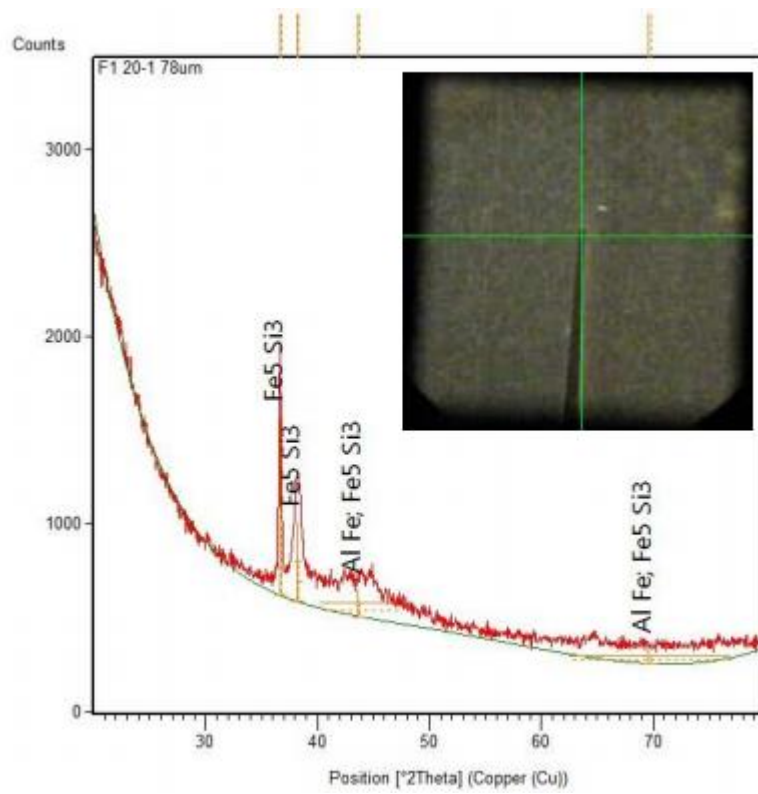


Fig. 5.10 Indexed XRD pattern of the $\text{Al}_{63.63}\text{Fe}_{18.18}\text{Si}_{18.18}$ alloy (F1).

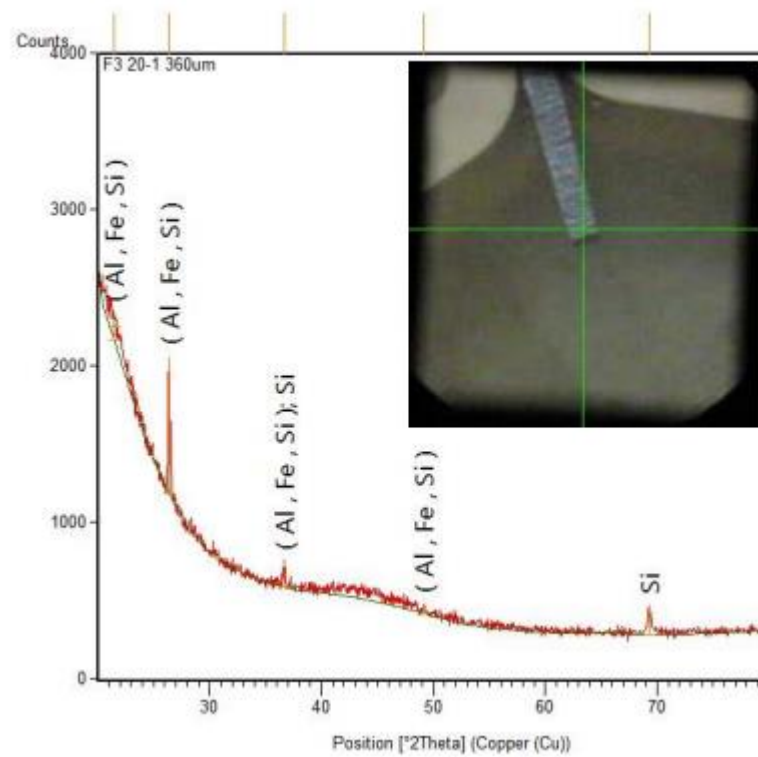


Fig. 5.11 Indexed XRD pattern of the $\text{Al}_{53.85}\text{Fe}_{23.08}\text{Si}_{23.08}$ alloy (F3).

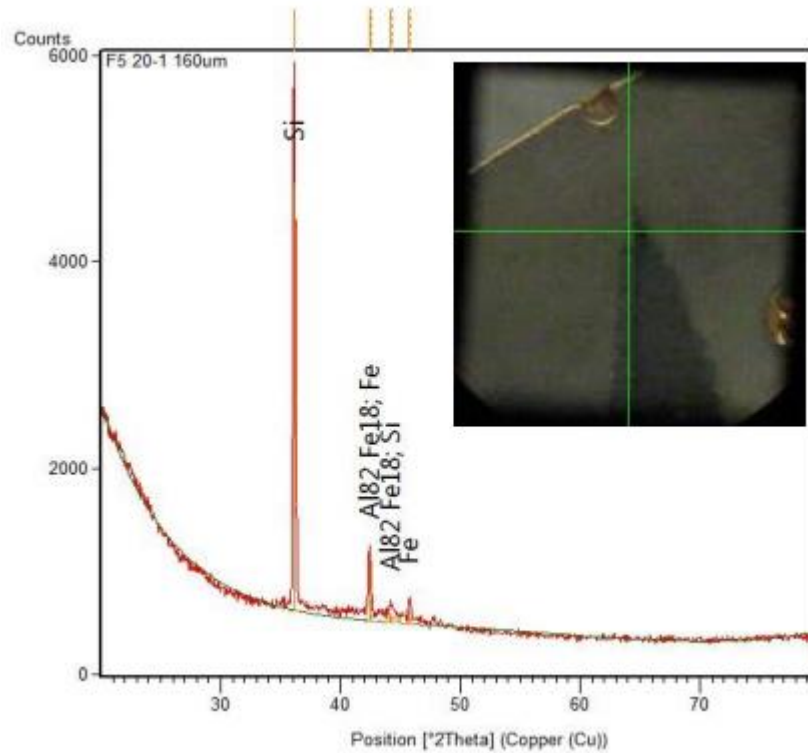


Fig. 5.12 Indexed XRD pattern of the $\text{Al}_{50}\text{Fe}_{25}\text{Si}_{25}$ alloy (F5).

5.3 Al-Co-Si Alloy System

5.3.1 Composition Design of the Al-Co-Si Alloys

For all the Al-Si-based alloys produced by melt spinning to date, the largest GFR was found in the Al-Co-Si alloy system, whereby fully amorphous ribbons of up to 20 μm in thickness were generated for alloys containing 15-45 at.% Si and 5-22 at.% Co (Inoue et al. 1988). To further investigate this alloy system, ten potential glass forming compositions were identified for wedge casting (Table 5.2) based on calculations of efficiently packed clusters in conjunction with their position on the ternary phase diagram where those compositions lying on liquidus lines were selected (Fig. 5.13). High packing efficiency was found in Co-centred clusters with N of 12, Al-centred clusters with N of 15, and Si-centred clusters with N of 10. The packing efficiencies of the $\text{Al}_{56.25}\text{Co}_{18.75}\text{Si}_{25}$ alloy (Co8) with two types of efficiently packed clusters were listed separately according to the cluster of different centre atoms.

Table 5.2: Investigated Al-Co-Si compositions (at.%) based on Miracle's atomic packing model: R is the radius ratio between the centre atom and first shell atoms, R* is the critical radius ratio, Δ is the difference to critical radius ratio, N is the coordination number, and Note is the designation.

	R	R*	Δ (%)	N	Note
Al ₇₅ Co _{12.5} Si _{12.5}	1.044	1.116	-6.42	15	Co1
Al _{68.75} Co _{6.25} Si ₂₅	1.064	1.116	-4.67	15	Co2
Al _{63.63} Co _{18.18} Si _{18.18}	0.844	0.799	5.60	10	Co3
Al _{63.63} Co _{9.09} Si _{27.27}	0.850	0.799	6.36	10	Co4
Al _{61.54} Co _{15.38} Si _{23.08}	0.930	0.902	3.05	12	Co5
Al _{61.54} Co _{23.08} Si _{15.38}	0.924	0.902	2.43	12	Co6
Al _{56.25} Co _{12.5} Si _{31.25}	1.088	1.116	-2.47	15	Co7
Al _{56.25} Co _{18.75} Si ₂₅	1.083	1.116	-2.95	15	Co8
	0.861	0.799	7.79	10	Co8
Al _{56.25} Co ₂₅ Si _{18.75}	1.078	1.116	-3.43	15	Co9
Al _{53.85} Co _{23.08} Si _{23.08}	0.940	0.902	4.21	12	Cox

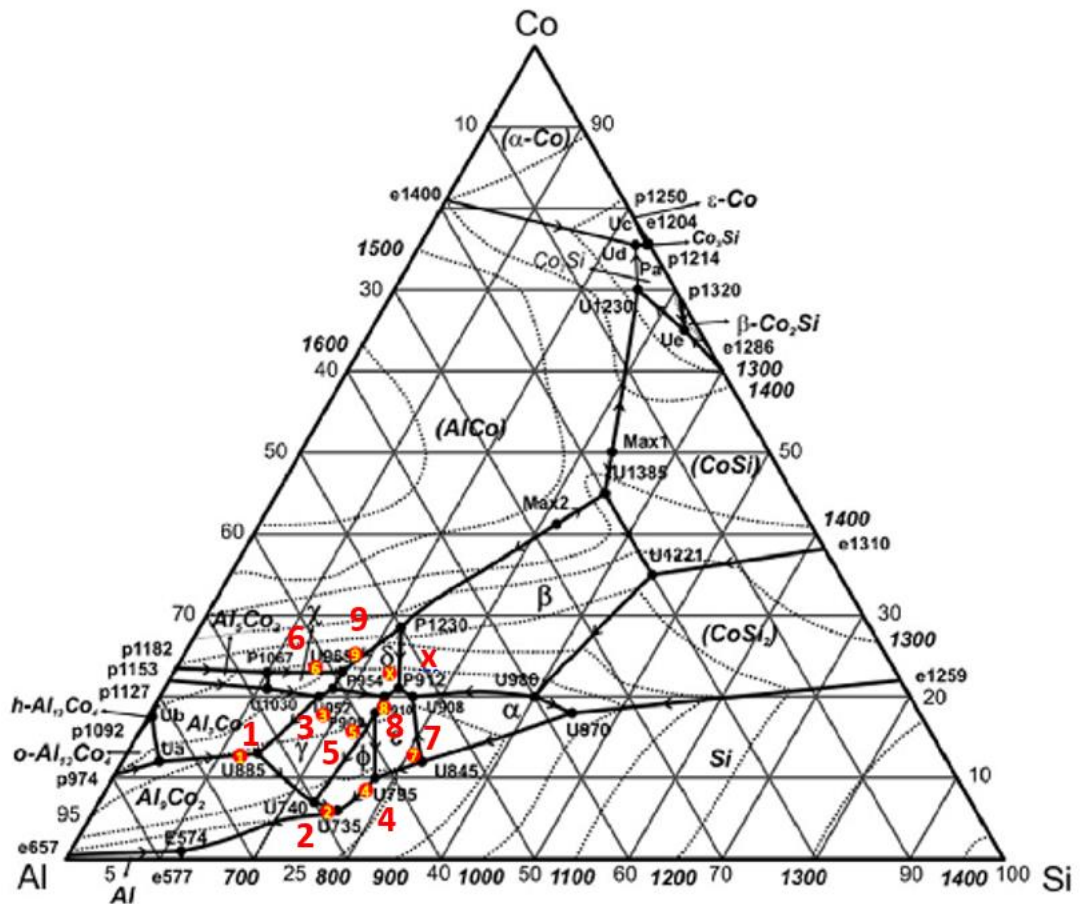


Fig. 5.13 Location of the ten candidate alloys on the Al-Co-Si phase diagram.

5.3.2 Copper Mould Casting of the Al-Co-Si Alloys

The alloys were arc melted and suction cast into the wedge-shaped copper moulds. Except for the Al lean compositions ($\text{Al}_{56.25}\text{Co}_{25}\text{Si}_{18.75}$ and $\text{Al}_{53.85}\text{Co}_{23.08}\text{Si}_{23.08}$), the alloys were difficult to cast due to their high viscosity (i.e. Fig. 5.14i-j). The alloys were cast into the copper moulds (Fig. 5.14a-h) by 40-50% of current and 25-50% of valve open. The well-shaped wedges were used for the microstructure inspection using SEM in the next section.

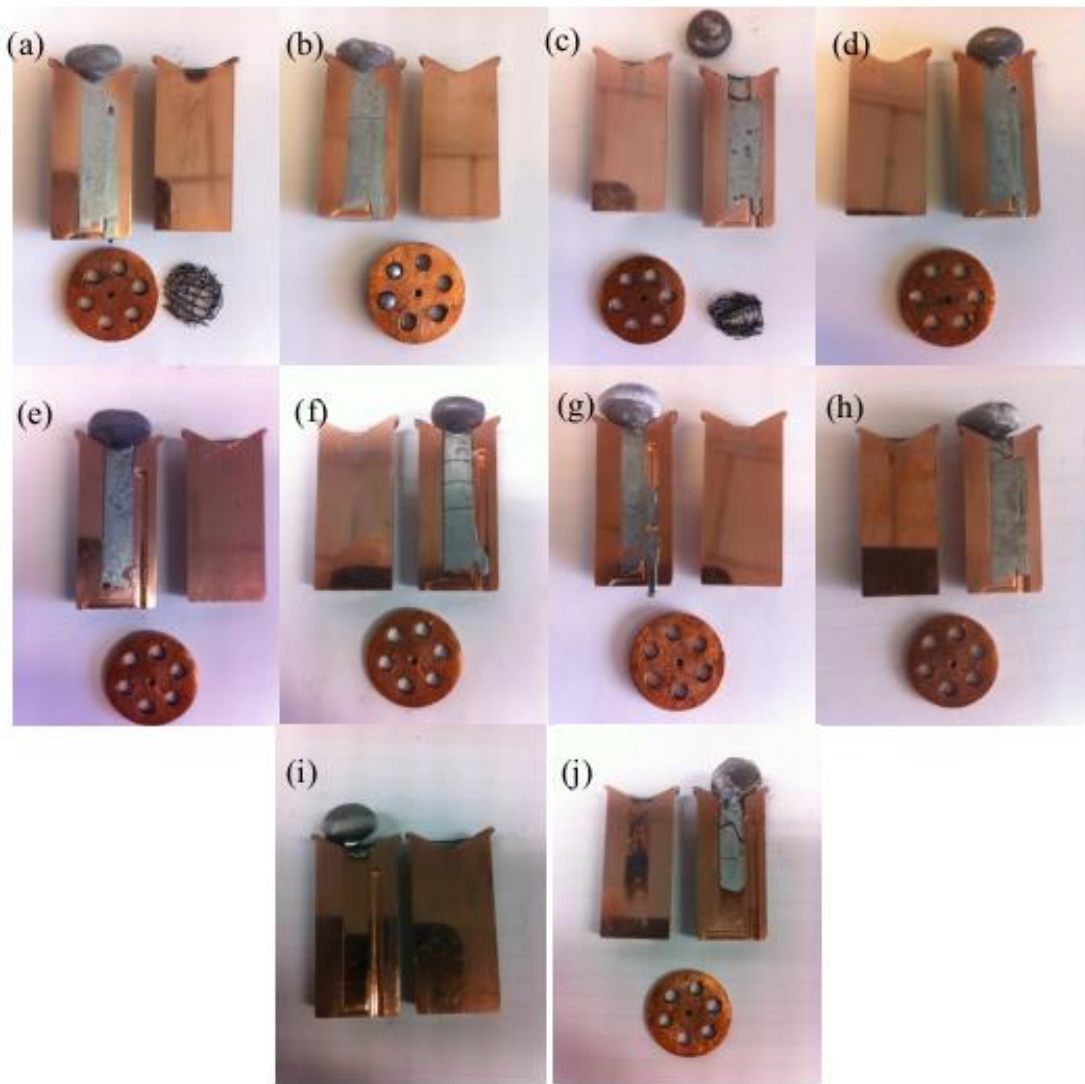


Fig. 5.14 The Al-Co-Si wedges produced using the 20:1 mould with compositions of (a) Co1, (b) Co2, (c) Co3, (d) Co4, (e) Co5, (f) Co6, (g) Co7, (h) Co8, (i) Co9, and (j) Cox.

5.3.3 Scanning Electron Microscopy of the Al-Co-Si Alloys

5.3.3.1 Al₇₅Co_{12.5}Si_{12.5} and Al_{68.75}Co_{6.25}Si₂₅ alloys

The various zones of the castings were again investigated by SEM. For the Al₇₅Co_{12.5}Si_{12.5} alloy (Co1), the wedge tip had a width of 78µm and 147µm after casting into 20:1 and 10:1 copper moulds, respectively. The latter had a fully crystallised tip, with the former having secondary crystalline phases present at 80µm in width from the edge of the wedge (Fig. 5.15a-b). In Al_{68.75}Co_{6.25}Si₂₅ alloy (Co2), the wedge tip had a width of 50µm and 240µm for the 20:1 and 10:1 mould, respectively. Fine crystalline phases were present at both tips (Fig. 5.15c), with dendrites observed at 380µm (Fig. 5.15d) and 400µm in width for wedges by 20:1 mould and 10:1 mould.

5.3.3.2 Al_{63.63}Co_{18.18}Si_{18.18} and Al_{63.63}Co_{9.09}Si_{27.27} alloys

The width of wedge tip was 240µm and 400µm in the Al_{63.63}Co_{18.18}Si_{18.18} alloy (Co3). Dendrites were present at both tips (Fig. 5.16a-b). For the Al_{63.63}Co_{9.09}Si_{27.27} alloy (Co4), the tips had a width of 75µm and 325µm for wedges by the 20:1 and 10:1 copper mould, respectively. The 10:1 wedge is fully crystallised from the tip; fine crystals initiated at the centre of the featureless matrix at 75µm in width in the 20:1 wedge (Fig. 5.16c-d).

5.3.3.3 Al_{61.54}Co_{15.38}Si_{23.08} and Al_{61.54}Co_{23.08}Si_{15.38} alloys

For the Al_{61.54}Co_{15.38}Si_{23.08} alloy (Co5), wedge tips were 190µm and 265µm in width for the 20:1 and 10:1 copper mould, respectively (Fig. 5.17a). For the Al_{61.54}Co_{23.08}Si_{15.38} alloy (Co6), wedge tips were 220µm and 190µm in width for the 20:1 and 10:1 copper mould, respectively (Fig. 5.17b). Dendrites were present at both tips indicating low GFA in these two compositions.

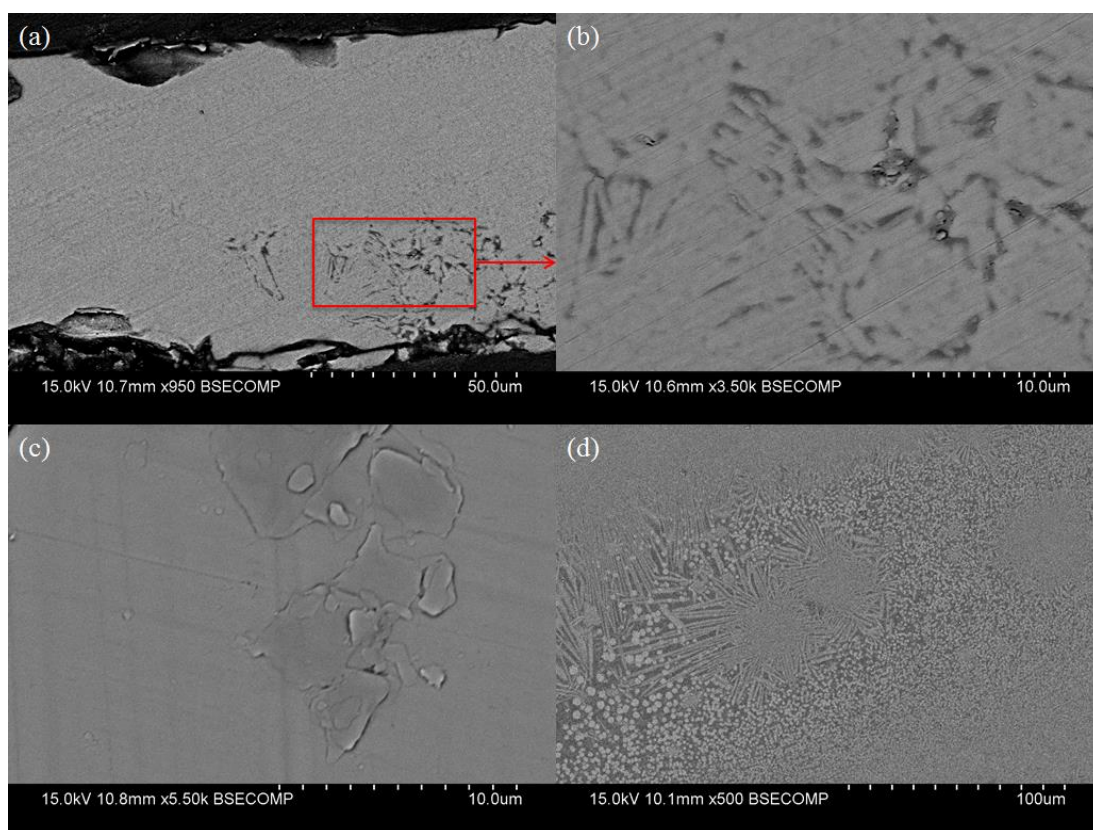


Fig. 5.15 SEM micrographs of (a-b) $\text{Al}_{75}\text{Co}_{12.5}\text{Si}_{12.5}$ wedges (Co1); (c-d) $\text{Al}_{68.75}\text{Co}_{6.25}\text{Si}_{25}$ wedges (Co2).

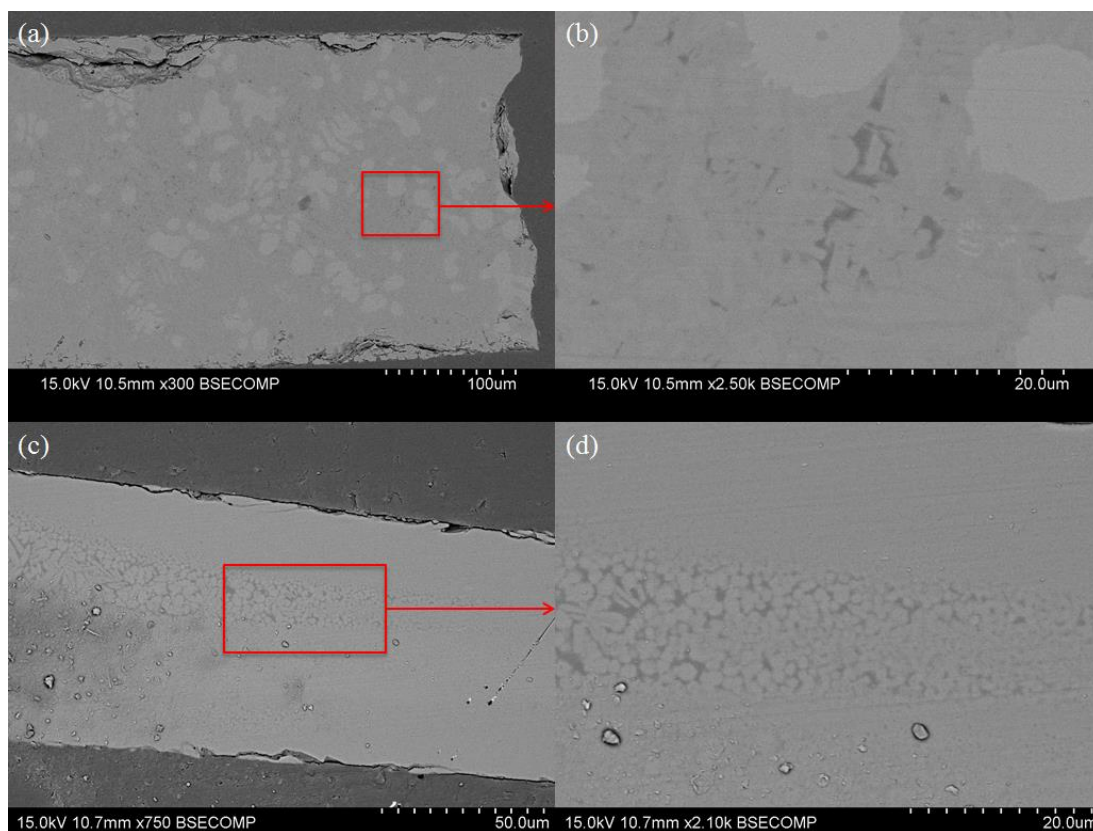


Fig. 5.16 SEM micrographs of (a-b) $\text{Al}_{63.63}\text{Co}_{18.18}\text{Si}_{18.18}$ wedges (Co3); (c-d) $\text{Al}_{63.63}\text{Co}_{9.09}\text{Si}_{27.27}$ wedges (Co4).

5.3.3.4 $\text{Al}_{56.25}\text{Co}_{12.5}\text{Si}_{31.25}$, $\text{Al}_{56.25}\text{Co}_{18.75}\text{Si}_{25}$, and $\text{Al}_{61.54}\text{Co}_{15.38}\text{Si}_{23.08}$ alloys

For the $\text{Al}_{56.25}\text{Co}_{12.5}\text{Si}_{31.25}$ alloy (Co7), wedge tips were both 100 μm by 10:1 and 20:1 copper moulds. Dendrites were present in the wedge (Fig. 5.18a-b). In the $\text{Al}_{56.25}\text{Co}_{18.75}\text{Si}_{25}$ alloy (Co8), wedge tips cast with 10:1 and 20:1 copper mould were 560 μm and 75 μm in width, respectively. A featureless matrix appeared at the wedge tip (Fig. 5.18c) but fine crystals were present at 120 μm in width and extended to 330 μm in width for the thin wedge and to 1mm in width for the thick wedge (Fig. 5.18d). For the $\text{Al}_{53.85}\text{Co}_{23.08}\text{Si}_{23.08}$ alloy (CoX), the width of tips was 830 μm and 740 μm for thick and thin wedges, respectively. Dendrites were present in both matrixes from the beginning of tips in $\text{Al}_{56.25}\text{Co}_{12.5}\text{Si}_{31.25}$ (Co7) and $\text{Al}_{61.54}\text{Co}_{15.38}\text{Si}_{23.08}$ (CoX), thereby indicating that GFA was low (Fig. 5.16e-f).

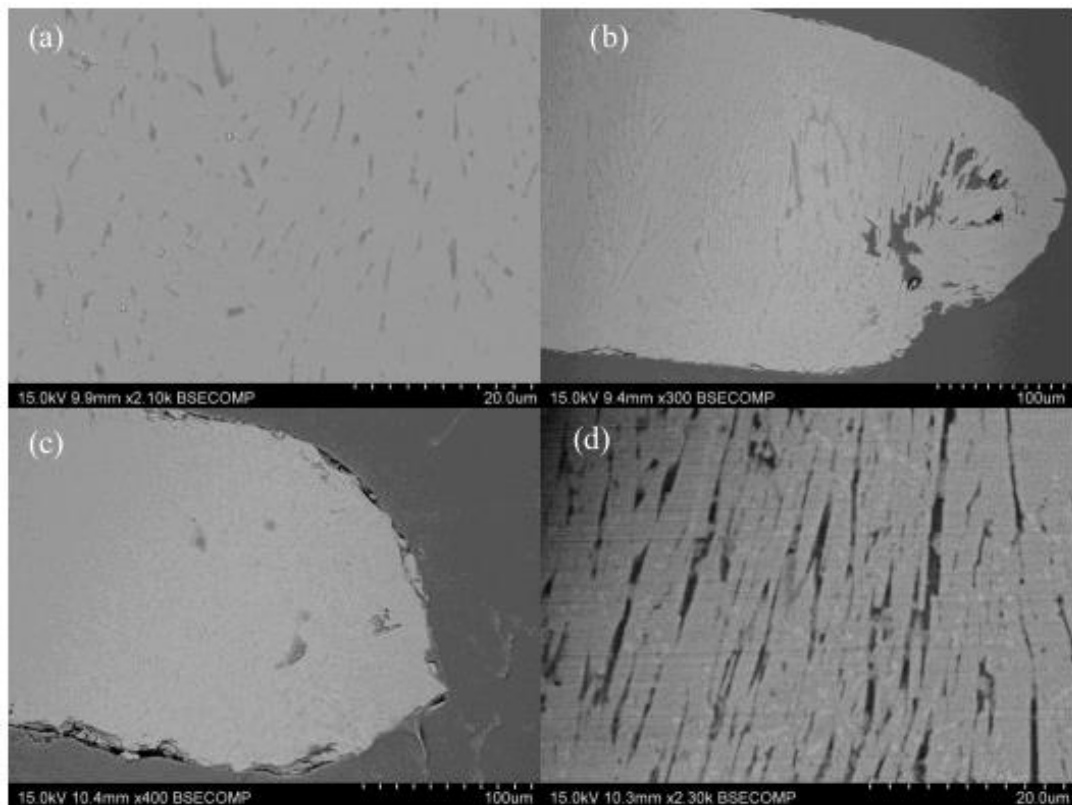


Fig. 5.17 SEM micrographs of (a-b) $\text{Al}_{61.54}\text{Co}_{15.38}\text{Si}_{23.08}$ wedges (Co5); (c-d) $\text{Al}_{61.54}\text{Co}_{23.08}\text{Si}_{15.38}$ wedges (Co6).

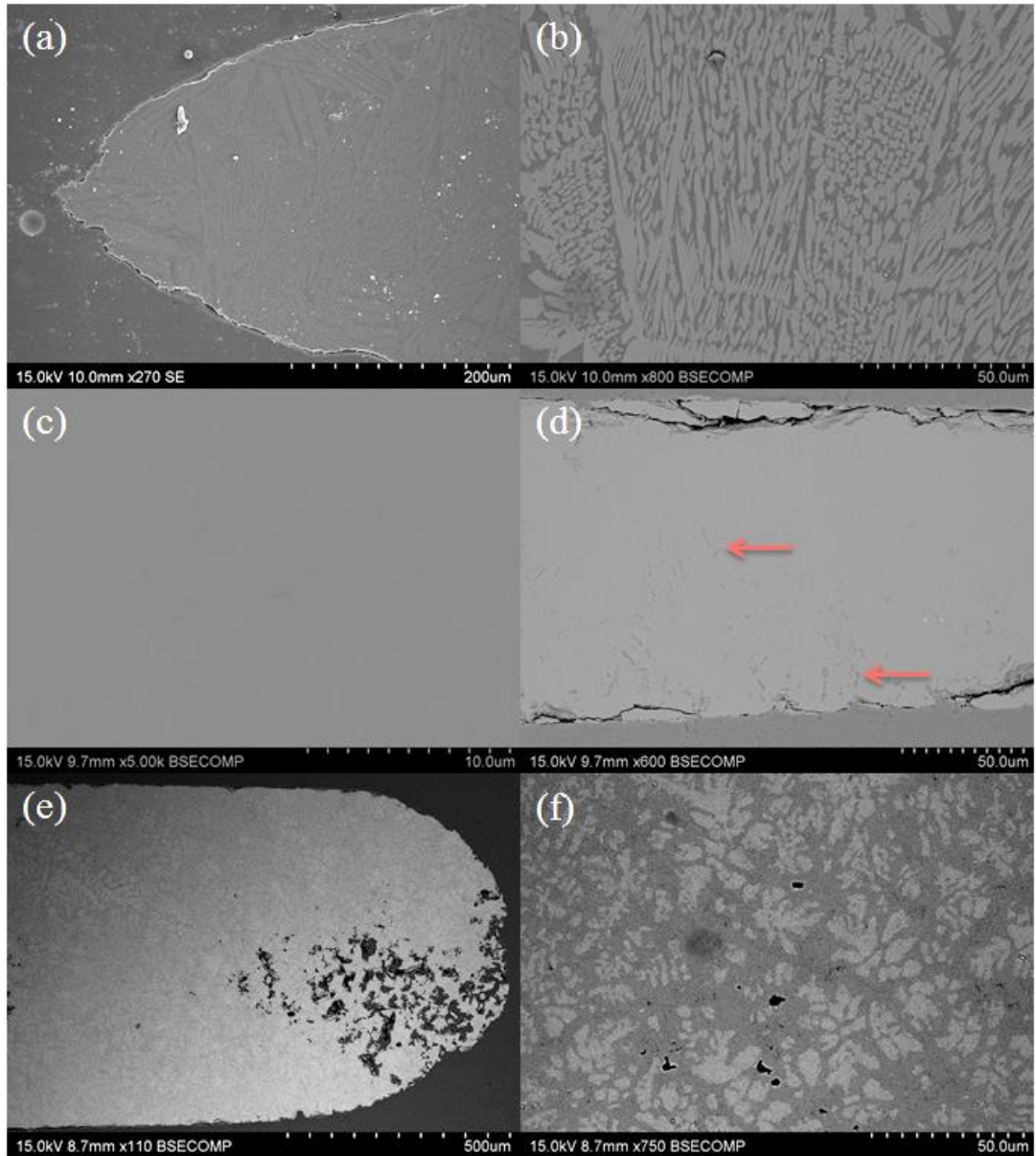


Fig. 5.18 SEM micrographs of (a-b) $\text{Al}_{56.25}\text{Co}_{12.5}\text{Si}_{31.25}$ wedges (Co7); (c-d) $\text{Al}_{56.25}\text{Co}_{18.75}\text{Si}_{25}$ wedges (Co8); (e-f) $\text{Al}_{53.85}\text{Co}_{23.08}\text{Si}_{23.08}$ wedges (CoX).

Microstructural evolution as a function casting thickness for the various alloy compositions are summarized in the Fig. 5.19. The $\text{Al}_{75}\text{Co}_{12.5}\text{Si}_{12.5}$ (Co1), $\text{Al}_{63.63}\text{Co}_{9.09}\text{Si}_{27.27}$ (Co4) and $\text{Al}_{56.25}\text{Co}_{18.75}\text{Si}_{25}$ (Co8) alloys had featureless matrixes of 78 μm , 75 μm , and 120 μm in width. There were fine crystals up to 400 μm in width in the $\text{Al}_{68.75}\text{Co}_{6.25}\text{Si}_{25}$ alloy (Co2), with dendrites forming in the centre of the matrix. This result indicated that GFA in these Al-Co-Si alloys is higher than the Al-Fe-Si alloys. The alloy with the largest critical casting thickness (i.e. highest GFA) was $\text{Al}_{56.25}\text{Co}_{18.75}\text{Si}_{25}$ (Co8) with a featureless region of 120 μm in width.

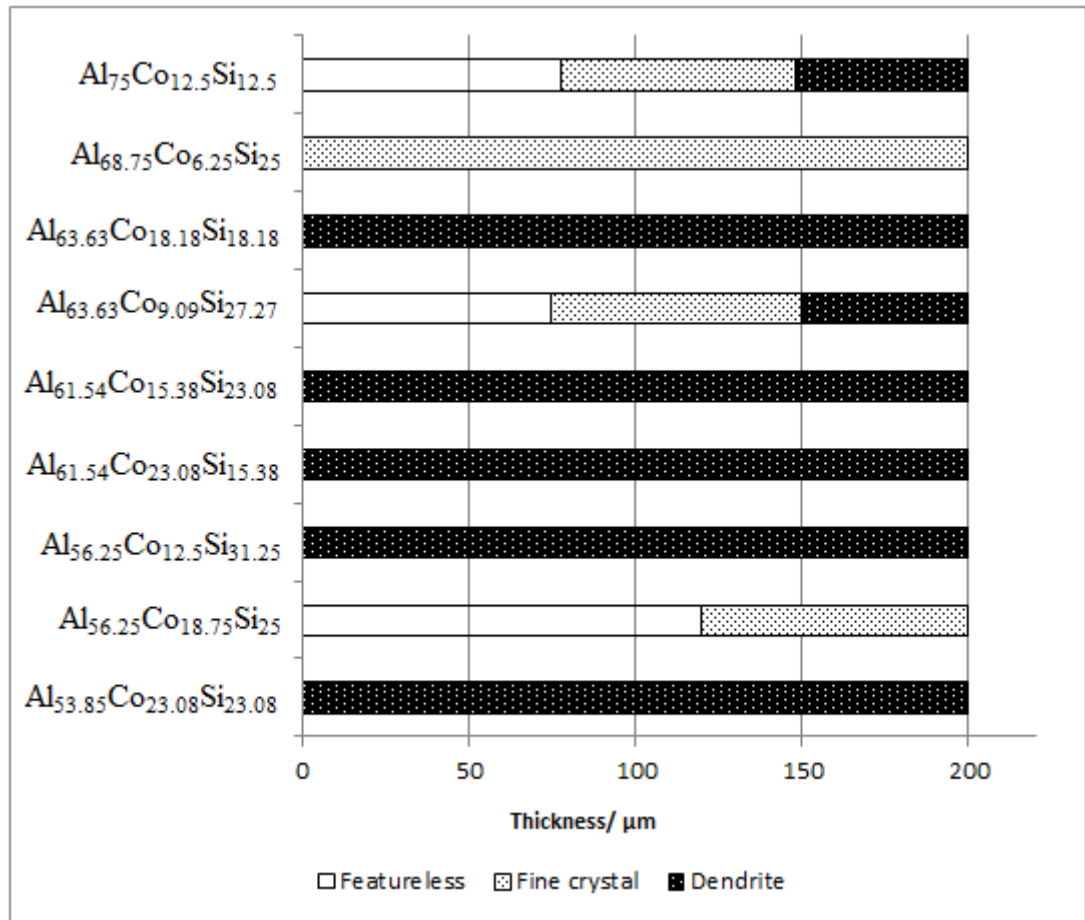


Fig. 5.19 The structures generated in the Al-Co-Si alloys as a function of wedge width.

5.3.4 X-Ray Diffraction of the Al-Co-Si Alloys

The crystalline phases generated in the Al-Co-Si alloys, as observed by SEM, were investigated by XRD. SEM micrographs revealed featureless regions at the wedge tips of $\text{Al}_{75}\text{Co}_{12.5}\text{Si}_{12.5}$ (Co1), $\text{Al}_{63.63}\text{Co}_{9.09}\text{Si}_{27.27}$ (Co4), $\text{Al}_{56.25}\text{Co}_{18.75}\text{Si}_{25}$ (Co8), and fine crystals up to 350μm in width in $\text{Al}_{68.75}\text{Co}_{6.25}\text{Si}_{25}$ (Co2). The various types of crystalline phase found in these alloys are described below.

The SEM micrograph in Fig. 5.15b shows the $\text{Al}_{75}\text{Co}_{12.5}\text{Si}_{12.5}$ alloy (Co1) has a grey phase surrounded by a dark phase at 75μm in width, and XRD (Fig. 5.21) indicating that they are Si-lean $\text{Al}_{13}\text{Co}_4$ (light) and Si (dark) phases, as labeled in the XRD spectrum. For the $\text{Al}_{68.75}\text{Co}_{6.25}\text{Si}_{25}$ alloy (Co2), dendrites initiated in fine crystalsmatrix at 350μm in width (Fig. 5.15d), with the white dots, grey dendrites,

and dark phases identified as Co, Al_3Co , and $\text{Al}_{0.82}\text{Si}_{0.18}$ in XRD spectrum, respectively (Fig. 5.22). For the $\text{Al}_{63.63}\text{Co}_{9.09}\text{Si}_{27.27}$ alloy (Co4), XRD at a width of $50\mu\text{m}$ indicated no significant peaks present in the matrix (Fig. 5.23); the small peaks present might be due to the presence of $\text{Al}_{3.21}\text{Si}_{0.47}$ fine crystal nuclei at $75\mu\text{m}$ in width adjacent to the amorphous matrix. The XRD spectrum in Fig. 5.24 reveals fine crystals present in featureless matrix of the $\text{Al}_{56.25}\text{Co}_{18.75}\text{Si}_{25}$ alloy (Co8), and this phase was identified to be $\text{Al}_{14}\text{Co}_5\text{Si}_2$.

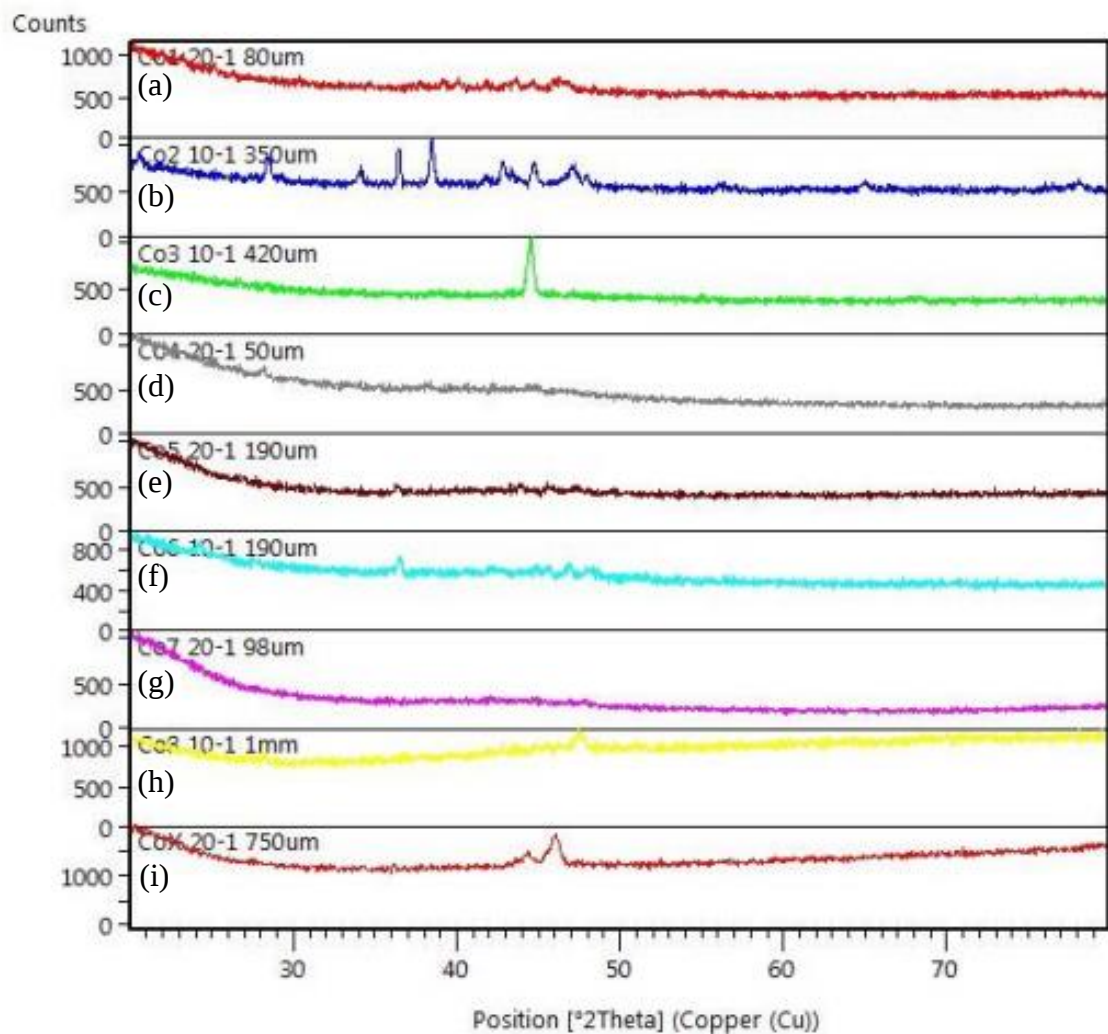


Fig. 5.20 XRD patterns of Al-Co-Si wedges for compositions of (a) $\text{Al}_{75}\text{Co}_{12.5}\text{Si}_{12.5}$ (b) $\text{Al}_{68.75}\text{Co}_{6.25}\text{Si}_{25}$ (c) $\text{Al}_{63.63}\text{Co}_{18.18}\text{Si}_{18.18}$ (d) $\text{Al}_{63.63}\text{Co}_{9.09}\text{Si}_{27.27}$ (e) $\text{Al}_{61.54}\text{Co}_{15.38}\text{Si}_{23.08}$ (f) $\text{Al}_{61.54}\text{Co}_{23.08}\text{Si}_{15.38}$ (g) $\text{Al}_{56.25}\text{Co}_{12.5}\text{Si}_{31.25}$ (h) $\text{Al}_{56.25}\text{Co}_{18.75}\text{Si}_{25}$ (i) $\text{Al}_{53.85}\text{Co}_{23.08}\text{Si}_{23.08}$.

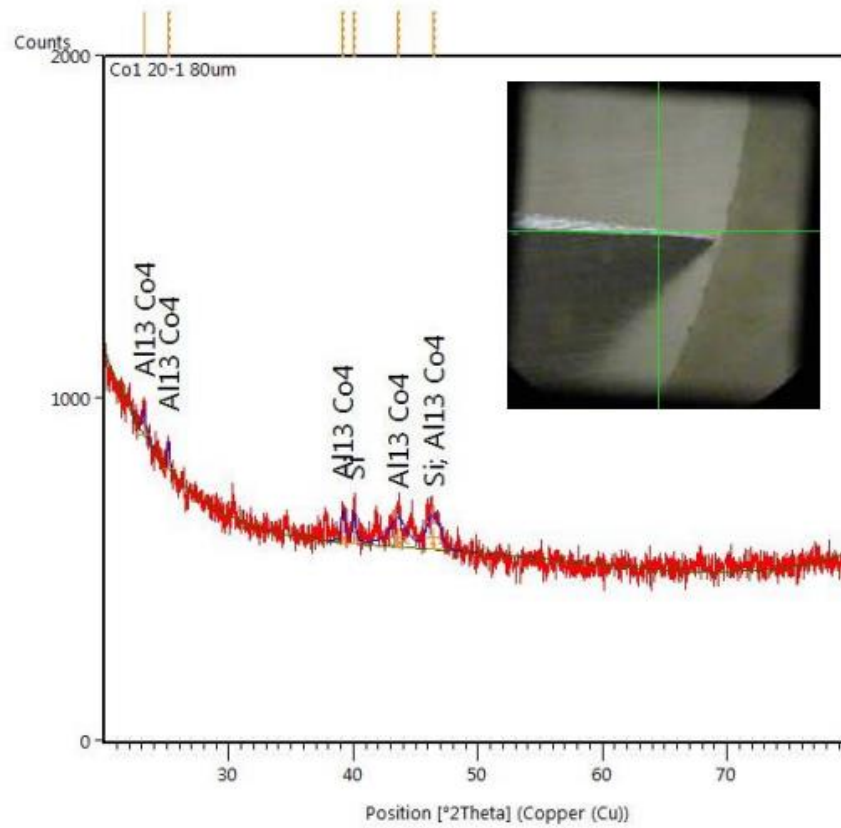


Fig. 5.21 Indexed XRD pattern of the Al₇₅Co_{12.5}Si_{12.5} alloy (Co1).

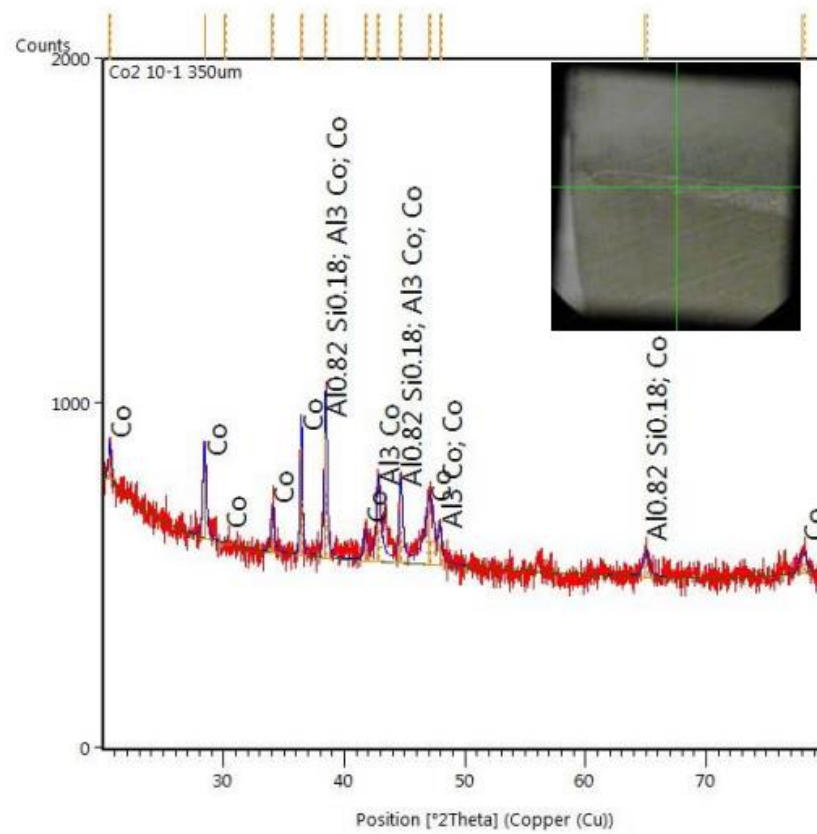


Fig. 5.22 Indexed XRD pattern of the Al_{68.75}Co_{6.25}Si₂₅ alloy (Co2).

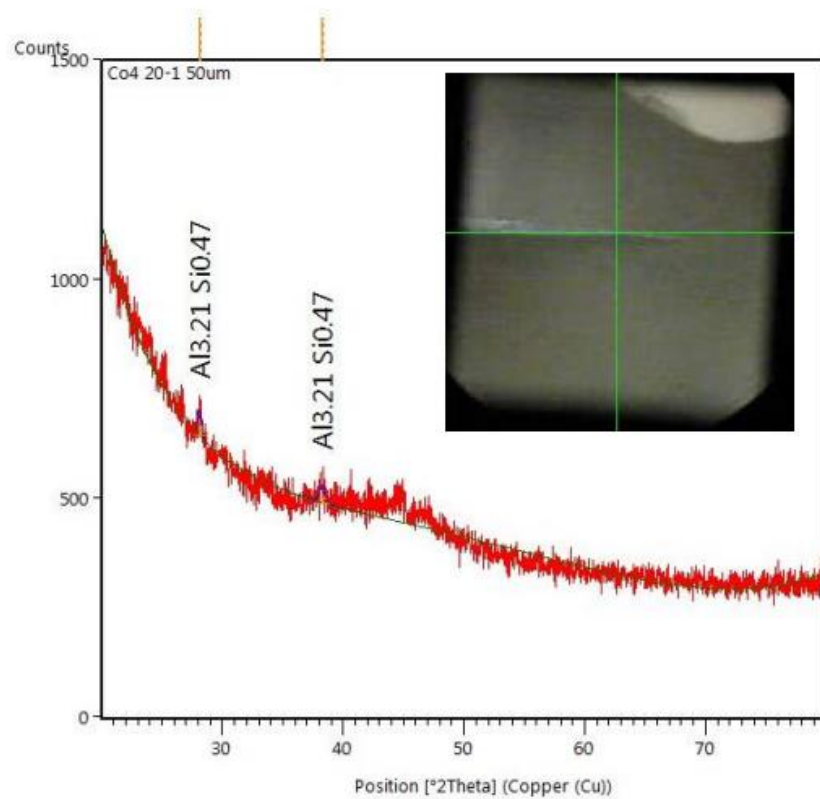


Fig. 5.23 Indexed XRD pattern of the $\text{Al}_{63.63}\text{Co}_{9.09}\text{Si}_{27.27}$ alloy (Co4).

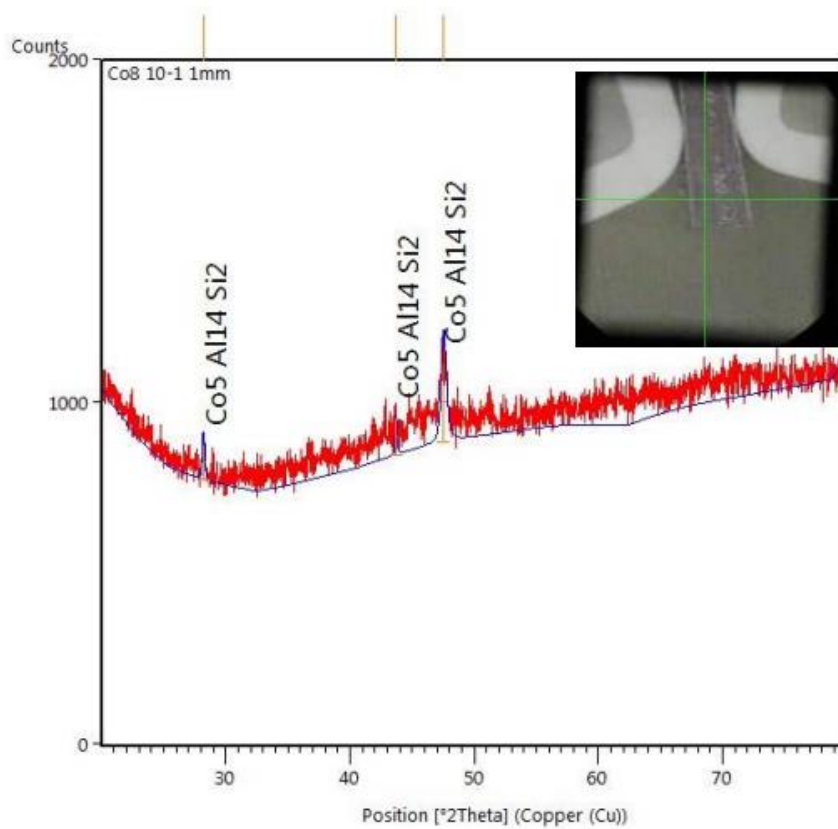


Fig. 5.24 Indexed XRD pattern of the $\text{Al}_{56.25}\text{Co}_{18.75}\text{Si}_{25}$ alloy (Co8).

5.3.5 Bi-clusters Composition of the Al-Co-Si Alloys

The $\text{Al}_{56.25}\text{Co}_{18.75}\text{Si}_{25}$ alloy (Co8) was found to have the largest critical casting thickness of 120 μm in width (i.e. highest GFA). From Table 5.2, two possible efficiently packed clusters with CN of 10 and 15, respectively, were computed for this alloy. This implies that the sluggish crystallisation kinetics associated with efficient packing around multiple species played a positive role towards glass-forming in this system; as the Co and Si are solutes in the Al-rich Al-Co-Si alloys, they are more likely to be the centre atom of clusters and surrounded by the Al atoms. Therefore, the silicon centred clusters and cobalt centred clusters were combined to select a composition with relatively higher viscosity in the solidification for good glass formation. As calculated that silicon centred clusters had high packing efficiency with N of 10 and cobalt centred clusters had high packing efficiency with N of 12, $\text{Al}_{74.18}\text{Co}_{7.64}\text{Si}_{18.18}$ is constructed, and four surrounding compositions with a variation of 2 at.% in silicon and cobalt (+2Si, -2Si, +2Co, -2Co) were also inspected for comparison. The $\text{Al}_{74.18}\text{Co}_{7.64}\text{Si}_{18.18}$ wedge had a tip of 75 μm and the bright secondary phases were initiated in the matrix at the width of 195 μm (Fig. 5.25a); the crystal phases along the wedge were increased in both size and number density, until the dendrites present at the width of 320 μm (Fig. 5.25b). The width of wedge tips is 18 μm , 190 μm , 290 μm and 95 μm in $\text{Al}_{76}\text{Co}_8\text{Si}_{16}$ (-2Si) wedge, $\text{Al}_{72}\text{Co}_8\text{Si}_{20}$ (+2Si) wedge, the $\text{Al}_{76}\text{Co}_6\text{Si}_{18}$ (-2Co) wedge, and $\text{Al}_{72}\text{Co}_{10}\text{Si}_{18}$ (+2Co) wedge. Fine crystals were present in the silicon lean composition of $\text{Al}_{76}\text{Co}_8\text{Si}_{16}$ with dendrites appeared at 108 μm in width; dendrites appeared in all other three compositions.

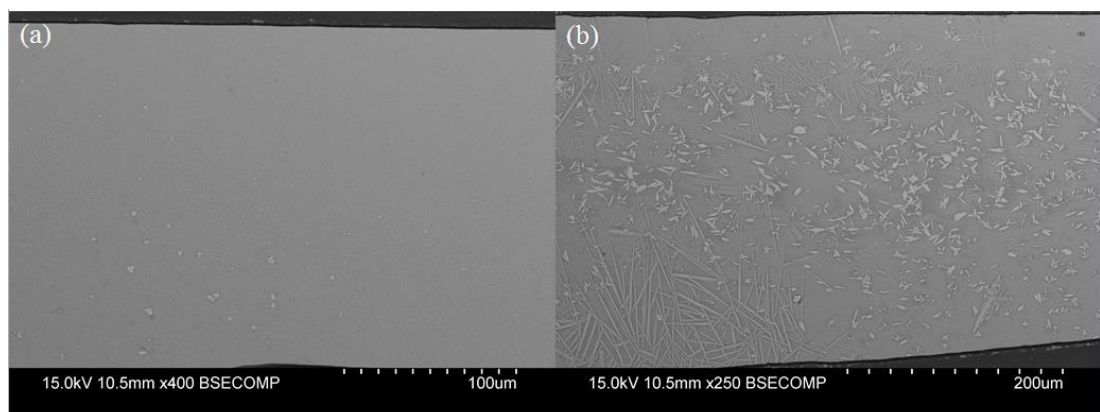


Fig. 5.25 SEM micrographs of the $\text{Al}_{74.18}\text{Co}_{7.64}\text{Si}_{18.18}$ wedge at (a) 195 μm and (b) 320 μm .

Chapter 6

Glass Formation in Al-Ni-Si and Al-Ni-Co-Si Alloys

6.1 Introduction

The propensity for glass formation in the Al-Fe-Si and Al-Co-Si ternary alloy systems was reported in the chapter 5. In addition to these systems, Al-Ni-Si alloys are another significant type of Al-LTM-Si system requiring further investigation since it has been shown that: (i) Al-Ni-RE alloys have better GFA than Al-Fe-RE (Audebert et al. 1997), and (ii) in metal-metal-type alloys, the addition of Ni also improved GFA in Al-Mg-Cu alloys (Guo et al. 2001). In previous investigations, it was believed that the addition of Ni to Al-based alloys stabilized close packed clusters around Ni, and hence promoted glass formation (Guo et al. 2001). However, no critical thickness measurements have been reported for Al-Ni-Si alloys by copper mould casting. In this chapter, the GFA of a series of Al-Ni-Si ternary alloys were investigated via the design of potential glass-forming compositions followed by wedge casting and structural analysis of the cast alloys. Given the relatively high GFA found in Al-Ni-Si and Al-Co-Si systems and the topological and electronic similarities between Ni and Co, the effect of the partial substitution of Ni with Co on GFA in the quaternary Al-Ni-Co-Si system was also investigated in this chapter.

6.2 Al-Ni-Si Alloys

6.2.1 Composition Design of Al-Ni-Si Alloys

To test the GFR in the Al-Ni-Si system, the packing efficiency was firstly calculated for efficiently packed clusters (see Appendix A). The compositions with the highest packing efficiency were found in Al-centred clusters with coordination number (N) of 15, Ni-centred clusters with $N = 12$, and Si-centred clusters with $N = 10$. The

potential glass-forming alloys that correspond well with liquidus lines were then selected to ensure a minimum local driving force for crystallization. The corresponding compositions are given in Table 6.1 which also lists associated radius ratios, packing efficiency, and coordination numbers of the efficiently packed clusters. The selected compositions which are based on efficiently-packed cluster configurations (determined in Table 6.1) are also shown in Fig. 6.1a indicating their ‘coincidental’ proximity to liquidus lines, peritectic and eutectic reactions.

Table 6.1: Investigated Al-Ni-Si compositions (at.%) based on Miracle’s atomic packing model: R is the radius ratio between the centre atom and first shell atoms, R* is the critical radius ratio, Δ is the deviation from the critical radius ratio, and N is the coordination number, P is the point number marked in the phase diagram, and Note is the alloy designation.

Compositions	R	R*	Δ (%)	N	P	Note
Al _{69.23} Ni _{15.38} Si _{15.38}	0.910	0.902	0.93	12	1	N15-15
Al _{63.63} Ni _{9.09} Si _{27.27}	0.850	0.799	6.40	10	2	S27-9
Al _{54.54} Ni _{27.27} Si _{18.18}	0.856	0.799	7.13	10	3	S27-18
Al _{54.54} Ni _{18.18} Si _{27.27}	0.862	0.799	7.87	10	4	S18-27
Al ₅₀ Ni ₂₅ Si ₂₅	1.094	1.116	-1.96	15	5	A25-25
Al _{61.54} Ni _{15.38} Si _{23.08}	0.926	0.902	2.67	12	6	N15-23
Al _{38.46} Ni _{23.08} Si _{38.46}	0.970	0.902	7.58	12	7	N23-38
Al _{15.38} Ni _{30.76} Si _{53.85}	1.000	0.902	10.89	12	8	N31-54
Al _{68.25} Ni _{12.5} Si _{18.75}	1.059	1.116	-5.09	15	9	A13-19
Al ₅₀ Ni _{18.75} Si _{31.25}	1.099	1.116	-1.50	15	x	A19-31
Al _{31.85} Ni ₂₅ Si _{43.75}	1.143	1.116	2.37	15	y	A25-44
Al _{84.62} Ni _{7.69} Si _{7.69}	0.886	0.902	1.82	12	7-7	N7-7
Al _{83.33} Ni _{8.33} Si _{8.33}	0.887	0.884	0.33	11	8-8	N8-8
Al _{81.82} Ni _{9.09} Si _{9.09}	0.822	0.799	2.23	10	9-9	S9-9
Al ₈₀ Ni _{6.67} Si _{13.33}	1.038	1.047	-0.83	14	7-13	A7-13
Al _{73.33} Ni _{6.67} Si ₂₀	1.053	1.047	0.61	14	7-20	A7-20
Al ₈₇ Ni ₂ Si ₁₁	N/A	N/A	N/A	N/A	2-11	U2-11
Al _{74.13} Ni _{7.69} Si _{18.18}	0.900	0.902	-0.19	12	8-18	N8-18

(a) The Al-Ni-Si alloys

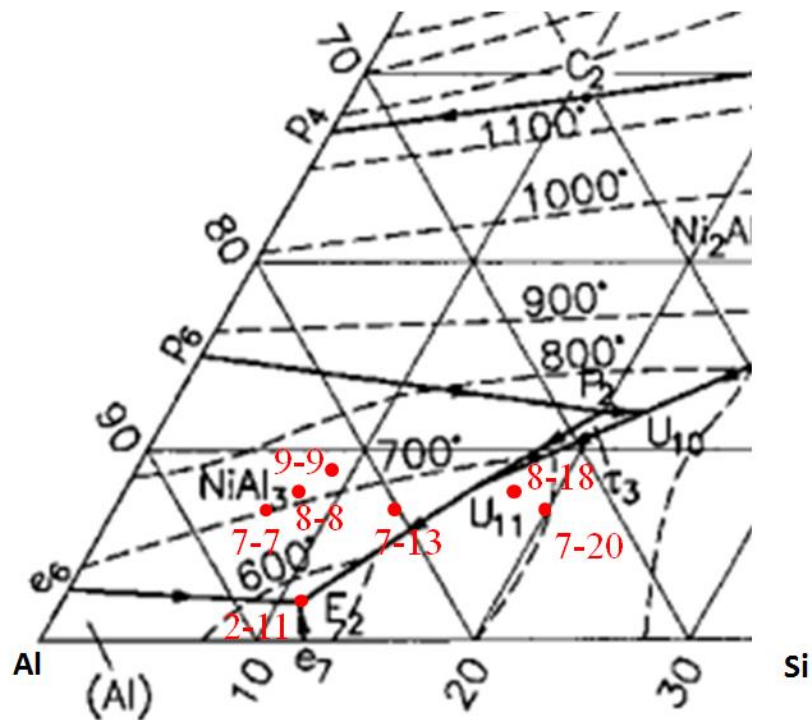
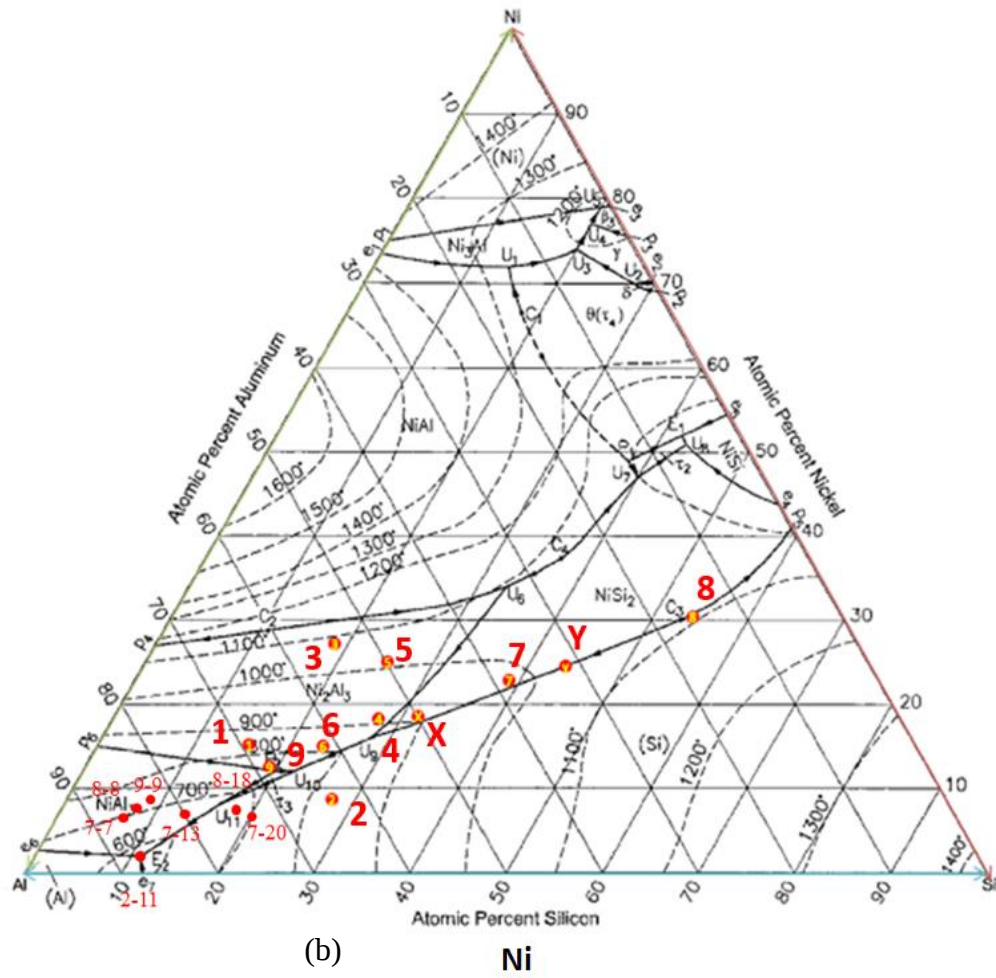


Fig. 6.1 Investigated compositions superimposed on: (a) overall, and (b) Al-rich end of the liquidus projection of the Al-Ni-Si system (Raghavan 2005).

Given the relatively high GFA found in this alloy system for prior mentioned cluster-based compositions, a more extensive range of alloy compositions was explored (shown more closely in Fig. 6.1b), particularly with liquidus temperatures below 800°C in the Al-rich region of the phase diagram, given that the considerably lower liquidus temperature aptly satisfies the driving force criteria. Efficiently-packed cluster-based compositions in this region consisted of Si-centred clusters with $N = 10$; Ni-centred clusters with $N = 11$ and 12 and Al-centred clusters with $N = 14$. The radius ratio, packing efficiency, and coordination numbers are also listed in Table 6.1. In addition to the cluster-based compositions, the deep eutectic point located at $\text{Al}_{87}\text{Ni}_2\text{Si}_{11}$ was also inspected for GFA, given the possible deep undercooling that can be achieved at eutectic reactions.

6.2.2 Copper Mould Casting of the Al-Ni-Si Alloys

Compositions listed in Table 6.1 were prepared from 99.9% Al, 99.999+% Si and 99.98% Ni using a mini arc melter in a Ti-gettered argon atmosphere. Wedge-shaped samples were produced by suction casting into copper moulds using 30-60% current and 25-100% open valve. Due to the broad composition range over a large area of the phase diagram (Fig. 6.1), there was a variation in both the melting point and viscosity of the alloys. Compositions of N1, N2, N4, N6, N9 (Fig. 6.2a,b,d,f,i) have a small amount of alloy drawn out of the copper mould by vacuum, which is probably due to their relatively low melting temperatures (Fig. 6.1). The composition N3 (Fig. 6.2c) was cast twice in the 20:1 copper mould as the first trial did not succeed, likely due to premature crystallization that led to a high casting viscosity probably because of this alloy's considerably high melting temperature of over 1100°C.

6.2.3 Scanning Electron Microscopy of Al-Ni-Si Alloys

The microstructure on the cross-sections of wedge-cast samples was inspected directly using a Hitachi S3400 SEM with in both secondary electron and backscattered electron modes. The voltage was 15 kV; the probe current was 105 μA ; the working distance was 10 mm. EDS line scan and mapping were used for the qualitative analysis of chemical compositions for regions or phases of interest.

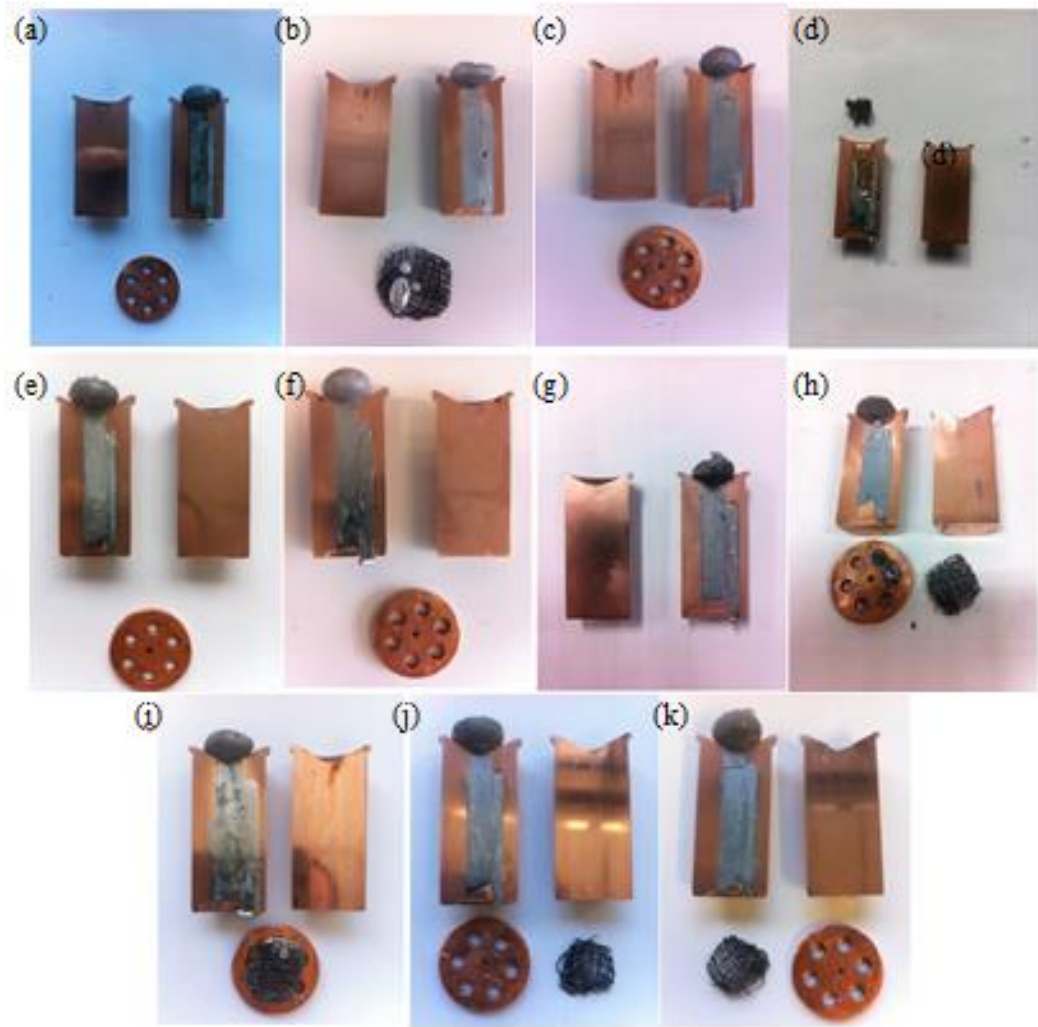


Fig. 6.2 The Al-Ni-Si wedges produced using 20:1 moulds with compositions of: (a) N1, (b) N2, (c) N3, (d) N4, (e) N5, (f) N6, (g) N7, (h) N8, (i) N9, (j) Nx, and (k) Ny.

6.2.3.1 $\text{Al}_{69.23}\text{Ni}_{15.38}\text{Si}_{15.38}$, $\text{Al}_{63.63}\text{Ni}_{9.09}\text{Si}_{27.27}$, $\text{Al}_{54.54}\text{Ni}_{27.27}\text{Si}_{18.18}$, and $\text{Al}_{54.54}\text{Ni}_{18.18}\text{Si}_{27.27}$ alloys

$\text{Al}_{69.23}\text{Ni}_{15.38}\text{Si}_{15.38}$ (N1) wedge tips had the width of $210\mu\text{m}$ and $75\mu\text{m}$ by 10:1 and 20:1 moulds, respectively. Crystalline dendrites were observed at the tip of the 10:1 wedge casting, however, a featureless zone was evident at the tip of the 20:1 wedge casting, where crystallites begin to appear at a casting thickness of $108\mu\text{m}$ (Fig. 6.3a). The $\text{Al}_{63.63}\text{Ni}_{9.09}\text{Si}_{27.27}$ (N2) wedge samples had tips of $6\mu\text{m}$ and $54\mu\text{m}$ in width when cast in the 20:1 and 10:1 copper moulds, respectively. A featureless zone of up to $50\mu\text{m}$ in width was observed for the 20:1 casting and up to $70\mu\text{m}$ width in the 10:1 wedge casting (Fig. 6.3b). Dendrites were clearly present in both wedge tips of the $\text{Al}_{54.54}\text{Ni}_{27.27}\text{Si}_{18.18}$ (N3) (Fig. 6.3c) and $\text{Al}_{54.54}\text{Ni}_{18.18}\text{Si}_{27.27}$ (N4) (Fig. 6.3d), alloys,

indicating that GFA is negligible for these lower Al-content compositions with higher melting points.

6.2.3.2 $\text{Al}_{50}\text{Ni}_{25}\text{Si}_{25}$, $\text{Al}_{61.54}\text{Ni}_{15.38}\text{Si}_{23.08}$, $\text{Al}_{38.46}\text{Ni}_{23.08}\text{Si}_{38.46}$, and $\text{Al}_{15.38}\text{Ni}_{30.76}\text{Si}_{53.85}$ alloys

The $\text{Al}_{50}\text{Ni}_{25}\text{Si}_{25}$ (N5) wedge tips were $90\mu\text{m}$ and $180\mu\text{m}$ for the 20:1 and 10:1 wedge casting, respectively. Crystalline structures were present in both tips (Fig. 6.4a). The $\text{Al}_{61.54}\text{Ni}_{15.38}\text{Si}_{23.08}$ alloy samples (N6) had tips of $60\mu\text{m}$ and $33\mu\text{m}$ in thickness for the 10:1 and 20:1 castings, and here coarse crystallites appear at casting thicknesses of $93\mu\text{m}$ and $90\mu\text{m}$ for these samples (Fig. 6.4b). The $\text{Al}_{38.46}\text{Ni}_{23.08}\text{Si}_{38.46}$ (N7) wedge tips were $55\mu\text{m}$ and $100\mu\text{m}$ for 20:1 and 10:1 castings, and large dendrites were present at the tips of both sample castings (Fig. 6.4c). The $\text{Al}_{15.38}\text{Ni}_{30.76}\text{Si}_{53.85}$ (N8) wedges had as-cast tips of $85\mu\text{m}$ and $250\mu\text{m}$ in width for the 20:1 and 10:1 samples; similarly for this low Al-content composition coarse crystallites were present in both tips (Fig. 6.4d).

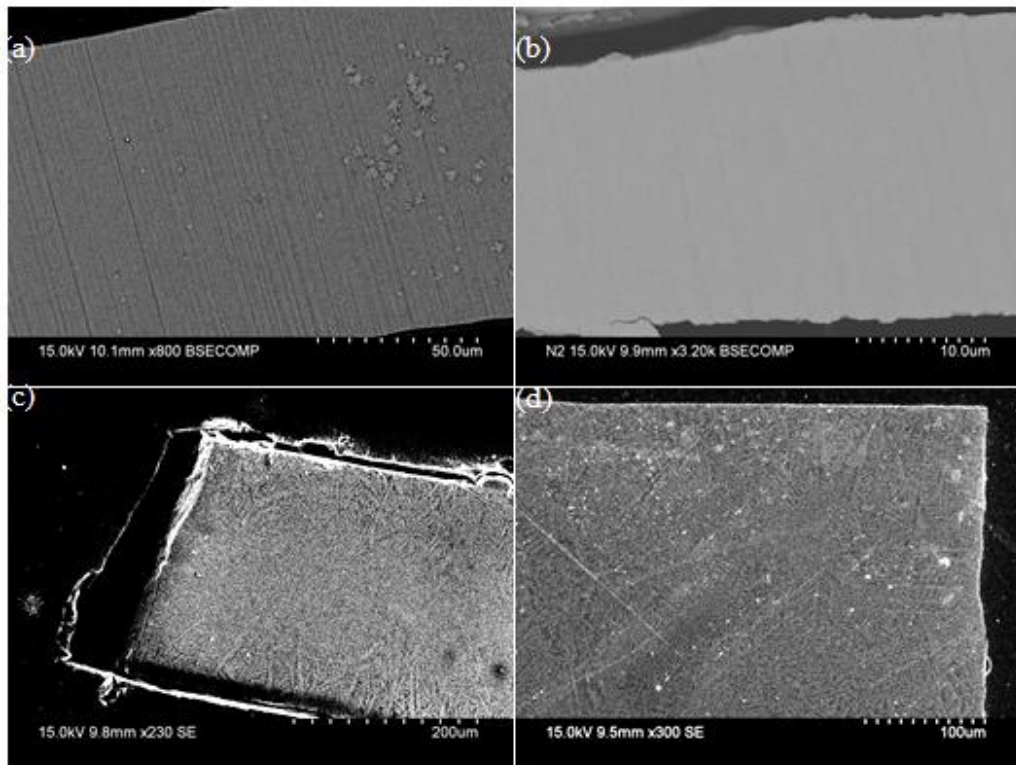


Fig. 6.3 Microstructure of: (a) $\text{Al}_{69.23}\text{Ni}_{15.38}\text{Si}_{15.38}$ (N1), (b) $\text{Al}_{63.63}\text{Ni}_{9.09}\text{Si}_{27.27}$ (N2), (c) $\text{Al}_{54.54}\text{Ni}_{27.27}\text{Si}_{18.18}$ (N3), (d) $\text{Al}_{54.54}\text{Ni}_{18.18}\text{Si}_{27.27}$ (N4).

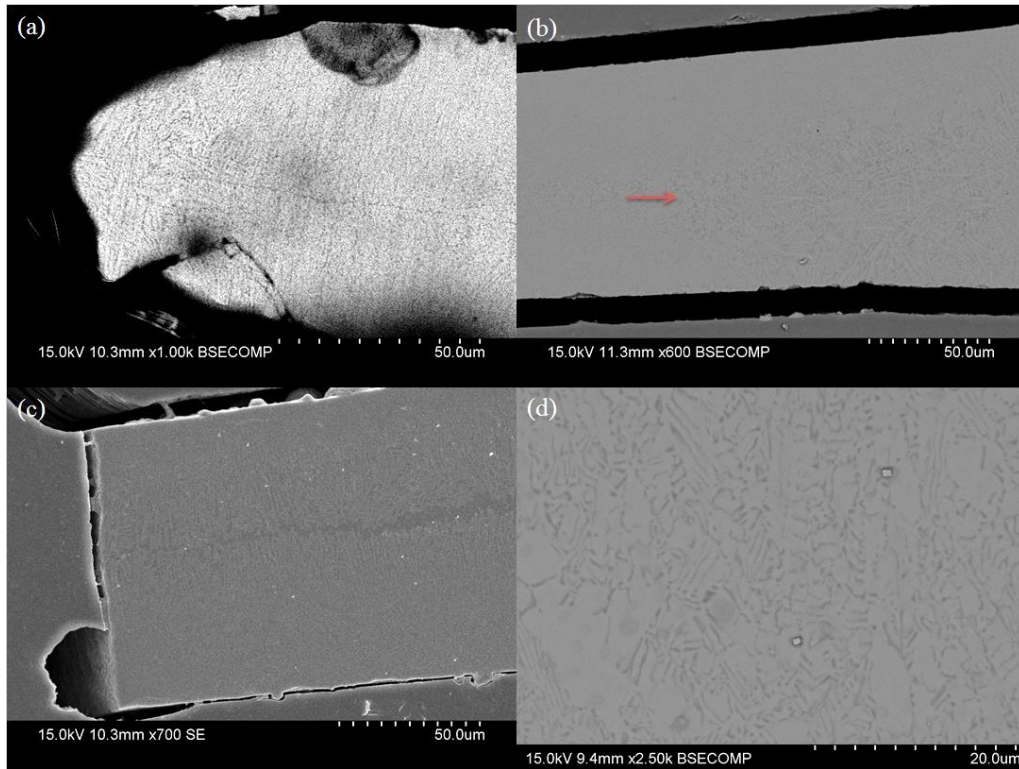


Fig. 6.4 Microstructure of: (a) $\text{Al}_{50}\text{Ni}_{25}\text{Si}_{25}$ (N5), (b) $\text{Al}_{61.54}\text{Ni}_{15.38}\text{Si}_{23.08}$ (N6), (c) $\text{Al}_{38.46}\text{Ni}_{23.08}\text{Si}_{38.46}$ (N7), (d) $\text{Al}_{15.38}\text{Ni}_{30.76}\text{Si}_{53.85}$ (N8).

6.2.3.3 $\text{Al}_{68.25}\text{Ni}_{12.50}\text{Si}_{18.75}$, $\text{Al}_{50}\text{Ni}_{18.75}\text{Si}_{31.25}$, and $\text{Al}_{31.85}\text{Ni}_{25}\text{Si}_{43.75}$ alloys

The wedge tip thickness of 20:1 and 10:1 samples for the $\text{Al}_{68.25}\text{Ni}_{12.50}\text{Si}_{18.75}$ alloy (N9) were 80 μm and 100 μm , respectively. Crystalline phases were present in the 10:1 wedge, however a featureless zone was present at tip of the 20:1 wedge sample (Fig. 6.5a), where crystalline phases begin to appear at a wedge thickness of 160 μm , likely due to the higher cooling rate provided by the narrower wedge geometry (Fig. 6.5b). The $\text{Al}_{50}\text{Ni}_{18.75}\text{Si}_{31.25}$ (Nx) alloy samples exhibited wedge tips of 55 μm and 95 μm in width for the 20:1 and 10:1 geometries. Crystalline phases appear to nucleate and coarsen at the centre of the 20:1 casting (Fig. 6.5c) but extend across the entire wedge in the 10:1 casting - again likely due to the higher cooling rate associated with the 20:1 geometry and the slower cooling rate experienced at the centre of the casting. The $\text{Al}_{31.85}\text{Ni}_{25}\text{Si}_{43.75}$ (Ny) wedge sample tips were 75 μm and 320 μm in thickness for the 20:1 and 10:1 configurations and highly directional dendrites were present in both of these samples (Fig. 6.5d).

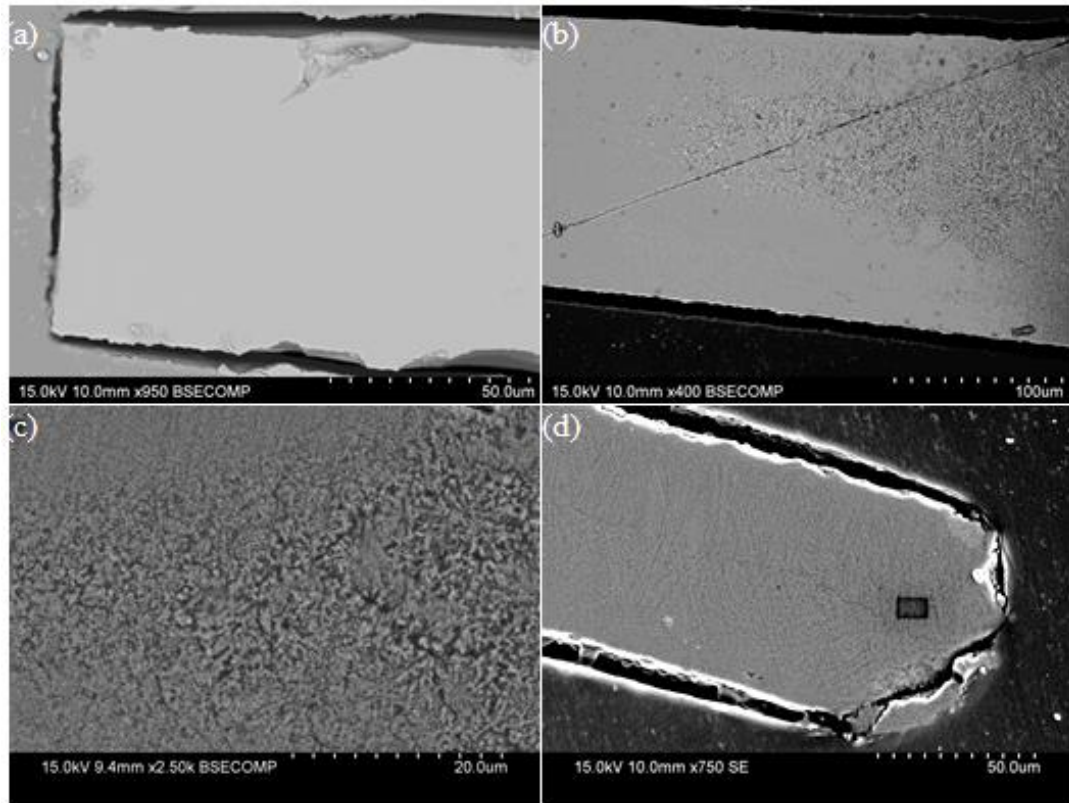


Fig. 6.5 Microstructure of: (a-b) $\text{Al}_{68.25}\text{Ni}_{12.50}\text{Si}_{18.75}$ (N9), (c) $\text{Al}_{50}\text{Ni}_{18.75}\text{Si}_{31.25}$ (Nx), (d) $\text{Al}_{31.85}\text{Ni}_{25}\text{Si}_{43.75}$ (Ny).

6.2.3.4 $\text{Al}_{84.62}\text{Ni}_{7.69}\text{Si}_{7.69}$, $\text{Al}_{83.33}\text{Ni}_{8.33}\text{Si}_{8.33}$, and $\text{Al}_{81.82}\text{Ni}_{9.09}\text{Si}_{9.09}$ alloys

The $\text{Al}_{84.62}\text{Ni}_{7.69}\text{Si}_{7.69}$ (7-7) wedge cast in the 20:1 copper mould had tip with width of $33\mu\text{m}$; a large bright contrast crystallite was present (Fig. 6.6a) in this casting. EDS mapping indicated that this is a Ni-rich Al-Ni-Si phase (Fig. 6.6a insert). Given the size of this crystallite, it was considered to be a casting/processing defect, where sometimes during the arc melting and vacuum casting process, large un-melted crystallites still in strong contact with the chilled copper hearth can be dragged into a casting, creating this kind of casting defect. It is quite clear that this crystallite has not triggered further crystallization in this region, which is also an indicator that this is not related to the GFA of this alloy. Much finer crystallites were found to precipitate at a wedge thickness of $45\mu\text{m}$ and dendrites initiated at $80\mu\text{m}$ in this sample. The $\text{Al}_{83.33}\text{Ni}_{8.33}\text{Si}_{8.33}$ (8-8) composition exhibited a wedge tip of $220\mu\text{m}$ in thickness consisting of coarse dendritic crystallites (Fig. 6.6c). A similar result was realized for the $\text{Al}_{81.82}\text{Ni}_{9.09}\text{Si}_{9.09}$ (9-9) alloy where the wedge produced using the 20:1 copper mould was $240\mu\text{m}$ in width with a fine crystal zone at the edge of the

casting closest to the mould walls 25 μm wide was observed progressively coarsening towards the centre of the casting (Fig. 6.6d).

6.2.3.5 $\text{Al}_{80}\text{Ni}_{6.67}\text{Si}_{13.33}$, $\text{Al}_{73.33}\text{Ni}_{6.67}\text{Si}_{20}$, and $\text{Al}_{87}\text{Ni}_2\text{Si}_{11}$ alloys

The $\text{Al}_{80}\text{Ni}_{6.67}\text{Si}_{13.33}$ (7-13) alloy wedge casting exhibited a largely crystallised tip 380 μm in width (Fig. 6.7a). Crystallisation appeared uniform throughout the tip region, indicating slow crystal nucleation and growth kinetics for this composition and the possibility that the matrix surrounding these crystallites may be amorphous. Similarly in the $\text{Al}_{73.33}\text{Ni}_{6.67}\text{Si}_{20}$ (7-20) wedge, which had an as-cast tip 120 μm wide shows nucleation at the mould walls and island-like nucleation centres with larger dendrites emanating from these sites within a dark matrix (Fig. 6.7a). The microstructure of deep eutectic point $\text{Al}_{87}\text{Ni}_2\text{Si}_{11}$ (2-11) was quite different from all compositions (Fig. 6.7b); which might be due to the abundance of Al atoms and low amount of Ni. EDS analysis at the wedge tip of 100 μm width indicated that the dark phase is α -Al and the brighter contrast regions are Al-Si rich as indicated in (Fig. 6.7d) and correspond well with the Al-Si binary eutectic reaction composition. Nickel appears to be uniformly distributed within the limits of detection. The morphology implied that, although the driving force of crystallization is very low at this deep eutectic point, the deficiency of solute atoms such as Ni and Si required for sufficient efficiently-packed topologies and increased entropy tends to lead to a high nucleation rate of α -Al rather than an amorphous phase.

6.2.3.6 $\text{Al}_{74.13}\text{Ni}_{7.69}\text{Si}_{18.18}$ alloys

Previous sections in this chapter have demonstrated that the GFA at Al-rich corner (i.e. Al-content > 80 at.%) was not necessarily better than those explored with higher melting temperatures between 700°C and 900°C. Further, the Al-rich Al-Ni-Si compositions are not comparable in GFA to the Al-Ni-RE alloys. This indicates that the driving force criteria may only be effective when the amount of solute is above certain level (i.e. a higher entropy or atomic diversity is essential to arrest crystallisation kinetics) or when specific efficiently-packed topologies are achieved which may have been the case for $\text{Al}_{84.62}\text{Ni}_{7.69}\text{Si}_{7.69}$ (7-7) which showed the highest GFA of the alloys examined in the Al-rich region. In this section, a composition of $\text{Al}_{74.13}\text{Ni}_{7.69}\text{Si}_{18.18}$ (8-18), which simultaneously corresponds to two efficiently-packed solute-centred clusters was selected. SEM micrographs in Fig. 6.8 show the wedge tip, with a width of 160 μm and the first crystalline structures appearing at a

casting thickness of 400 μm . This is the largest featureless zone identified in Al-Si based alloys to date.

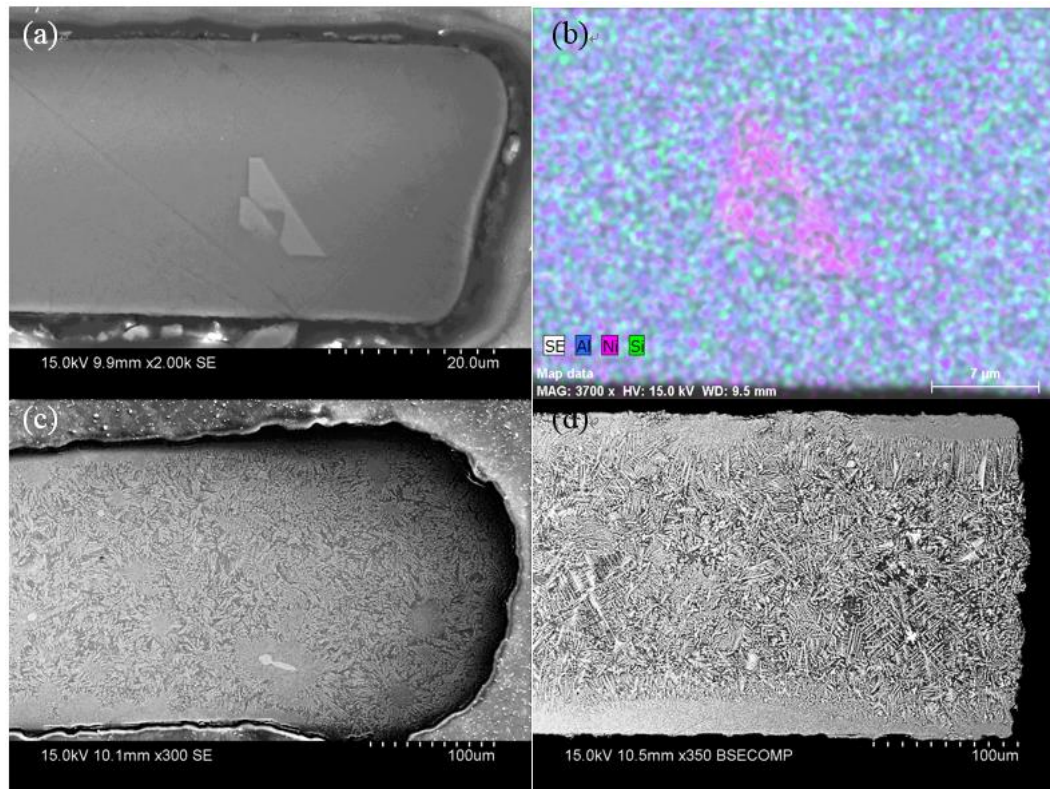


Fig. 6.6 Microstructure of: (a-b) $\text{Al}_{84.62}\text{Ni}_{7.69}\text{Si}_{7.69}$ (7-7) with EDS mapping; (c) $\text{Al}_{83.33}\text{Ni}_{8.33}\text{Si}_{8.33}$ (8-8); (d) $\text{Al}_{81.82}\text{Ni}_{9.09}\text{Si}_{9.09}$ (9-9).

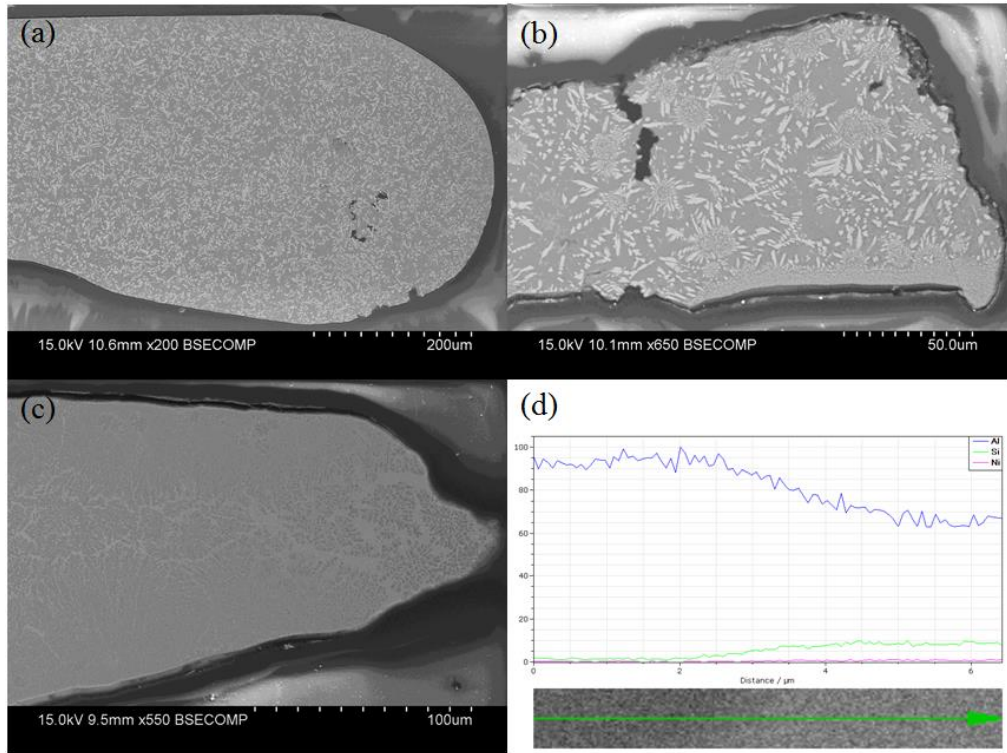


Fig. 6.7 Microstructure of: (a) $\text{Al}_{80}\text{Ni}_{6.67}\text{Si}_{13.33}$ (7-13); (b) $\text{Al}_{73.33}\text{Ni}_{6.67}\text{Si}_{20}$ (7-20); (c) deep eutectic $\text{Al}_{87}\text{Ni}_2\text{Si}_{11}$ (2-11) with (d) EDS line scan.

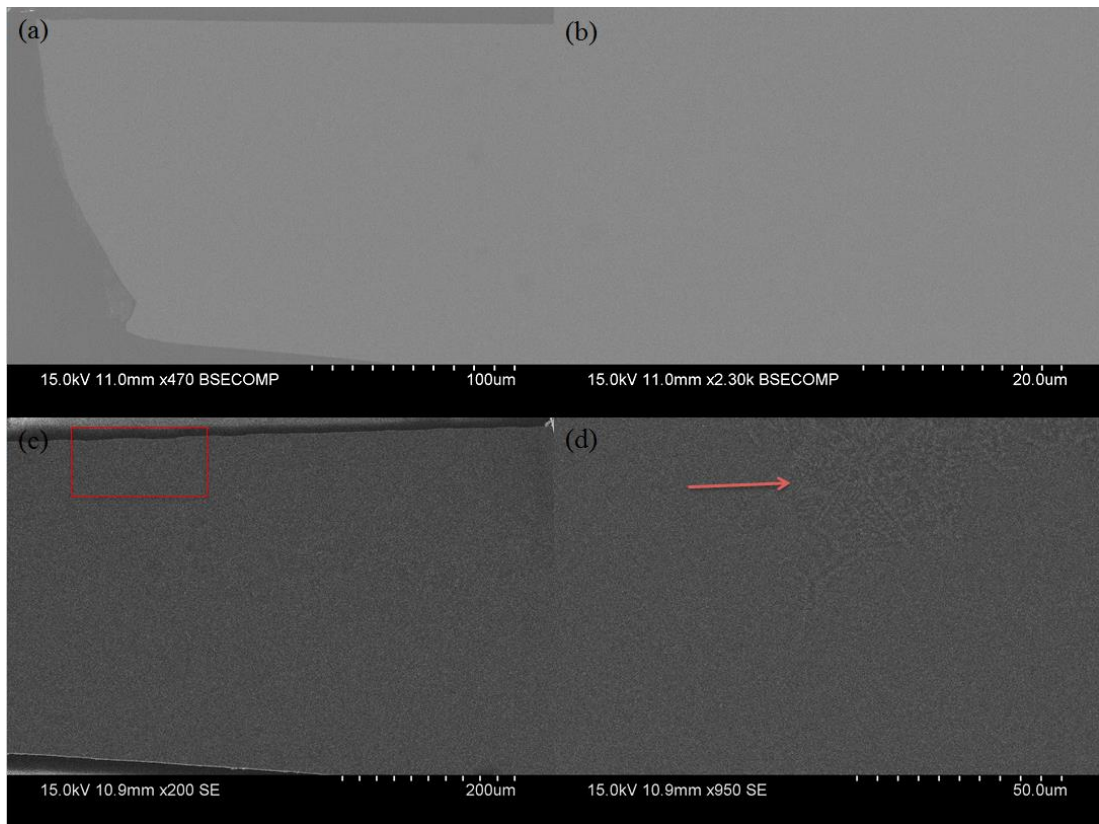


Fig. 6.8 Microstructure of $\text{Al}_{74.13}\text{Ni}_{7.69}\text{Si}_{18.18}$ at: (a-b) 160 μm; (c-d) 400 μm.

The GFA of the Al-Ni-Si alloys examined in this work are summarized in Fig. 6.9. Of the ternary systems studied in this thesis, the Al-Ni-Si system has shown the highest propensity for glass-formation with the $\text{Al}_{74.13}\text{Ni}_{7.69}\text{Si}_{18.18}$ (8-18) alloy exhibiting a featureless zone at the wedge tip and the presence of fine crystals at a casting thickness of 400 μm . GFA in this system will be discussed in more detail in the following sections.

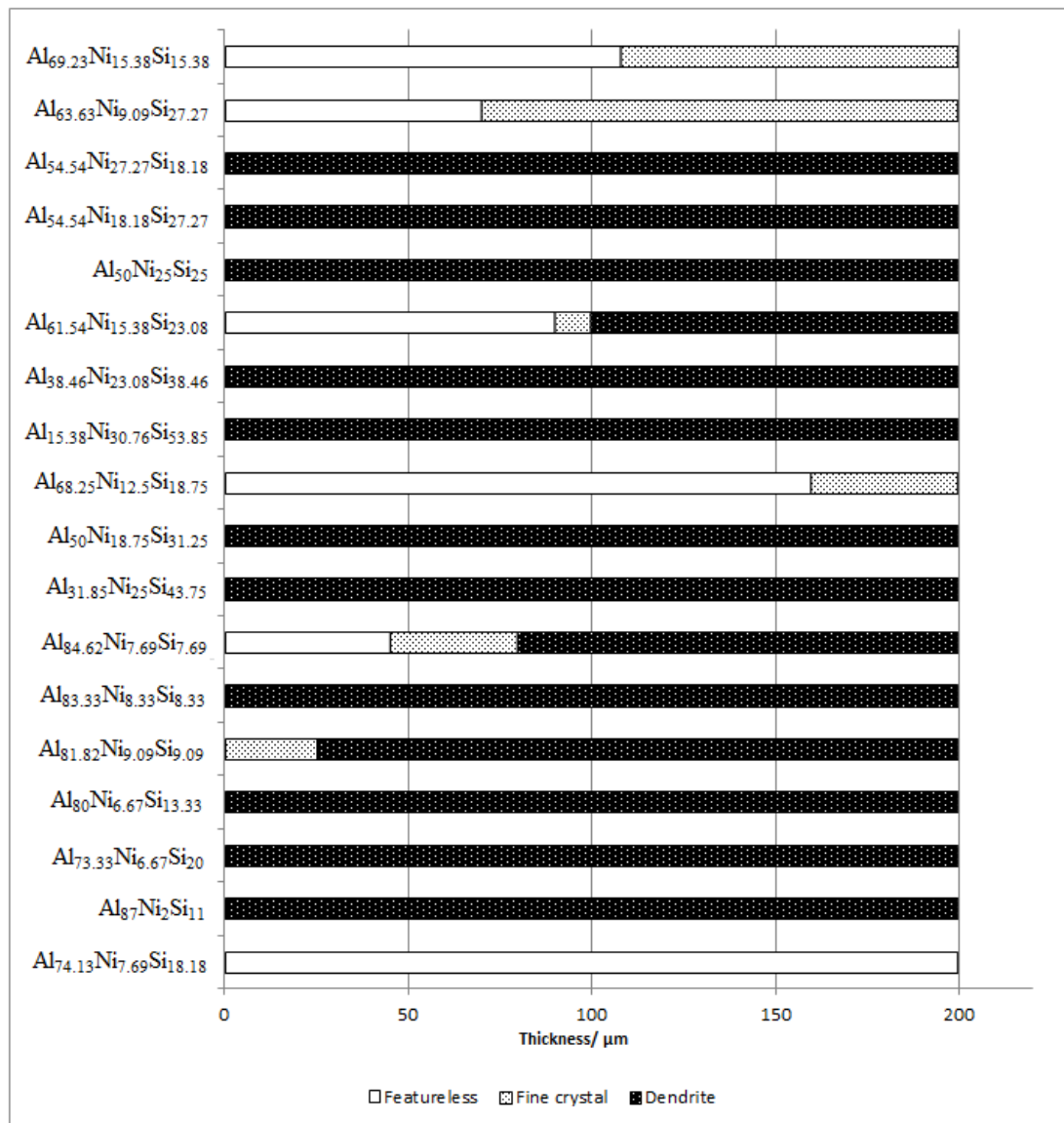


Fig. 6.9 Different microstructures in Al-Ni-Si alloys.

6.2.4 X-Ray Diffraction for Al-Ni-Si Alloys

Due to the relatively small size of the amorphous region in these wedge-cast samples and the interactive area associated with the spot size (500 μm diameter) of the XRD

micro-capillary set up used (see section 3.5.1), crystalline phases were detected in the majority of samples, hence laboratory scale XRD proves insufficient to compare the GFA of different compositions for this case. Crystalline phases in proximity to wedge tips and crystallised zones were investigated. The angular range of scanning was 20° to 80° , and the step size and time was 0.02° and 2s, respectively. The XRD spectra of the alloys are given in Fig. 6.10. There are peaks in each spectrum, thereby indicated that crystalline phases are present. Similar to other wedges, peaks were present in XRD spectra of the $\text{Al}_{74.13}\text{Ni}_{7.69}\text{Si}_{18.18}$ (8-18) sample (Fig. 6.11) and those of the N1, N2, N6, N9 alloys. Two major crystalline peaks evident in many traces at approximately 37° and $4^\circ 2\theta$ were later found to be due to copper induction tape attached remotely to the sample mounting blocks.

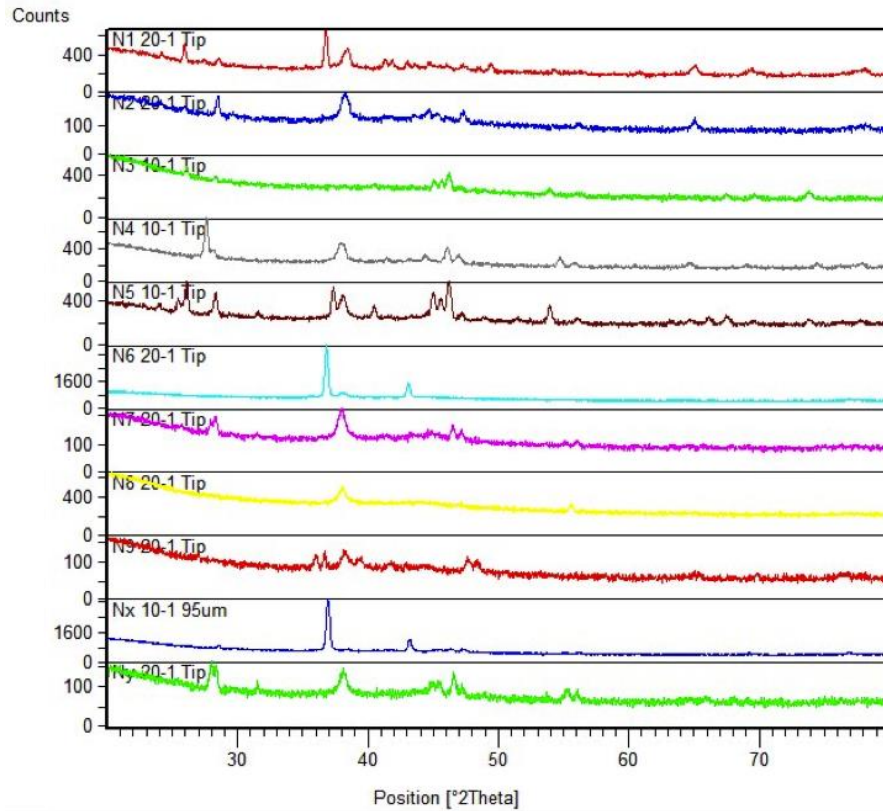
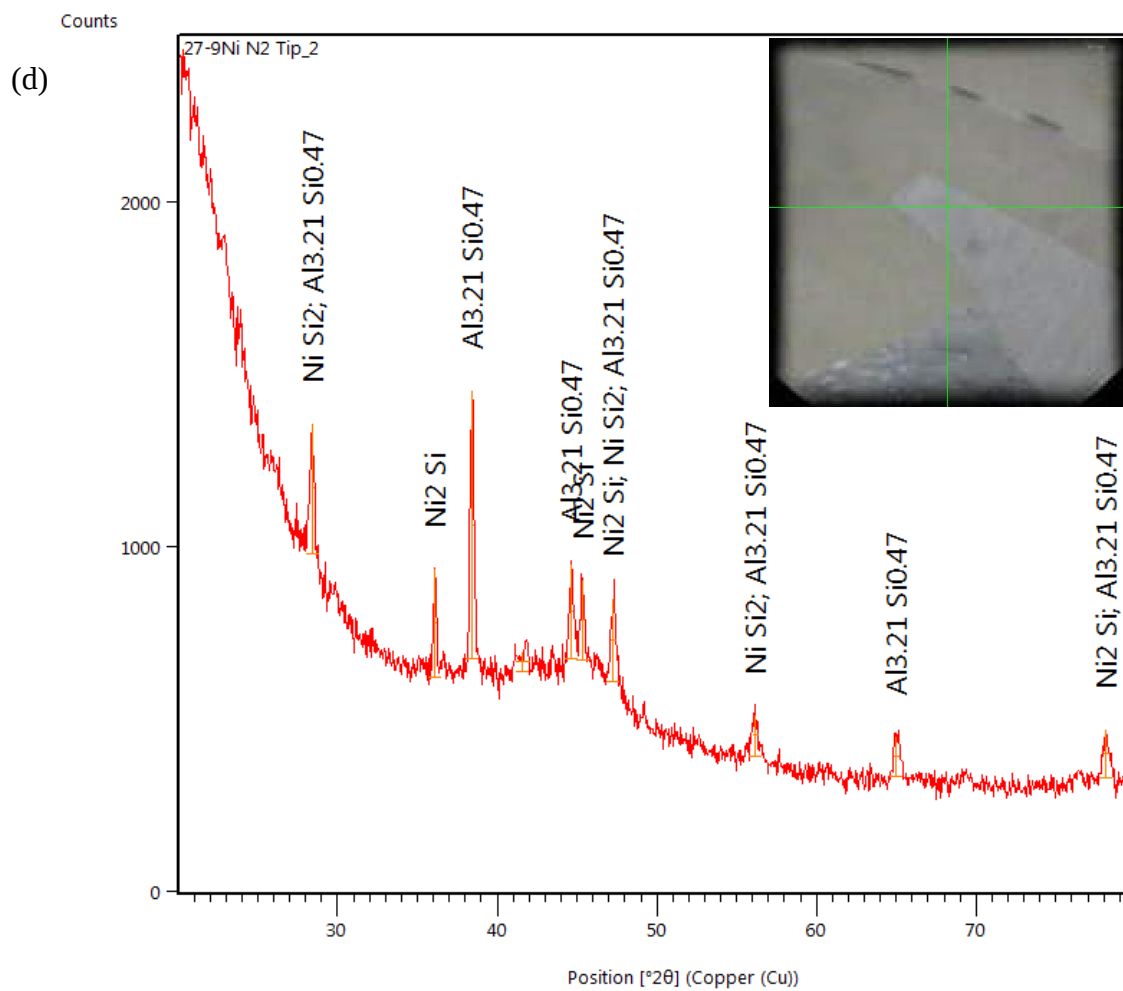
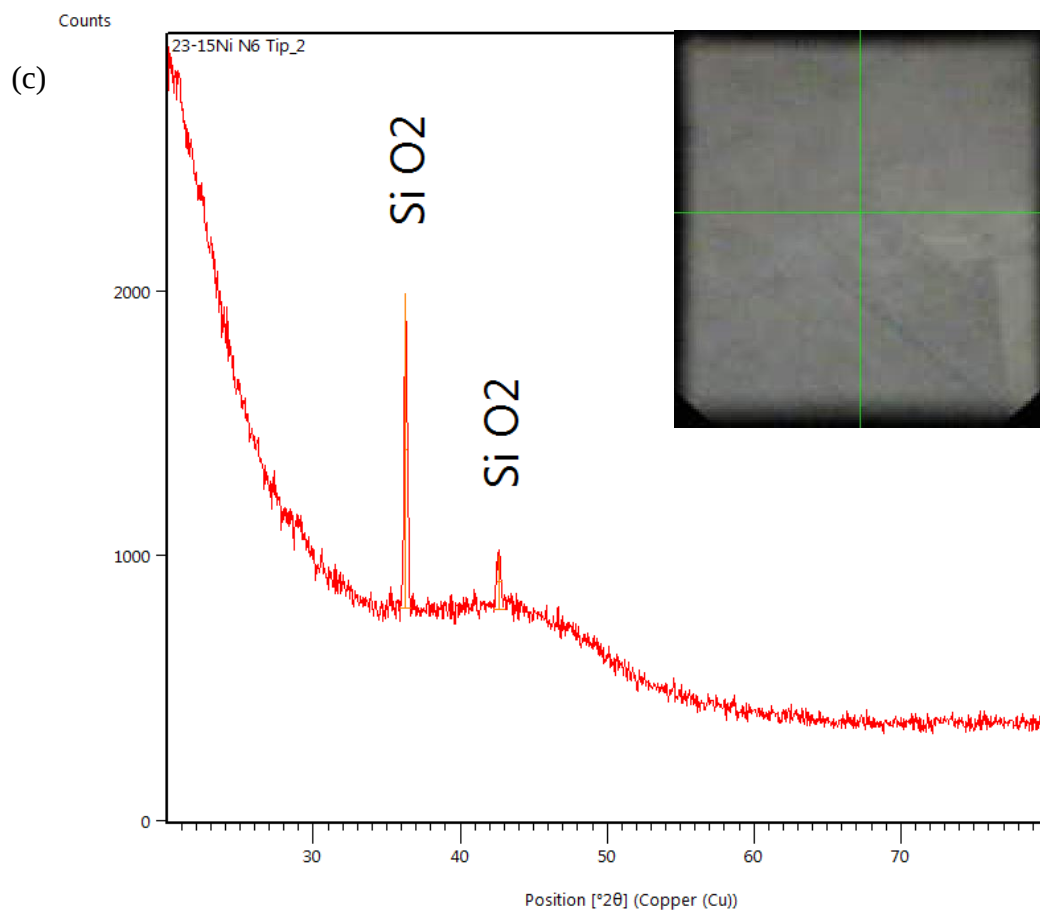


Fig. 6.10 X-ray Diffraction spectra of the Al-Ni-Si alloys given in Table 6.1.

The faces of wedge tips for selected Al-Ni-Si alloys with notably large featureless zones were also scanned for crystallinity and it can be seen in Fig. 6.11 that the characteristic amorphous halo between 40° and $50^\circ 2\theta$ is present to some extent in all samples.



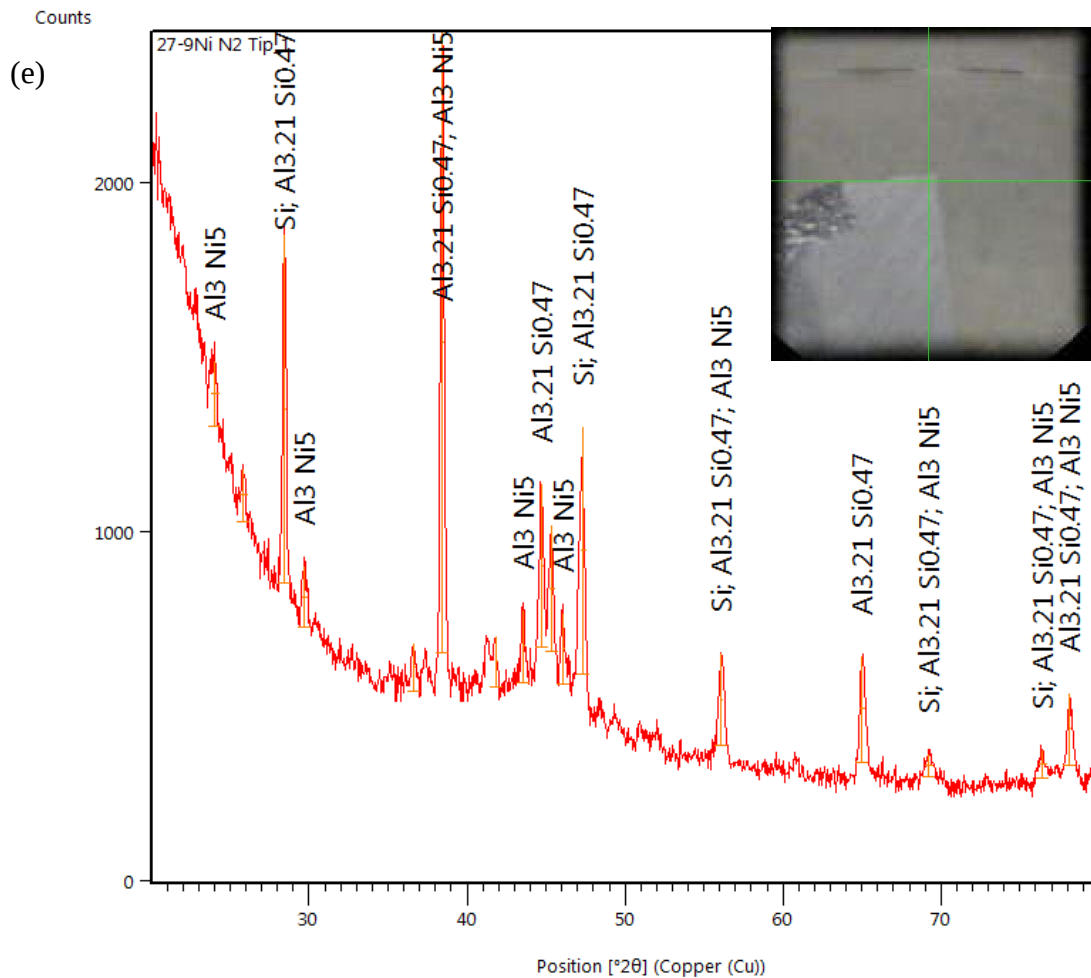


Fig. 6.11 XRD spectra from the front area of wedges with featureless zones: (a) $\text{Al}_{69.23}\text{Ni}_{15.38}\text{Si}_{15.38}$ (N1) 20:1 (b) $\text{Al}_{61.54}\text{Ni}_{15.38}\text{Si}_{23.08}$ (N6) 20:1 (c) $\text{Al}_{61.54}\text{Ni}_{15.38}\text{Si}_{23.08}$ (N6) 10:1 (d) $\text{Al}_{63.63}\text{Ni}_{9.09}\text{Si}_{27.27}$ (N2) 10:1 (e) $\text{Al}_{63.63}\text{Ni}_{9.09}\text{Si}_{27.27}$ (N2) 20:1.

6.2.5 Focused Studies on the $\text{Al}_{74.13}\text{Ni}_{7.69}\text{Si}_{18.18}$ Amorphous Alloy

The $\text{Al}_{74.13}\text{Ni}_{7.69}\text{Si}_{18.18}$ sample produced in Section 6.2.1 showed the highest GFA of the alloys studied and thus was selected for further investigation.

6.2.5.1 Transmission Electron Microscopy (TEM)

A thin foil from the centre and edge of the featureless wedge tip was prepared using a focused ion beam (FIB) and placed on a TEM grid using a micro-force cantilever. Upon exposure to the TEM 200keV electron beam, there was a clear reaction between the sample microstructure and the beam during imaging, indicating a very low thermal stability of this alloy. Resultant TEM micrographs showed nanocrystals of between 50 and 100nm were present in both foils (Fig. 6.12) and large dark contrast regions of around 700 nm had evolved which were not seen in prior SEM or FIB imaging. The inset SAED image in Figs. 6.12a and 6.12c confirms the presence of both nanocrystals and some larger crystallites. Similar instabilities under TEM

observation were also reported by Legresy et al. (1988) and given the low crystallisation temperatures of amorphous alloys found in this system, of between 127 and 177°C (Tsai et al. 1988b; Gögebakan et al. 2009), this response to a high energy electron beam would be expected.

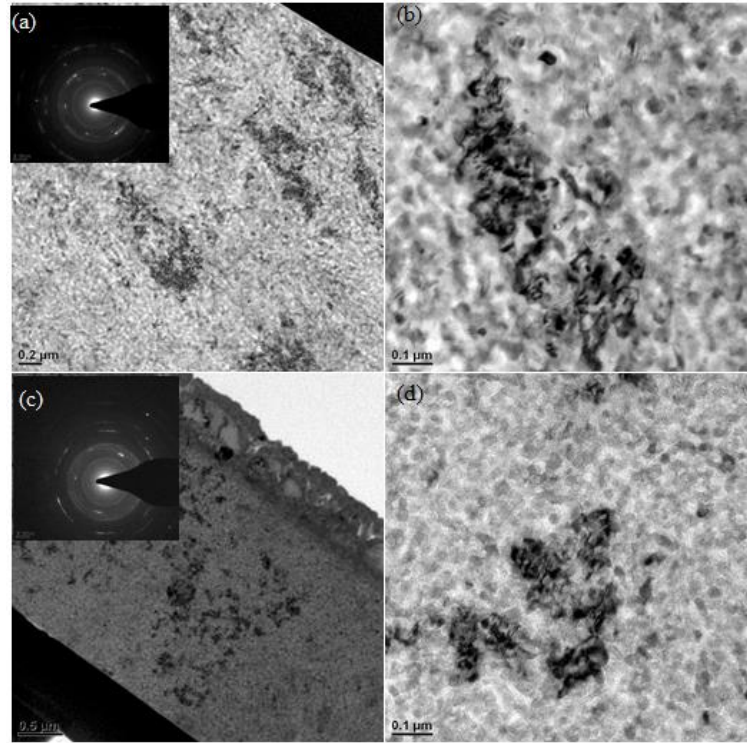


Fig. 6.12 TEM micrographs of $\text{Al}_{74.13}\text{Ni}_{7.69}\text{Si}_{18.18}$ foils from wedge tip at: (a-b) centre, (c-d) edge; SAED were inserted in (a) and (c) for corresponding figures.

6.2.5.2 NanoSEM Microstructural Investigation

Given the instability of the $\text{Al}_{74.13}\text{Ni}_{7.69}\text{Si}_{18.18}$ amorphous alloy using TEM, a high resolution Nova NanoSEM was used to probe the microstructure of the as-cast alloy in more depth. Even at high resolution, the tip region was found to exhibit little contrast that would be associated with a crystalline microstructure (Fig. 6.13a). In this high resolution analysis, crystalline structures were first observed at a wedge thickness of 300 μm (Fig. 6.13b), which rapidly coarsened and become more defined throughout the entire wedge section as wedge thickness increased to 400 μm (Fig. 6.13c-d) becoming a large dendritic structure beyond 500 μm in thickness.

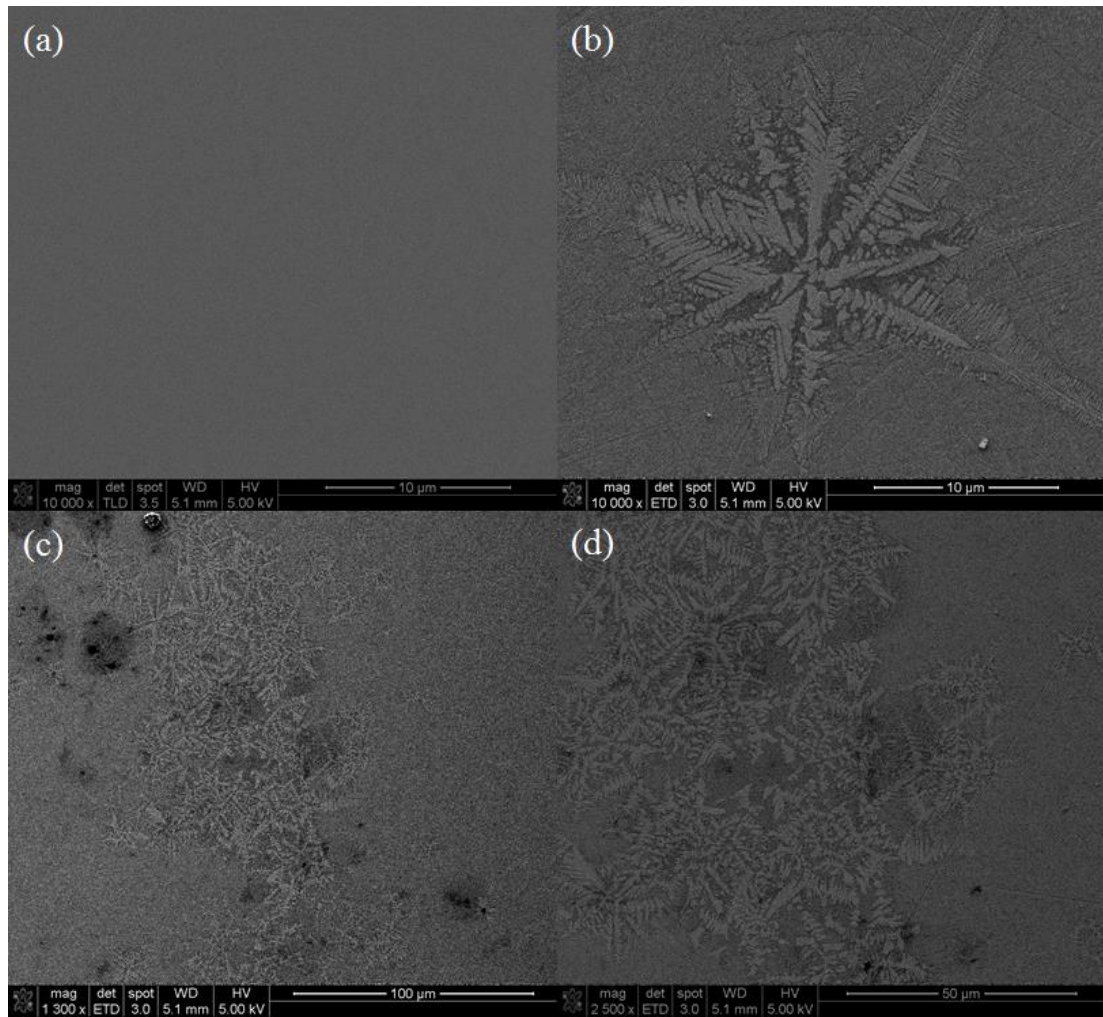


Fig. 6.13 Nano-SEM micrographs of $\text{Al}_{74.13}\text{Ni}_{7.69}\text{Si}_{18.18}$ at (a) 160 μm (b) 300 μm , and (c-d) 400 μm .

6.2.5.3 Mechanical Properties

Vickers microhardness testing was carried out on the tip region of the $\text{Al}_{74.13}\text{Ni}_{7.69}\text{Si}_{18.18}$ amorphous alloy for a range of applied loads (Fig. 6.14a); the average hardness was $372 \pm 71 \text{ HV}$. Closely inspecting the indents using SEM, no obvious cracks, shear bands or crystals are observed (inset to Fig. 6.14a), indicating that this amorphous alloy is quite ductile and that there are no brittle intermetallics present.

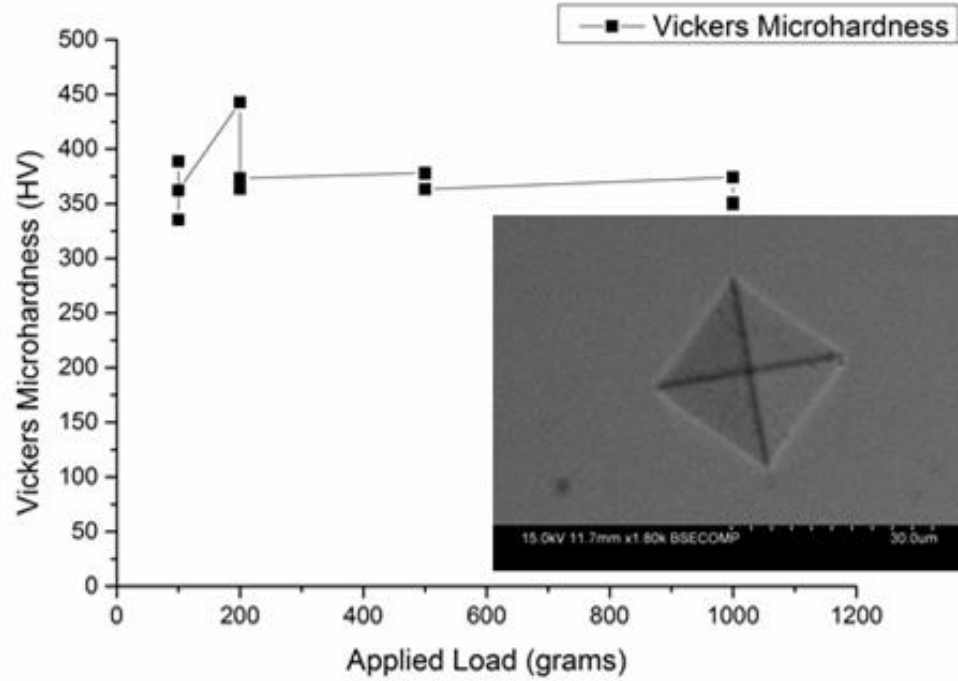


Fig. 6.14 Microhardness with an insert of a SEM micrograph of indentation.

6.3 Al-Ni-Co-Si Alloys

6.3.1 Quaternary Alloy Design and Processing

Given that the highest GFA was found in the Al-Co-Si and Al-Ni-Si ternary systems studied in this thesis, a range of quaternary alloys was cast by partially substituting Ni for Co in the highest glass forming alloy composition found, $\text{Al}_{74.13}\text{Ni}_{7.69}\text{Si}_{18.18}$, in an attempt to improve GFA. This is similar to the successful approach used to discover BMGs in the Al-Ni-Co-RE alloys (Yang et al. 2009). In this work, Ni partially substituted by 2, 4 and 6 at.% Co. As sufficient heat and high cooling rate was found essential for the glass formation in the previous section, different casting conditions were also used for each composition in order to further establish the role of processing conditions on the generation of an amorphous microstructure. These are listed in Table 6.2.

Table 6.2: Casting conditions of quaternary $\text{Al}_{74}\text{Si}_{18}\text{Ni}_6\text{Co}_2$, $\text{Al}_{74}\text{Si}_{18}\text{Ni}_4\text{Co}_4$, and $\text{Al}_{74}\text{Si}_{18}\text{Ni}_2\text{Co}_6$ with various arc current and vacuum forces

Composition	Ni	Co	Current	Valve	Note
$\text{Al}_{74}\text{Si}_{18}\text{Ni}_6\text{Co}_2$	6%	2%	50%	20%	6-2-1
	6%	2%	40%	30%	6-2-2
	6%	2%	40%	10%	6-2-3
$\text{Al}_{74}\text{Si}_{18}\text{Ni}_4\text{Co}_4$	4%	4%	40%	20%	4-4-1
	4%	4%	50%	10%	4-4-2
	4%	4%	30%	10%	4-4-3
$\text{Al}_{74}\text{Si}_{18}\text{Ni}_2\text{Co}_6$	2%	6%	40%	20%	2-6-1
	2%	6%	50%	10%	2-6-2
	2%	6%	30%	10%	Fail
	2%	6%	35%	10%	2-6-3

6.3.2 Scanning Electron Microscopy of Al-Ni-Co-Si Alloys

6.3.2.1 $\text{Al}_{74}\text{Si}_{18}\text{Ni}_6\text{Co}_2$ quaternary alloy

The results shown in Figs 6.15 and 6.16 reveal that 2% Co did not improve GFA in Al-Ni-Co-Si alloys compared to the $\text{Al}_{74.13}\text{Ni}_{7.69}\text{Si}_{18.18}$ base alloy. With respect to the casting conditions, compared to the 6-2-1 sample, the 6-2-2 sample tip exhibited smaller microstructural features in the centre of the casting, likely due to the lesser degree of superheating applied by the lower melting current, leading to a faster cooling rate (Fig. 6.15a-d). A discontinuous region around $14\mu\text{m}$ in width consisting of very fine crystallites was also observed at the sample edge (immediate chill zone) which was not observed for the 6-2-1 condition. The wedge cast under condition 6-2-3 (40% current and 10% valve open) shown in Fig. 6.16a, yields a largely different microstructure, which may be due to the smaller alloy volume leading to increased heat with the same arc current or, given the small valve opening, may indicate that shear rate during casting may also have a significant effect on microstructure. Compared to 6-2-1 and 6-2-2 with fully crystallized wedge tips, fine crystals were observed in a $50\mu\text{m}$ wide edge region were observed, which were also present at a wedge thickness of $1000\mu\text{m}$ (Fig. 6.16b-d).

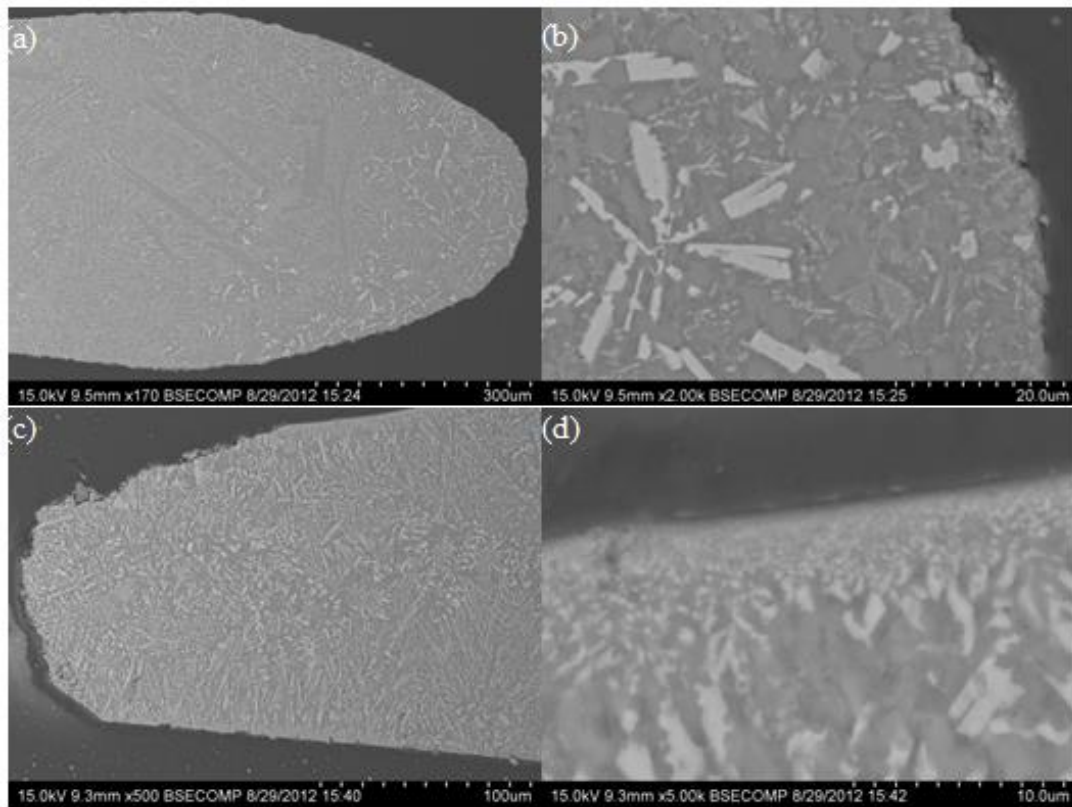


Fig. 6.15 SEM micrographs of $\text{Al}_{74}\text{Si}_{18}\text{Ni}_6\text{Co}_2$ (a-b) 6-2-1 wedge tip of 500 μm in width; (c-d) 6-2-2 wedge tip of 120 μm in width.

6.3.2.2 $\text{Al}_{74}\text{Si}_{18}\text{Ni}_4\text{Co}_4$ quaternary alloys

A featureless microstructure the width of 75 μm was found in the wedge tip of the $\text{Al}_{74}\text{Si}_{18}\text{Ni}_4\text{Co}_4$ alloy using the 4-4-1 casting conditions (40% arc current), shown in Fig. 6.17a-b and fine crystals become evident at the centre of the wedge at a thickness of 90 μm . However, increasing the arc current to 50% for the 4-4-2 casting condition, which provides a higher melt superheat appears to result in a completely crystalline microstructure, furthermore, the wedge tip achieved was quite large at 255 μm in width, which is considerably larger than the featureless zone observed in the 4-4-1 casting condition sample. By decreasing current from 40% to 30% with same 10% valve open, the $\text{Al}_{74}\text{Si}_{18}\text{Ni}_4\text{Co}_4$ (4-4-3) wedge (Fig. 6.18a) produced a larger featureless region, with crystallites appearing at the centre of the wedge at a thickness of 190 μm (Fig. 6.18b). Secondary bright phases were initiated at a thickness of 250 μm (Fig. 6.18c). An amorphous skin was still maintained up to a thickness of 500 μm . (Fig. 6.18d) The $\text{Al}_{74}\text{Si}_{18}\text{Ni}_4\text{Co}_4$ alloy had the largest featureless zone observed, in the quaternary Al-Ni-Co-Si alloys.

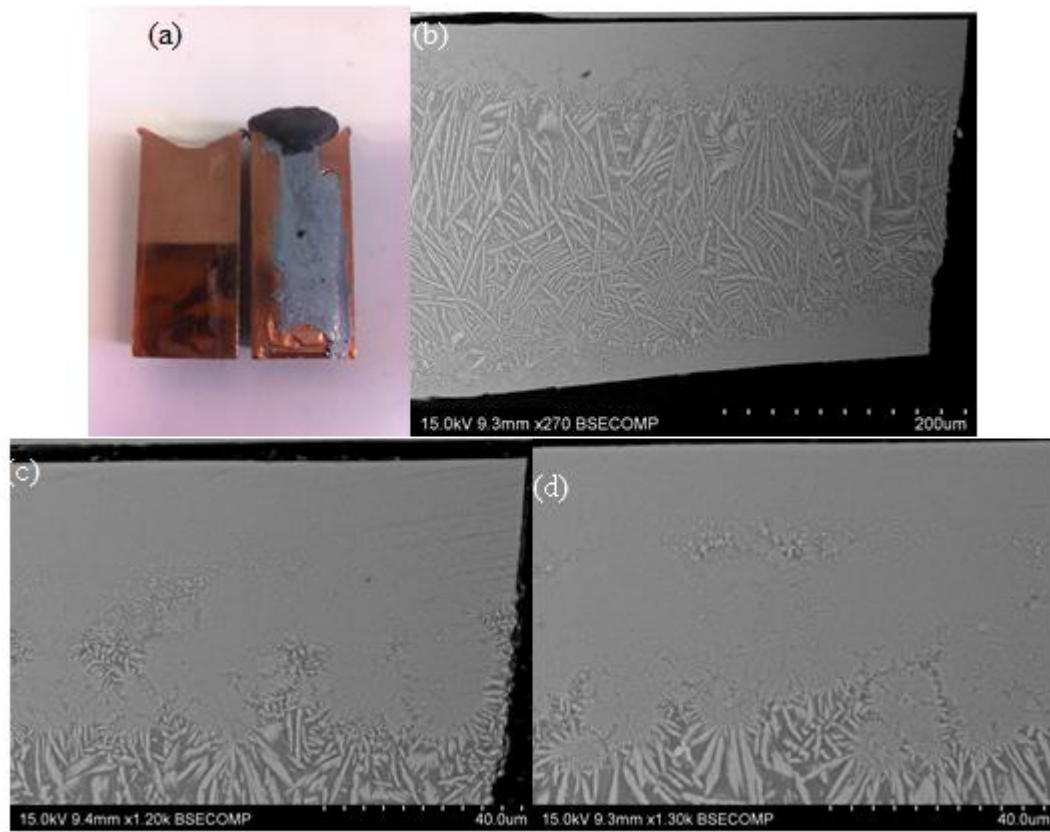


Fig. 6.16 $\text{Al}_{74}\text{Si}_{18}\text{Ni}_6\text{Co}_2$ (6-2-3) wedge (a), and micrographs at (b-c) 275 μm and (d) 1000 μm .

6.3.2.3 $\text{Al}_{74}\text{Si}_{18}\text{Ni}_2\text{Co}_6$ quaternary alloys

No featureless zones were observed in the $\text{Al}_{74}\text{Si}_{18}\text{Ni}_2\text{Co}_6$ alloys for any casting condition. This is largely due to the high melting point and premature solidification of these alloys, where wedge tips were often greater than 200 μm in thickness, perceivably larger than the GFA of the quaternary alloy system. The wedge tips of $\text{Al}_{74}\text{Si}_{18}\text{Ni}_2\text{Co}_6$ had the width of 330 μm and 275 μm by 40% and 50% current. Fine crystal regions about 90 μm wide were formed at the edges of the sample in contact with the Cu mould for 2-6-1 and 2-6-2 casting conditions with a relatively fine crystalline interior to the casting (Fig. 6.19a-d). The $\text{Al}_{74}\text{Si}_{18}\text{Ni}_2\text{Co}_6$ (2-6-3) wedge did not cast properly in the first trial using 30% arc current, presumably due to premature solidification before mould filling could be achieved. After re-melting the whole alloy piece using 35% arc current a wedge with a fine tip of 140 μm was formed, however, this contained large crystalline structures (Fig. 6.20a-d).

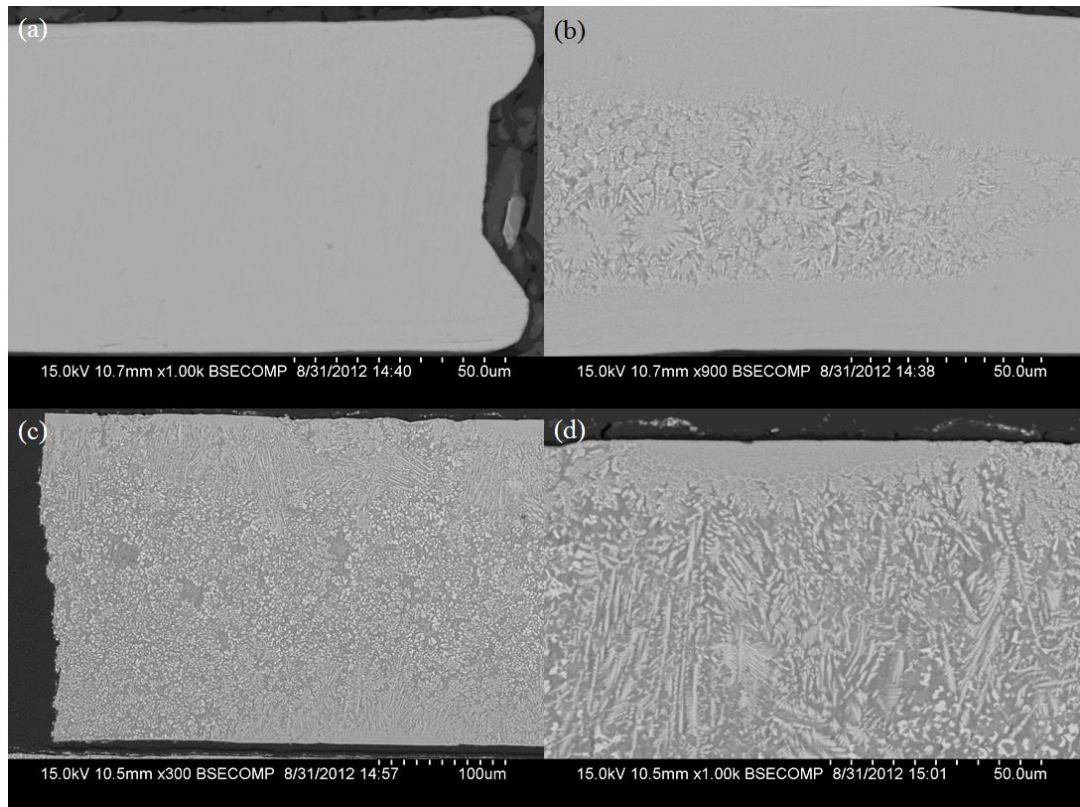


Fig. 6.17 SEM micrographs of $\text{Al}_{74}\text{Si}_{18}\text{Ni}_4\text{Co}_4$ (a-b) 4-4-1 tip by 40% current at $75\mu\text{m}$ in width with associated (c-d) 4-4-2 tip by 50% current at $255\mu\text{m}$ in width.

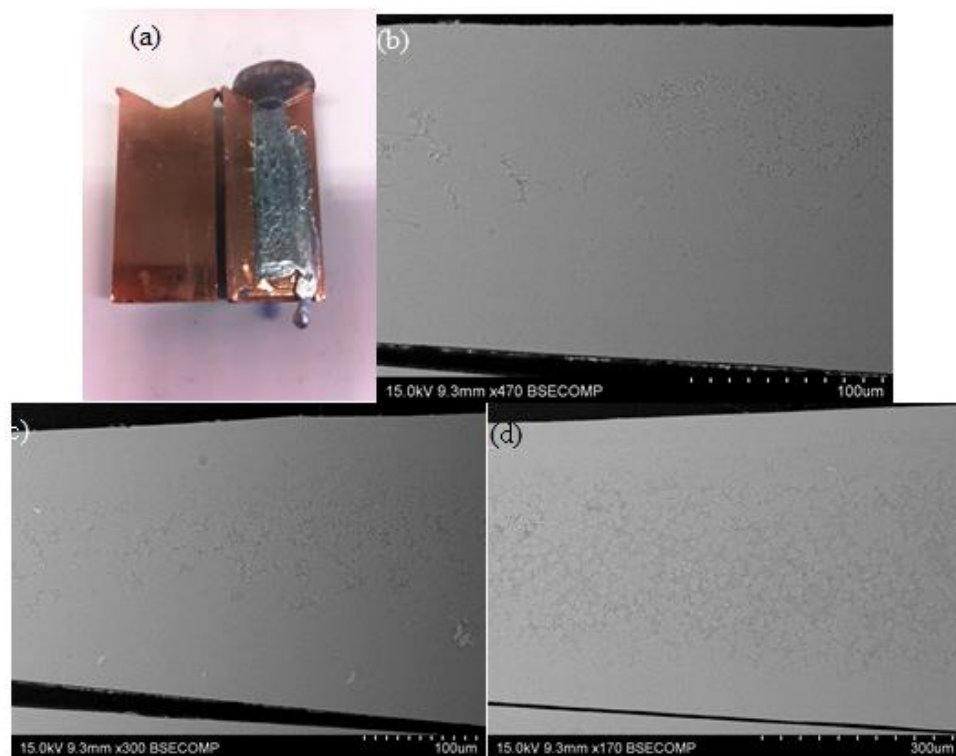


Fig. 6.18 The $\text{Al}_{74}\text{Si}_{18}\text{Ni}_4\text{Co}_4$ (4-4-3) wedge (a), and micrographs at (b) $190\mu\text{m}$, (c) $250\mu\text{m}$, and (d) $500\mu\text{m}$.

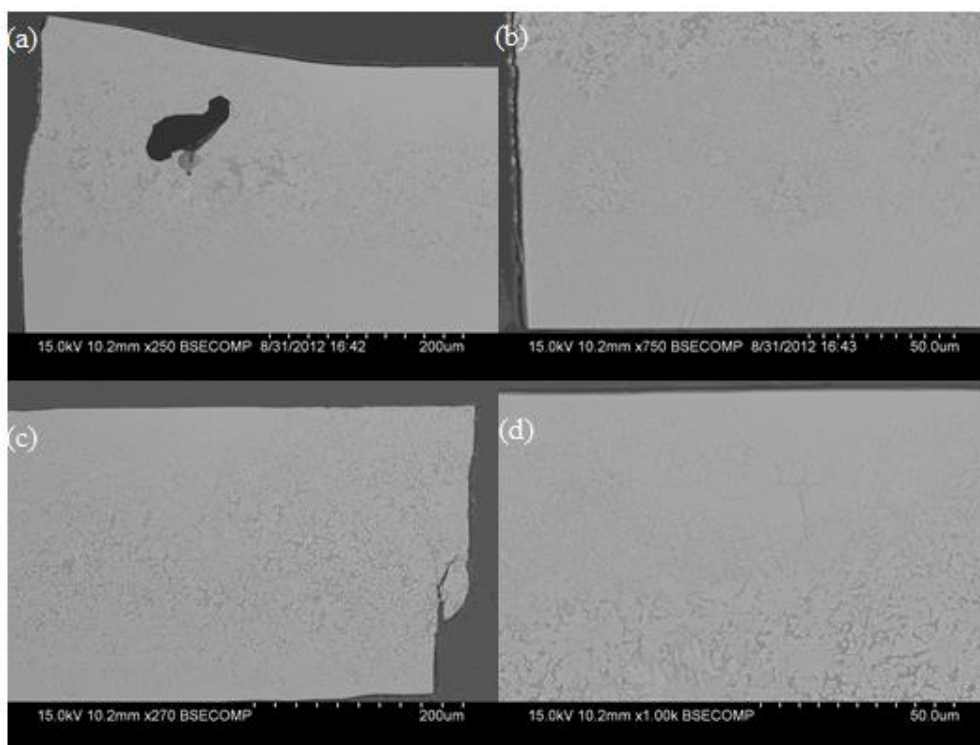


Fig. 6.19 SEM micrographs of $\text{Al}_{74}\text{Si}_{18}\text{Ni}_2\text{Co}_6$ (a-b) 2-6-1 tip at $330\mu\text{m}$ in width; (c-d) 2-6-2 tip at $275\mu\text{m}$ in width.

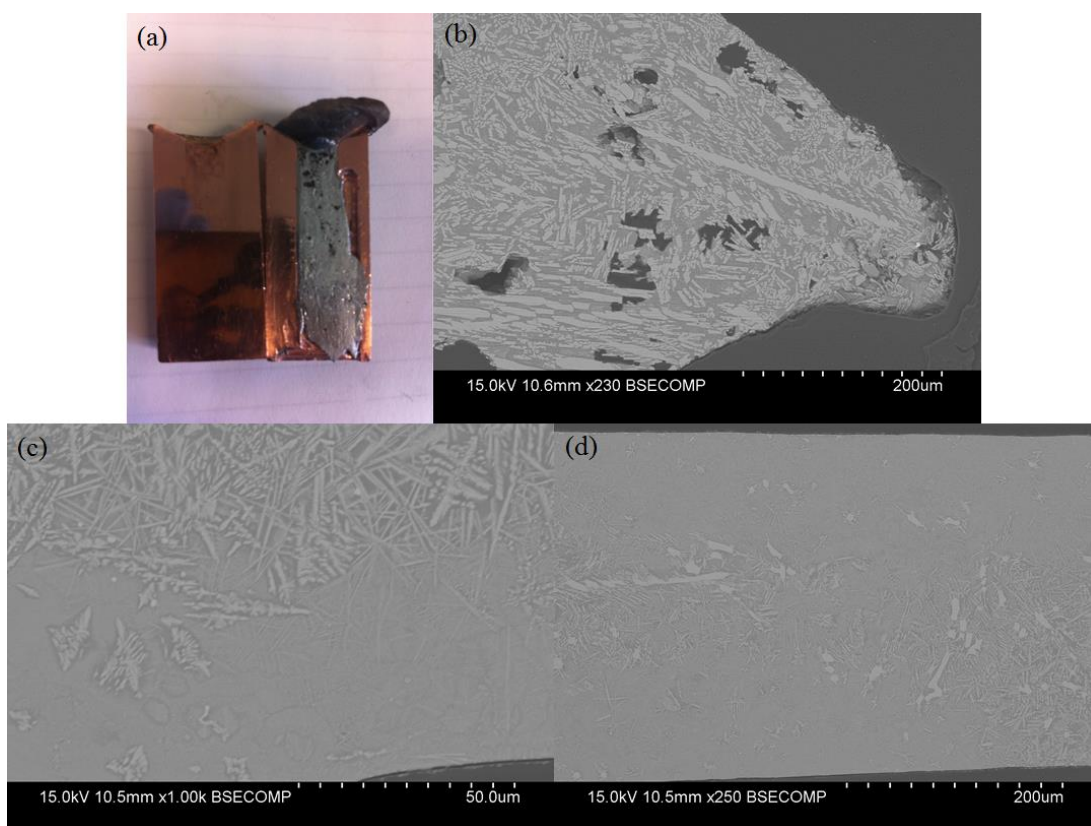


Fig. 6.20 $\text{Al}_{74}\text{Si}_{18}\text{Ni}_2\text{Co}_6$ (2-6-3) wedge (a), and micrographs at (b) $140\mu\text{m}$; (c) $500\mu\text{m}$; (d) $300\mu\text{m}$.

In summary, the GFA of $\text{Al}_{74}\text{Si}_{18}\text{Ni}_8$ after partial substitution of Ni with 2%, 4%, and 6% Co was investigated. Of these alloys, $\text{Al}_{74}\text{Si}_{18}\text{Ni}_4\text{Co}_4$ exhibited the thickest featureless zone of $190\mu\text{m}$ and it was observed that smaller alloy volumes and lower suction forces were found to support higher GFA in the quaternary Al-Ni-Co-Si alloys. When compared to the GFA of the parent ternary Al-Ni-Si and Al-Co-Si alloy families which have a maximum GFA of $400\mu\text{m}$ and $195\mu\text{m}$, respectively, it seems that the GFA of the quaternary system is largely dependent on the GFA of the containing ternary systems.

Chapter 7

Discussion

7.1 Introduction

Al-based alloys have long been known to be poor glass formers (see chapter 2), although recent work on quite complex Al-Ni-Co-La-Y systems have generated a glass with a casting diameter of over 1mm, that is, they are “bulk” metallic glasses (Yang et al. 2009). Other than these rather exotic systems, there are very few reports of the generation of Al-base metallic glasses containing a combination of early transition metal (ETM), late transition metal (LTM) and metalloid additions and without incorporating expensive rare earth (RE) additions. The most intensive studies into glass formation in Al-based alloys fall into two major categories: (i) Al-LTM-ETM and (ii) Al-LTM-RE (LTM = Fe, Co, Ni, Cu; ETM = Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W; RE = Y, La, Ce, Pr, Nd Sm, Gd, Tb, Dy, Ho, Er, Yb) systems.

While cooling rates of up to 10^6K/s are easily achieved by melt spinning (R A Dunlap et al. 1986), melt-spun ribbons of many Al-based alloys still showed the formation of various crystalline phases. As typical examples, no amorphous phase were found in melt-spun ribbons of Al-Si binary alloys (Uzun et al. 2004). In $\text{Al}_{93-x}\text{Si}_7\text{Ti}_x$ ternary alloys ($x = 0.6, 1, 2$), X-ray diffraction (XRD) revealed Al, Si, and Al_3Ti crystalline phases in the melt-spun ribbons (Ahmed 2008). In $\text{Al}_{70-x}\text{Fe}_5\text{Si}_{25}\text{Co}_x$ quaternary alloys, aluminum was substituted with Co but crystalline phases of Al, Si, Al_4FeSi_2 still formed (Kiliçaslan et al. 2013). All these (and many other studies see Chapter 2) reveal that the selection of elements is critical for generating good glass forming Al alloys.

As stated earlier, many investigations of glass formation in Al-base alloys have been carried out on metal-metal-base systems often containing RE additions, whereas

metal-metalloid-base systems without RE additions have been far less studied. This thesis is focused on the propensity for glass formation in Al-base alloys containing a combination of metalloids and early transition metals or late transition metals. The results were arranged three chapters depending on the specific types of elemental additions:

- (i) Chapter 4 – **Al-ETM-Si/Ge** ternary and quaternary alloy systems (ETM = Mn, Cr, Mo);
- (ii) Chapter 5 – **Al-LTM-Si** ternary alloy systems (LTM = Fe, Co), and
- (iii) Chapter 6 – **Al-LTM-Si** and **Al-LTM₁-LTM₂-Si** ternary and quaternary alloy systems (LTM₁= Ni; LTM₂= Co).

This chapter commences with a systematic discussion of the optimal GFR of the alloys under investigation and follows with specific sections on certain parameters affecting GFA such as atomic packing efficiency, heat of mixing and thermodynamic driving force.

7.2 Glass Forming Ranges

7.2.1 Al-Mn-Si/Ge alloys

The ability to produce amorphous Al-Mn-Si alloys has attracted attention due to their useful ferromagnetic properties at low temperature. Here, Al₅₀Mn₂₀Si₃₀ and Al₅₅Mn₂₀Si₂₅ ribbons of 10 μ m in thickness and 1mm in width were produced by melt spinning (R A Dunlap et al. 1986); the melt-spun ribbons were fully amorphous using a spinning rate of 60m/s (Dunlap et al. 1989). Ferromagnetic behaviour was demonstrated in the amorphous ribbons below 115K (Dunlap et al. 1989).

In this thesis, seven Al-Mn-base alloy compositions containing silicon and the partial substitution of silicon with germanium were produced by copper mould casting (see Chapter 4). On casting, none of the alloys appeared to be fully amorphous at their cone-shaped tip (section 4.2), and only the ternary Al₅₀Si₃₀Mn₂₀ alloy showed a featureless region after polishing. The results imply that Al-Mn-Si alloys have better GFA than Al-Mn-Ge alloys. The fully crystallised Al-Mn-Si-Ge and Al-Mn-Ge alloys indicated that the GFA does not increase by the substitution of Si with Ge, which may be due to two reasons. Firstly, the intrinsic GFA is very low in the Al-

Mn-Si alloys by the observation of a featureless region only at the edge of the matrix, and microalloying has no significant effect on the GFA. Secondly, the addition of germanium did not form a solid solution in the Al-Mn-Si matrix at this cooling rate, but introduced a new type of Ge-containing crystalline phases. Therefore, the GFA is not improved with the substitution of Ge.

7.2.2 Al-Cr-Si alloys

Glass formation in the Al-Si-Cr ternary system was first investigated by Inoue et al. (1988) using melt spinning, and the optimal GFR of their 20 μm thick ribbons was 5-18 at.% Cr and 25-40 at.% Si, as shown in the ternary diagram in Fig. 7.1. In this thesis, five Al-Cr-Si compositions were investigated using copper mould casting, and these are also plotted in Fig. 7.1. At the tip of as-cast wedges, a featureless matrix was observed in compositions of $\text{Al}_{61.54}\text{Cr}_{7.69}\text{Si}_{30.76}$ (Point 3) and $\text{Al}_{63.63}\text{Cr}_{18.18}\text{Si}_{18.18}$ (Point 2). The other three compositions showed no featureless zone at the wedge tip. Compared with the optimal GFR of the Al-Si-Cr ribbons (Inoue et al. 1988), the $\text{Al}_{61.54}\text{Cr}_{7.69}\text{Si}_{30.76}$ alloy studied herein had a featureless zone of $\sim 150 \mu\text{m}$, which is located in the optimal GFR of the melt-spun ribbons. Possibly due to the lower silicon content in the $\text{Al}_{63.63}\text{Cr}_{18.18}\text{Si}_{18.18}$ alloy (Point 2), the featureless zone of $40 \mu\text{m}$ at the wedge tip falls slightly outside Inoue's reported optimal range. Nevertheless, this composition is shown to extend the GFR of Al-Cr-Si alloys containing lower Si contents (shaded region in Fig. 7.1).

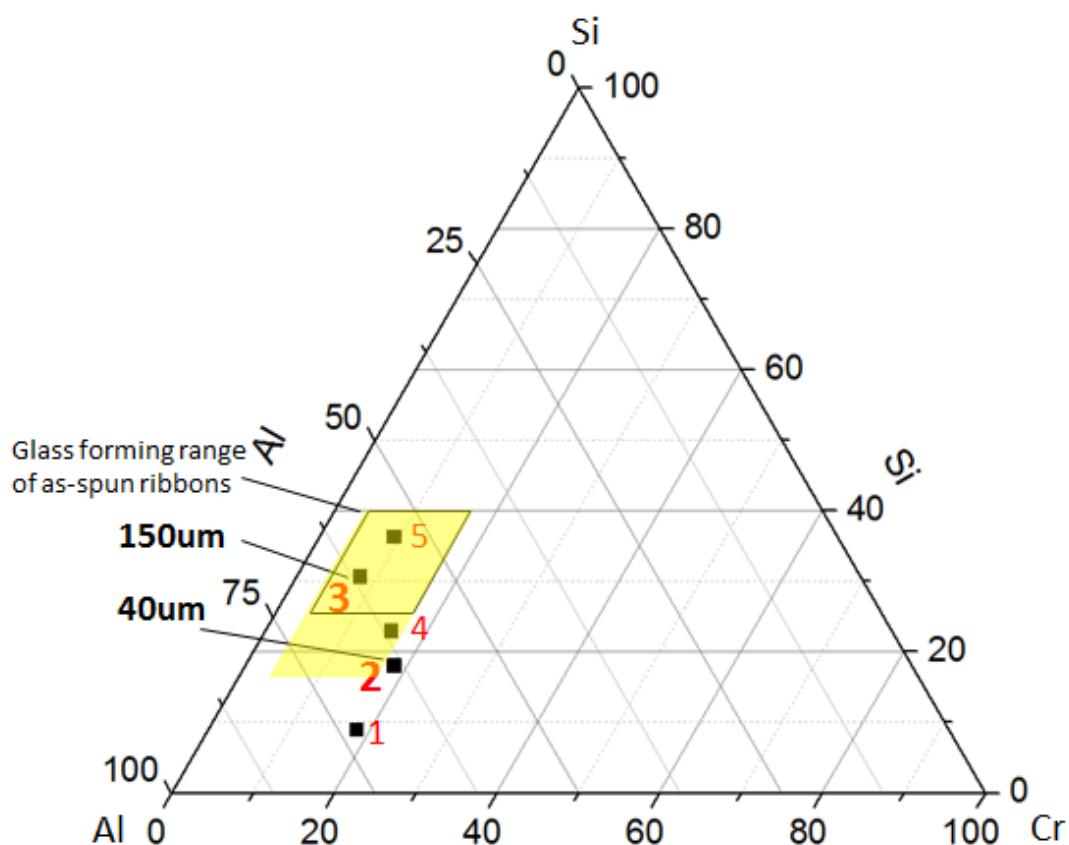


Fig. 7.1 GFR of the Al-Cr-Si compositions and those produced by Inoue et al. (1988) by melt spinning.

In another study on melt spinning of Al-Cr-Si alloys (Kimura et al. 1988), 20 μm thick amorphous ribbons were reported for compositions containing 7-22 at.% Cr and 24-37 at.% Si (Fig. 7.2). Quasi-crystalline ribbons were produced for compositions containing 17-22 at.% Cr and 15-23 at.% Si with mixed quasi-crystalline and aluminum phase produced for compositions containing for 6-20 at.% Cr and 0-23 at.% Si. Compared with this previous work (Fig. 7.2), the $\text{Al}_{63.63}\text{Cr}_{18.18}\text{Si}_{18.18}$ cast wedge, with a featureless zone of $\sim 40 \mu\text{m}$ at the wedge tip, falls in the quasi-crystalline region for melt-spun ribbons. The $\text{Al}_{61.54}\text{Cr}_{7.69}\text{Si}_{30.76}$ wedge with a featureless zone of $\sim 150 \mu\text{m}$ at tip, falls in the fully amorphous region of melt-spun ribbons. The trend of GFR by copper mould casting is in agreement with the GFR trend observed in melt spun ribbons. However, the current study revealed that the overall GFA in Al-Cr-Si system is limited and only up to 150 μm by this slower cooling casting method. Because no amorphous phases can be formed in rapidly solidified binary Al-Si ribbons (Kimura et al. 1988), it was believed that, in the ternary Al-Cr-Si alloys, the attractive interactions between Cr and Al, and the attractive interactions between Cr and Si changed the bonding nature

of repulsive Al-Si interaction (Inoue et al. 1988); this attractive interaction decreased the atomic mobility and increased the melt viscosity during solidification, thereby retarding crystallization and promoting the formation of fully amorphous melt-spun ribbons and the featureless zone at the copper mould-cast wedge tip.

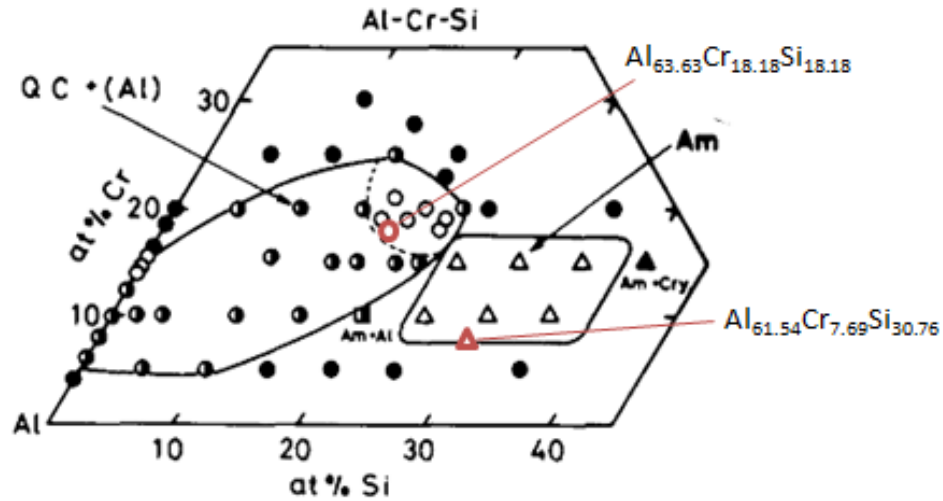


Fig. 7.2 Rapidly solidified phases in Al-Cr-Si ribbons: open circle, quasi-crystalline; solid circle, crystalline; semi-circle, quasi-crystalline with crystalline; open triangle, amorphous; semi-triangle, amorphous with crystal; semi-rectangular, amorphous with aluminum (Kimura et al. 1988). Two of Al-Cr-Si wedges with featureless zones are shown for comparison.

7.2.3 Al-Mo-Si alloys

In a previous investigation on melt spinning of Al-Mo-Si alloys, fully amorphous ribbons without any trace of crystalline phases was produced (Inoue et al. 1988). However, both the GFR and GFA were not provided for these alloys. While molybdenum has a very high melting point ($> 2600^{\circ}\text{C}$), it is a useful element to determine whether it increases the viscosity and thus GFA in Al-Si-based alloys. In this thesis, five compositions in compliance with efficiently packed clusters (see calculation method in Appendix A) were investigated and their composition is plotted in the Al-Mo-Si ternary phase diagram (Fig. 7.3). While these alloys are reported to form a fully amorphous phase by melt spinning, SEM micrographs of as-cast wedges produced by both the 10:1 and 20:1 copper mould configurations indicated that the GFA in Al-Mo-Si alloys was low. For the 10:1 copper mould, a narrow featureless region of width less than $44\text{ }\mu\text{m}$ and $60\text{ }\mu\text{m}$ was observed at the cast tip of $\text{Al}_{50}\text{Mo}_{31.25}\text{Si}_{18.75}$ (Point 4 in Fig. 7.3) and $\text{Al}_{54.54}\text{Mo}_{27.27}\text{Si}_{18.18}$ (Point 2 in

Fig. 7.3), respectively. No featureless matrix was observed in the high-Mo composition (Point 3). The melt exhibited a high viscosity for compositions at both Point 1 and Point 5, i.e. the melt only partially filled the mould cavity for the standard casting suction casting conditions. According to the isothermal lines in liquidus projection, the melting point of alloys at Point 1 and 5 are $> 1500^{\circ}\text{C}$ and $\sim 1700^{\circ}\text{C}$, respectively. The high melting points of these alloys may contribute to the high viscosity encountered during suction casting. The high viscosity found in compositions of high melting point impeded the flow, thereby preventing complete filling of the mould.

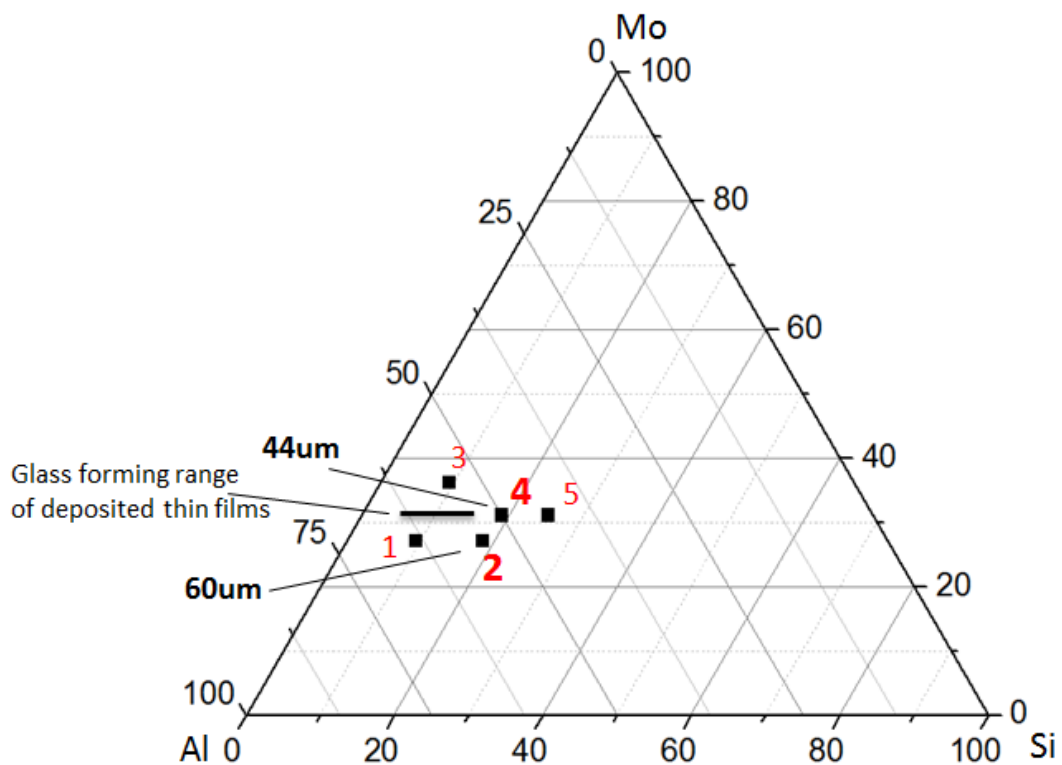


Fig. 7.3 GFR of the Al-Mo-Si compositions and those produced (Habazaki et al. 1994) by magnetron sputtering.

In a previous study on Al-Mo-Si alloys, a fully amorphous phase is possible in binary $\text{Al}_{66-54}\text{Mo}_{34-46}$ and ternary $\text{Al}_{53-63}\text{Mo}_{31}\text{Si}_{6-16}$ alloys when a thin film of thickness $\sim 6 \mu\text{m}$ is deposited on both a silicon and molybdenum substrate by magnetron sputtering (Habazaki et al. 1994). In the current study, the $\text{Al}_{50}\text{Mo}_{31.25}\text{Si}_{18.75}$ and $\text{Al}_{54.54}\text{Mo}_{27.27}\text{Si}_{18.18}$ alloys showing a featureless zone at the wedge tip are close to the composition of amorphous thin film, $\text{Al}_{53}\text{Mo}_{31}\text{Si}_{16}$. This indicates that the GFR of alloys in the form of thin films is similar to those produced

by slow cooling produced by copper mould casting. However, the GFA in all the Al-Mo-Si alloys in this thesis was low (featureless zone <60 μm at the wedge tips), thereby confirming that glass formation in this system is better investigated by rapid cooling techniques such as sputtering or melt spinning.

7.2.4 Al-Fe-Si alloys

Glass formation of melt-spun Al-Fe-Si alloys for 12-22 at.% Fe was investigated by Inoue et al. (1988). In this thesis, five Al-Fe-Si compositions in compliance with the most efficiently packed clusters were investigated, and these are plotted in the ternary diagram in Fig. 7.4.

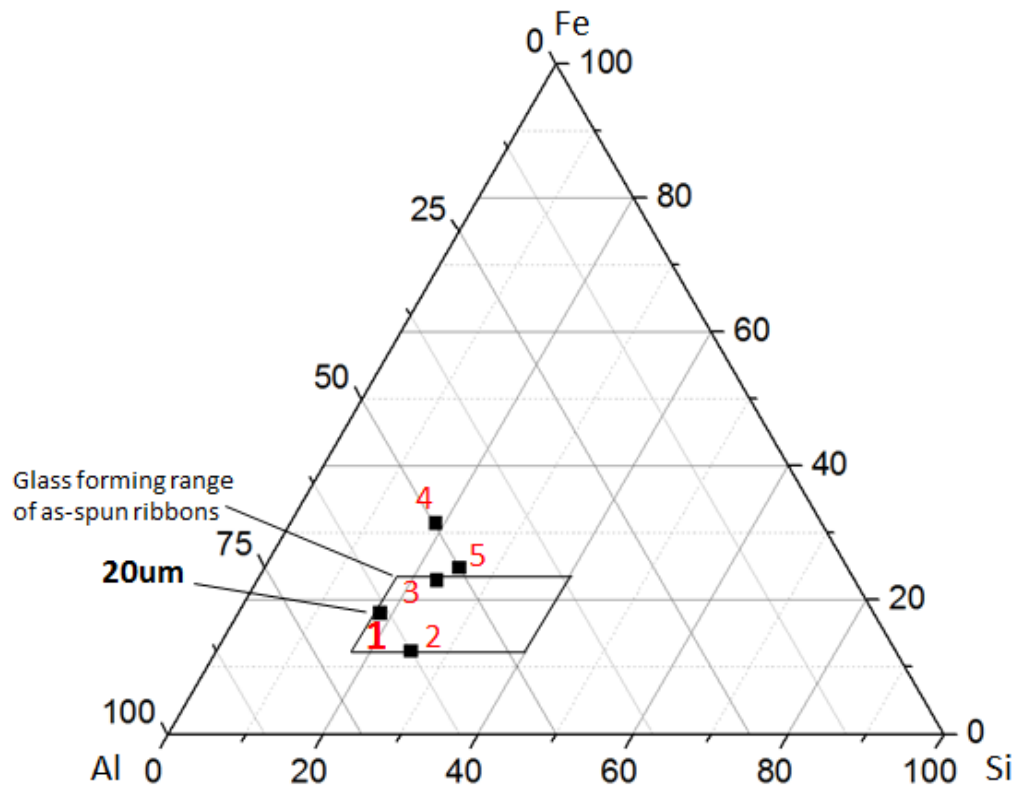


Fig. 7.4 GFR of the Al-Fe-Si compositions and those produced by Inoue et al. (1988) by melt spinning.

In another study on melt-spun ribbons of an $\text{Al}_{87}\text{Fe}_2\text{Si}_{11}$ alloy, the addition of up to 2 at.% Fe did not fully suppress crystallization, and promoted the formation of an Fe-containing amorphous phase between the Si nanoparticles and amorphous matrix, which acted as a diffusion barrier to impede oxide growth and refine the Si particles (Gaidarova 2007). In the current study, the Fe content of the Al-Fe-Si alloys was greater than 12.5 at.%, and the morphology of the phases is quite different to Gaidarova's alloys. As confirmed by XRD, different types of Fe-containing crystalline phases formed during casting, which resulted in crystallization even at the wedge tips. The competing process of various crystalline phases was also observed in melt-spun Al-Fe-Si ribbons (Bendersky et al. 2012), where the $\text{Al}_{65}\text{Fe}_{15}\text{Si}_{20}$ alloy showed a structural variation in different regions of the ribbons under SEM and along the perforated hole of the TEM foil.

7.2.5 Al-Co-Si alloys

Glass formation of Al-Co-Si alloys produced by melt spinning was investigated by Inoue et al. (1988) for compositions bounded by 15-42 at.% Si and 5-23 at.% Co. In this thesis, glass formation of ten compositions was investigated by copper mould casting and compared with the melt spinning data in Fig. 7.6.

In the present study, the highest GFA was observed for $\text{Al}_{74.18}\text{Co}_{7.64}\text{Si}_{18.18}$ (Point Y in Fig. 7.6) where a fine crystalline phase was present in the featureless matrix at a width of 195 μm . The second highest GFA was $\text{Al}_{56.25}\text{Co}_{18.75}\text{Si}_{25}$ which showed a crystalline zone at 120 μm from the wedge tip (Point 8 in Fig. 7.6), followed by $\text{Al}_{75}\text{Co}_{12.5}\text{Si}_{12.5}$ with a featureless region of 78 μm (Point 1 in Fig. 7.6), and $\text{Al}_{63.63}\text{Co}_{9.09}\text{Si}_{27.27}$ with featureless region of 75 μm (Point 4 in Fig. 7.6). Alloys 4, 8, Y exhibiting a featureless matrix by copper mould casting falls in the melt spinning range, but alloy 1 containing less silicon falls out of this range and, thus, extends the GFR of Al-Co-Si alloys. Alloy Y with the highest GFA is located near the edge rather than in the middle of the GFR of melt-spun ribbons; this can be explained by its topological characteristics, as discussed in the next section on atomic packing efficiency.

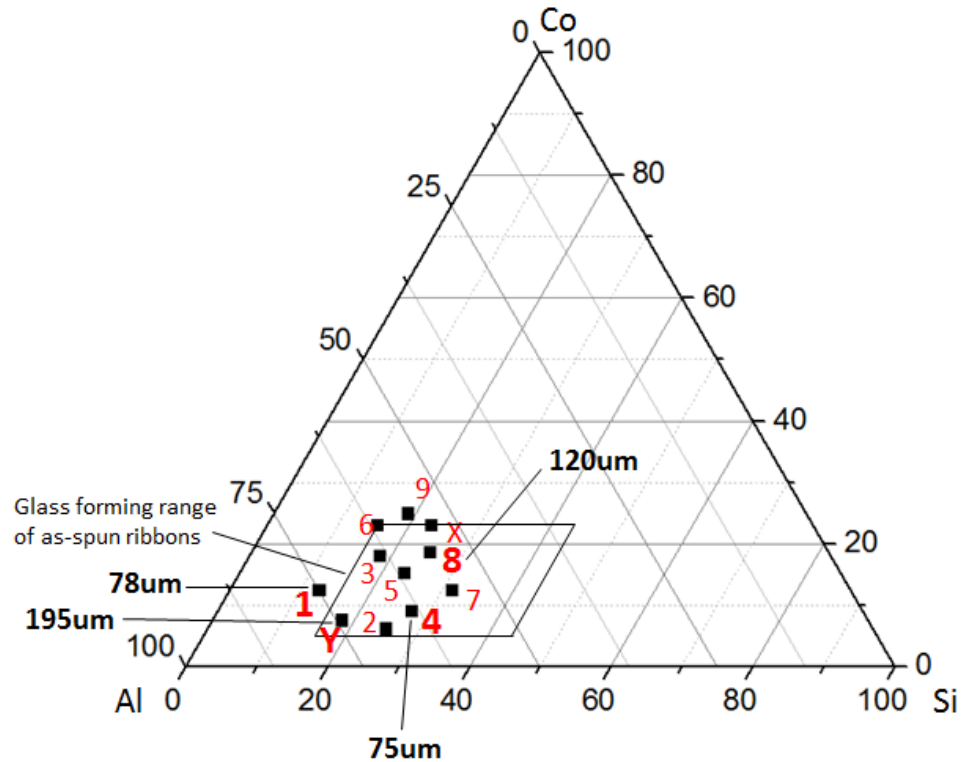


Fig. 7.6 GFR of the Al-Co-Si compositions and those produced by Inoue et al. (1988) by melt spinning.

7.2.6 Al-Ni-Si alloys

Over twenty Al-Ni-Si compositions were produced by copper mould casting to test the GFR and GFA of this alloy system. Fifteen major alloys are plotted in Fig. 7.7. A featureless matrix was observed in wedge tips of six compositions in the Al-Ni-Si system. The highest GFA was $\text{Al}_{74.18}\text{Ni}_{7.64}\text{Si}_{18.18}$ with featureless region of 400 μm in width (Point C in Fig. 7.7); the second highest GFA was $\text{Al}_{68.25}\text{Ni}_{12.50}\text{Si}_{18.75}$ with featureless region of 160 μm in width (Point 9); followed by $\text{Al}_{69.23}\text{Ni}_{15.38}\text{Si}_{15.38}$ (Point 1) with featureless region of 108 μm in width, $\text{Al}_{61.54}\text{Ni}_{15.38}\text{Si}_{23.08}$ (Point 6) with featureless region of 90 μm in width, $\text{Al}_{63.63}\text{Ni}_{9.09}\text{Si}_{27.27}$ (Point 2) with featureless region of 70 μm in width, and $\text{Al}_{84.62}\text{Ni}_{7.69}\text{Si}_{7.69}$ (Point a) with featureless region of 45 μm in width. The GFR for this system by melt spinning was reported to fall within the composition range 5-23 at.% Ni and 12-28 at.% Si (Inoue et al. 1988); compared with other compositions with dendrites and crystal phases, five compositions with featureless zones at wedge tips were located within the GFR of melt-spun ribbons. Only the $\text{Al}_{84.62}\text{Ni}_{7.69}\text{Si}_{7.69}$ alloy (Point a) is slightly out of the range. Compared with the other ternary Al-Si-based alloys studied herein, the Al-Ni-Si alloys showed the highest glass-forming ability.

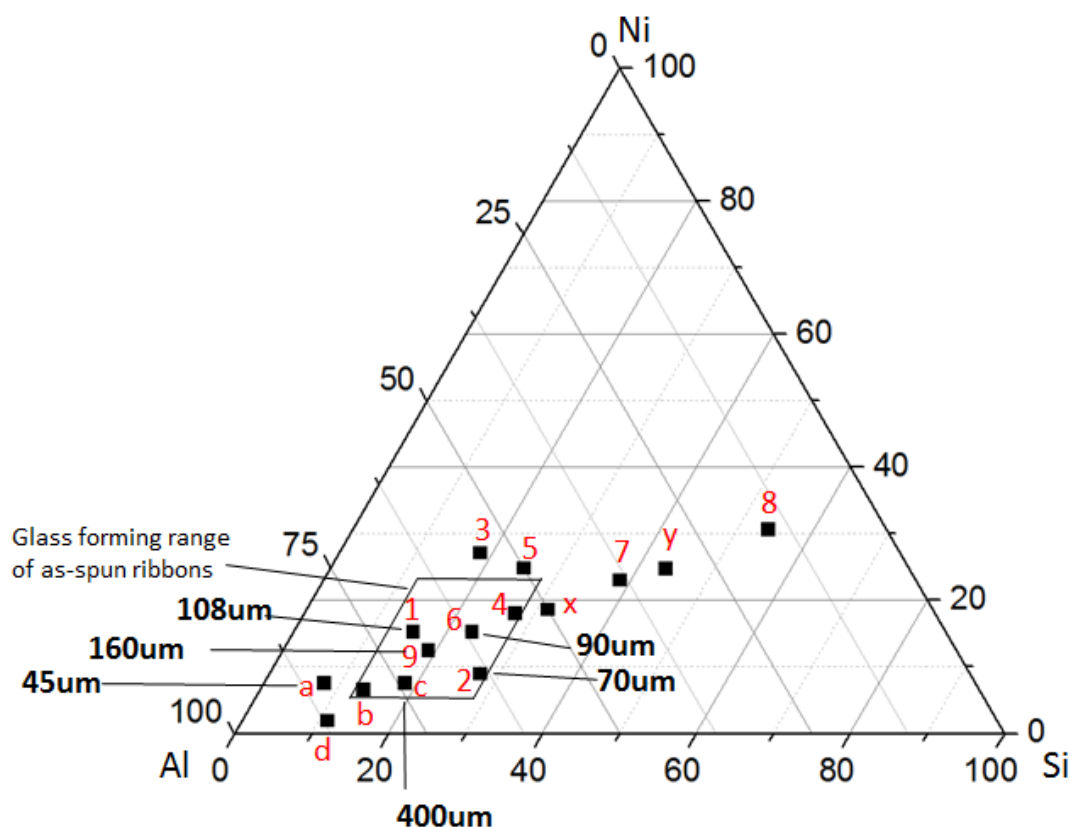


Fig. 7.7 GFR of the Al-Ni-Si compositions and those produced by Inoue et al. (1988) by melt spinning.

7.2.7 Summary

The metal-metalloid glasses generally contained 80% metals and 20% metalloids such as Au-Si, Pd-Si, and Pt-P etc. The metals could be one type or multiple metal elements, but the total amount of these elements is in general ~ 80 at.%. In the current study, the Al-Si-based alloys generated the widest featureless region formed at the composition close to 20% Si in both the Al-Ni-Si and Al-Co-Si systems. Previous research argued that a potential reason behind this trend is these alloys' atomic structure. Four metal atoms formed a cluster of the form of a tetrahedron, with the metalloid atom filling the interstice of the tetrahedron and, hence increasing the packing density of the clusters; the metal elements at the four corners of the tetrahedron are therefore limited in mobility to form long range order or crystalline phases. In the Al-Ni-Si and Al-Co-Si alloys studied herein, the widest featureless zones were found at a specific composition of 18.18 at.% Si, which may be attributed to the packing density of clusters from the kinetic viewpoint, as discussed in the next section.

7.3 Atomic Packing Efficiency

The atomic packing efficiency of specific clusters that represent the alloy compositions was calculated based on Miracle's model (Miracle et al. 2003, Miracle 2004, Miracle et al. 2006) and effective radius ratio method (Laws et al. 2010).

According to Miracle's model, the efficiently packed clusters with different number of atoms in the first shell can achieve a maximum packing efficiency or most densely packed stacks with a specific radius ratio between the centre atom and the surrounding atoms. In the potential glass forming composition region, given the radius of the constituent elements, the coordination number of efficiently packed clusters can be estimated. This method was expanded into multi-element systems using the effective radius ratio method. This method not only provided a range of glass forming candidates by comparing the ideal atomic radius ratio with average radius ratio between centre atom and first shell atoms, but also considered the contribution of each element in a cluster of the multi-element system with a specific coordination number. Therefore, this method was chosen as a guide in the selection of glass forming candidates in the ternary alloys studied in this thesis.

In Al-Ni-Si alloys, the radius ratios between solute atoms and solvent atoms were 0.80, 0.87 and 1.0. Within the known glass forming region, using the effective radius ratio method it was found that efficiently-packed silicon-centred clusters would have a coordination number $N=10$, nickel-centred clusters a coordination number $N=12$ and aluminium-centred clusters $N=15$. The selection of alloy compositions with the highest propensity for glass formation utilized these efficiently-packed cluster compositions of different atomic centres in reported glass forming regions in Al-Si-based ternary systems. The wedges with featureless zones were shown for compositions $\text{Al}_{63.63}\text{Ni}_{9.09}\text{Si}_{27.27}$ ($N=10$), $\text{Al}_{61.54}\text{Ni}_{15.38}\text{Si}_{23.08}$ ($N=12$), $\text{Al}_{69.23}\text{Ni}_{15.38}\text{Si}_{15.38}$ ($N=12$), and $\text{Al}_{68.25}\text{Ni}_{12.50}\text{Si}_{18.75}$ ($N=15$). In the effective radius ratio method, the packing efficiency was measured and displayed by the percentage of difference to the radius ratio of the ideally packed clusters; therefore the high packing efficiency is shown as a low value. Among the compositions with a featureless zone, $\text{Al}_{63.63}\text{Ni}_{9.09}\text{Si}_{27.27}$ (Point 2 in Fig. 7.7) derived from the Si-centred cluster ($N=10$) had the packing efficiency of 6.40%; $\text{Al}_{61.54}\text{Ni}_{15.38}\text{Si}_{23.08}$ (Point 6 in Fig. 7.7) built on the Ni-centred cluster ($N=12$) had the packing efficiency of 2.67%; $\text{Al}_{69.23}\text{Ni}_{15.38}\text{Si}_{15.38}$ (Point 1 in Fig. 7.7) based on the Ni-centred cluster ($N=12$) had the

packing efficiency of 0.93%; $\text{Al}_{68.25}\text{Ni}_{12.50}\text{Si}_{18.75}$ (Point 9 in Fig. 7.7) constructed on the Al-centred cluster (N=15) had the packing efficiency of -5.94%. As the featureless region was revealed in compositions with both the Si-centred clusters and the Ni-centred clusters, the global packing efficiency may be increased by the combination of these two types of solute-centred clusters, which led to $\text{Al}_{74.13}\text{Ni}_{7.69}\text{Si}_{18.18}$ containing both efficiently packed Si-centred clusters and Ni-centred clusters.

Fig. 7.8 shows representative efficiently packed clusters that correspond to these alloy compositions. The alloy that exhibited the highest GFA actually corresponds to two efficiently packed clusters, a Si-centred cluster with N=10 and a Ni-centred cluster with N=12, whereas other alloy compositions were only locally represented by single clusters with N=10, 12 or 15. This implies that at least two of the solute elements in the highest glass-forming alloy are efficiently packed, resulting in an increase in the global packing efficiency of the alloy (Miracle 2004). This can result in a higher alloy viscosity and more sluggish crystallisation kinetics (Busch et al. 2007) compared to other compositions, which is thought to be the reason behind the substantial increase in GFA of this alloy compared to others.

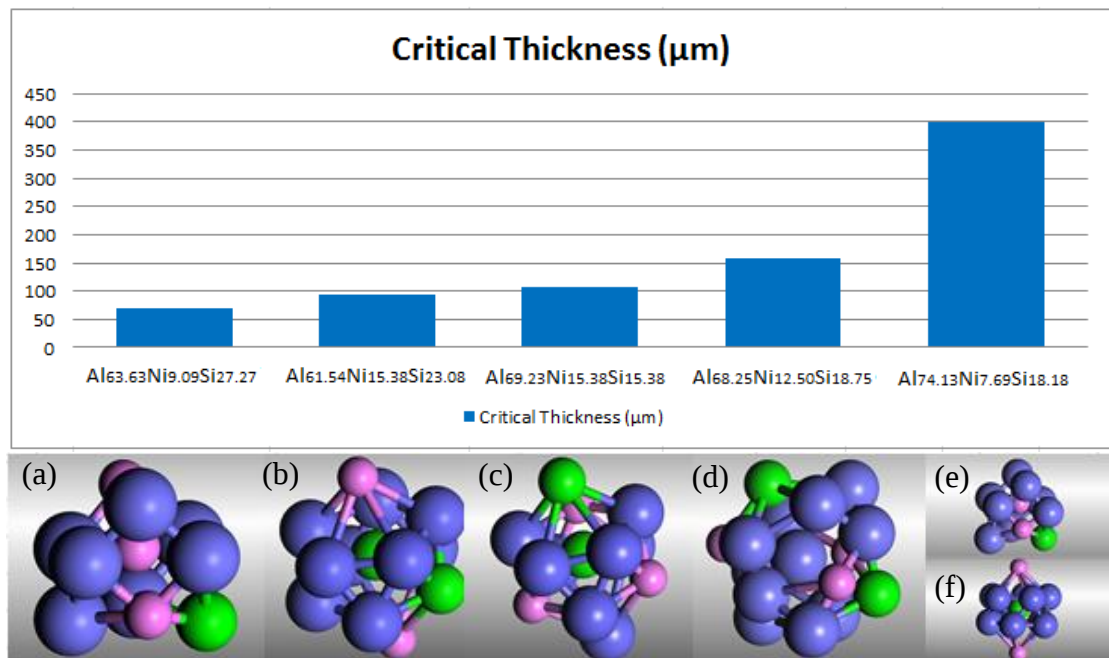


Fig. 7.8 Clusters of glass formers: (a) $\text{Al}_{63.63}\text{Ni}_{9.09}\text{Si}_{27.27}$ (N=10); (b) $\text{Al}_{61.54}\text{Ni}_{15.38}\text{Si}_{23.08}$ (N=12); (c) $\text{Al}_{69.23}\text{Ni}_{15.38}\text{Si}_{15.38}$ (N=12); (d) $\text{Al}_{68.25}\text{Ni}_{12.50}\text{Si}_{18.75}$ (N=15), (e-f) $\text{Al}_{74.13}\text{Ni}_{7.69}\text{Si}_{18.18}$ (N=10, 12); where blue is Al, green is Ni, pink is Si.

In Al-based alloys with RE elements, the efficiently packed cluster method was also reported to be an efficient approach in the search for compositions with high GFA. In early research of Al-Ni-Fe-Gd ribbons, it was found the best glass formers were away from the eutectic point (He et al. 1993). This triggered researchers to find a new method for designing the composition of glass formers. In Al-Ni-La alloys, the glass-forming composition of $\text{Al}_{86}\text{Ni}_9\text{La}_5$ was designed based on the efficiently packed clusters of $\text{Al}_{9.4}\text{Ni}$ and $\text{Al}_{17.5}\text{La}$, which is simulated from Ab initial molecular dynamic simulations and inverse Monte Carlo method; the critical thickness was 780 μm and nanocrystal regions was up to 980 μm (Sanders et al. 2006). Later in Al-Ni-Co-Y-La BMGs (Yang et al. 2009), amorphous rods with a diameter of 1 mm were produced; the composition with best GFA in ternary Al-Ni-Y alloys, $\text{Al}_{86}\text{Ni}_8\text{Y}_6$, were also predicted from efficiently packed binary clusters of $\text{Al}_{9.4}\text{Ni}$ and $\text{Al}_{16.9}\text{Y}$ (Yang et al. 2010).

Compared to binary clusters used in Al-Ni-La and Al-Ni-Y alloys, Al-Ni-Si alloy in the current study is built up by ternary efficiently packed clusters (Fig. 7.8e-f), which meant it considered all three elements in the design of the clusters. In the phase diagram of the Al-Ni-Si ternary system, it has a deep eutectic point, which indicated the possibility of the co-existence of three elements. Mapping of the featureless zones also showed the uniform distribution of solute elements, which confirmed the potential existence of the cluster structure. Therefore, the design of efficiently packed clusters considering all three elements may be more close to the real chemistry of featureless matrix. Furthermore, the widest featureless region found in the $\text{Al}_{74.13}\text{Ni}_{7.69}\text{Si}_{18.18}$ wedge indicated that the bi-cluster method with two efficiently packed ternary clusters is applicable in the development of Al-Ni-Si alloys. The bi-cluster method applied in Al-Ni-Si alloys extended the application range of the topological design principle, which might help accelerate the progress in exploring Al-based alloys with high GFA.

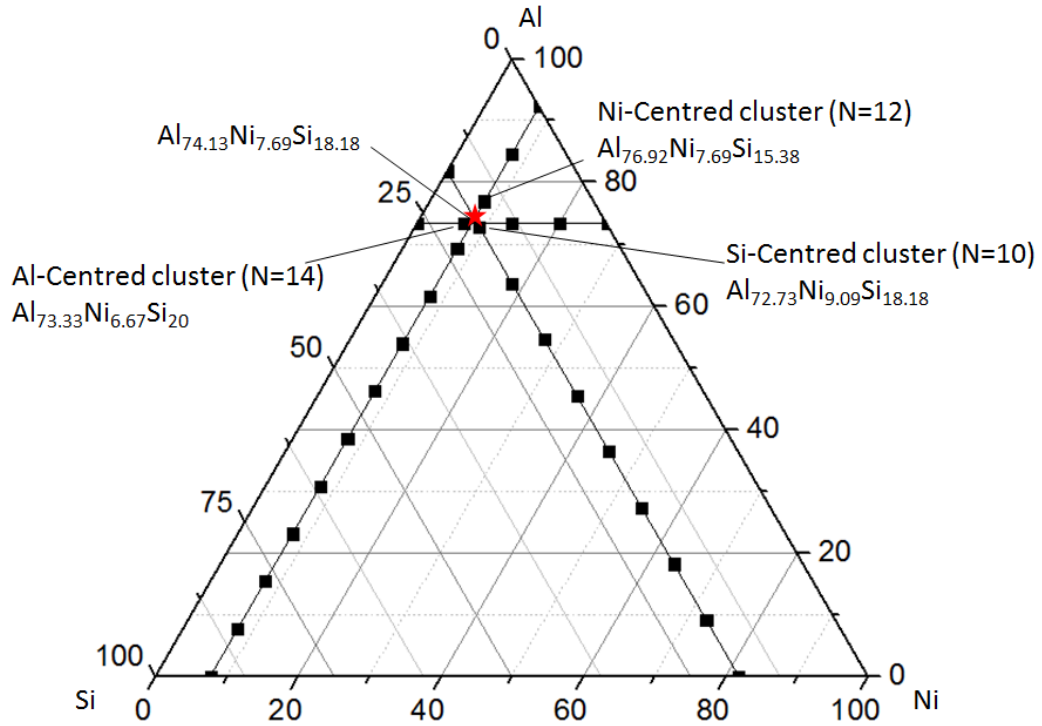


Fig. 7.9 Compositions of $\text{Al}_{74.13}\text{Ni}_{7.69}\text{Si}_{18.18}$ with three clusters efficiently packed around the constituent elements Al, Ni and Si.

As mentioned above, $\text{Al}_{74.13}\text{Ni}_{7.69}\text{Si}_{18.18}$ (Red point in Fig. 7.9) was constructed by two efficiently packed ternary clusters. When we examine the packing efficiency of clusters around the composition, the composition of $\text{Al}_{73.33}\text{Ni}_{6.67}\text{Si}_{20}$ with the Al-centred cluster (N=14) had packing efficiency of 0.61%; the $\text{Al}_{76.92}\text{Ni}_{7.69}\text{Si}_{15.38}$ with the Ni-centred cluster (N=12) had a packing efficiency of -0.18%; and $\text{Al}_{72.73}\text{Ni}_{9.09}\text{Si}_{18.18}$ with the Si-centred cluster (N=10) had a packing efficiency of 4.28%. As the difference is calculated by $\Delta = (R/R^* - 1) \times 100\%$, the negative value of -0.18% in packing efficiency means the average radius ratio between core atoms and 1st shell atoms is smaller than that of ideal packing with N=12; thus the 1st shell atoms are slightly larger than that in ideal packed cluster. Therefore, in this case, the atoms in the 1st shell are slightly compressed with each other to form an efficiently packed cluster. The positive packing efficiency of 0.61% and 4.28% means the core atom is slightly larger than that in an ideally packed cluster with N=14 and N=10, and the core atom is slightly compressed by the 1st shell atoms to form a efficiently packed cluster. All of these three Al-, Ni- and Si-centred clusters around $\text{Al}_{74.13}\text{Ni}_{7.69}\text{Si}_{18.18}$ have high packing efficiency; this may be helpful to form efficiently packed clusters with less effort in local chemical environment; and the interlock of efficiently packed clusters in the melt is likely to inhibit the atomic

rearrangement for crystallization. Therefore, we draw a potential self-consistence principle for efficiently packed cluster method that the compositions with clusters efficiently packed around all its elements are crystallization resistant and promote glass formation. On inspection of the ternary metallic glasses with elements with similar radius ratios including Zr-Fe-Al, Zr-Cu-Ni-Al, and Pd-[Cu, Co, Ni, Fe]-Si, the glass forming composition was located near the composition $\text{Al}_{74.13}\text{Ni}_{7.69}\text{Si}_{18.18}$ (Fig. 7.10). The alloys with similar radius ratio would have similar packing efficiency at this the composition. It indicated an internal relationship in terms of topology that compositions with clusters all efficiently packed around each constitute element are likely to possess good GFA.

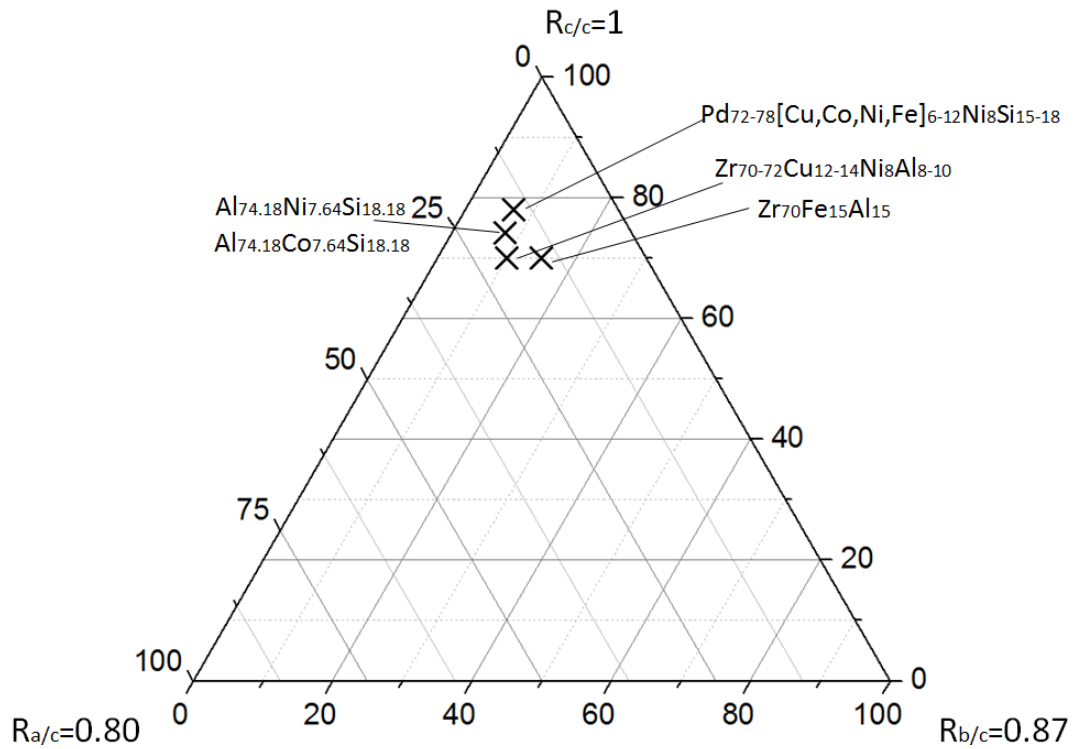


Fig. 7.10 Good glass formers with similar radius ratio.

The compositions studied in the Al-Co-Si and Al-Ni-Si systems provided evidence for the self-consistence principle; however, the featureless zone in the other alloys is relatively narrower than that of Al-Ni-Si and Al-Co-Si alloys. The first reason is the different atomic size that Mn, Cr, and Mo do not have the atomic radius ratio of $R_{a/c}=0.80$ and $R_{b/c}=0.87$ in Al-Ni-Si and Al-Co-Si alloys, therefore it is not a typical self-consistence system which are complied with the rule that clusters are efficiently packed around all elements. The second reason is that other factors such as the nature

of bonding may affect the efficiency in atomic packing. In the next section, heat of mixing are discussed which is known to play a significant role in the formation of metallic glasses.

7.4 Heat of Mixing Criterion

Besides efficiently packed clusters, the chemical interactions between the constituent elements are also considered to be a significant factor for the kinetic aspect of GFA. In previous studies of amorphous alloys, researchers found the negative heat of mixing between the constituent elements would improve GFA (Inoue et al. 2011). The heat of mixing is the enthalpy of mixing of binary liquid in an A-B system at equi-atomic composition (Takeuchi et al. 2005). A negative value means an attractive interaction between elements. The long range homogeneity with attractive interaction was summarized as one of three features in a new glassy structure (Inoue et al. 2011). This is because the strong chemical interaction between the atoms can stabilize the efficiently packed clusters and maintain the supercooled liquid below the solidification temperature. The heat of mixing of elements in Al-Si alloys are shown in Fig. 7.11.

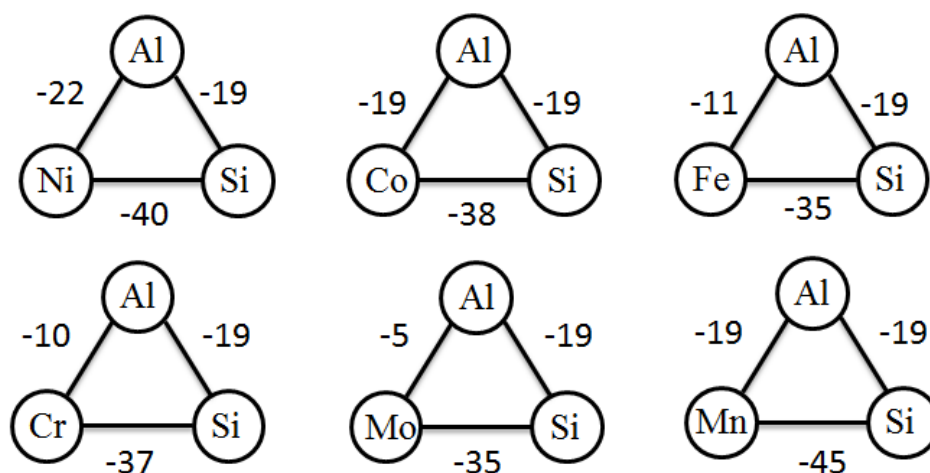


Fig. 7.11 Heat of mixing constituent elements.

The negative heat of mixing is dominant in all six ternary alloys studied in this thesis, which indicated that they have the potential to form efficiently packed clusters by providing attractive bonding among the different types of atoms. However, their bonding strength is varied due to the different heat of mixing of transition metal

elements in their alloy systems, which may possess various contributions to the stability of cluster structures. Among these transition metals, the heat of mixing of aluminum atoms and transition metal atoms follow the sequence Al-Ni(-22) > Al-Co(-19) > Al-Mn(-19) > Al-Fe(-11) > Al-Cr(-10) > Al-Mo(-5); while the heat of mixing of silicon atoms and transition atoms are in another sequence: Si-Mn (-45) > Si-Ni(-40) > Si-Co(-38) > Si-Cr(-37) > Si-Fe(-35) > Si-Mo(-35). The relationship between the thickness of featureless matrix and the negative heat of mixing are plotted in Fig. 7.12.

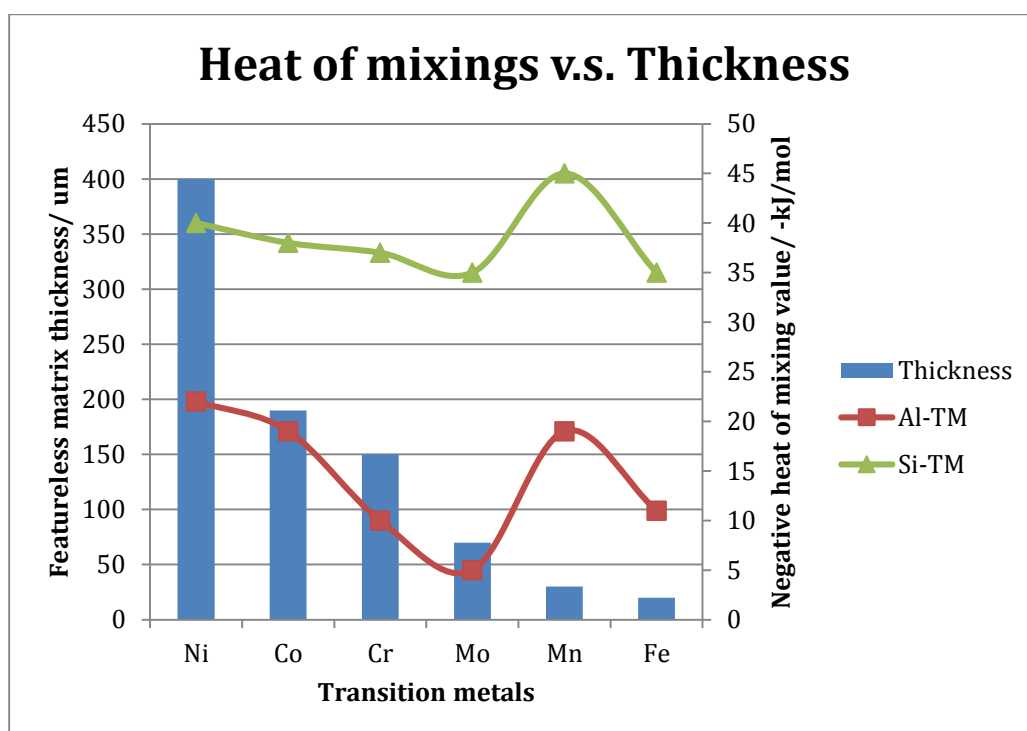


Fig. 7.12 Relationship between the negative heat of mixing and thickness of the featureless matrix in the alloys studied in this thesis.

The widest featureless zones were found in the Al-Ni-Si and Al-Co-Si systems, followed by the Al-Cr-Si and Al-Mo-Si systems. The negative values in heat of mixing are consistent in the first four elements of Ni, Co, Cr, and Mo, which reflected the positive effect of the attractive bonding nature on GFA. Fig. 7.12 showed that Fe has lower heat of mixing than that of Ni and Co, which could be the reason explaining why the GFA of Al-Fe-Si is much lower than that of Al-Co-Si and Al-Ni-Si. When the negative heat of mixing of Al-Fe and Fe-Si is low, the attractive interaction is less effective that the efficiently packed clusters would be more prone to be interrupted and crystal nuclei are easier to form; this promoted the

crystallization of matrix during cooling and restricted the size of featureless zones observed on the wedge tips after casting. Mn has a high negative value of heat of mixing, but the featureless region is only 30 μm at the edge; the possible reason is that Mn, Cr, and Mo do not have the atomic radius ratio as $R_{a/c}=0.80$ and $R_{b/c}=0.87$ in Al-Ni-Si and Al-Co-Si alloys, therefore it is not a typical self-consistence system in metalloid-containing alloys, which are complied with the rule that clusters are efficiently packed around all elements. So even though the negative heat of mixing is high in Al-Mn-Si alloys, the global packing efficiency is not high enough to form a large amorphous zone by copper mould casting.

7.5 Driving Force Criterion

In addition to the requirements of efficiently packed clusters forming in an alloy melt and the beneficial effects of a negative heat of mixing between each of the elements, the driving force criterion is also a significant thermodynamic requirement for estimating the composition dependency of GFA in multicomponent alloys. It is based on a calculation of the driving force for the formation of crystalline phases in the undercooled liquid states (Kim et al. 2005). Glass formation is a competitive process to the formation of more stable crystalline phases below the melting point. Hence, alloy compositions with a low thermodynamic driving force to form crystalline phases would be more likely to generate an amorphous alloy if the cooling rate is sufficiently rapid. Near the melting point, the driving force of crystalline phases is the same as the composition dependence of the liquidus temperature (Kim et al. 2004). As many compositions studied herein exhibiting high atomic packing efficiency fall along the liquidus lines, the liquidus projection in each system can be used for validating whether or not the driving force criterion is applicable in each of the ternary Al-Si-TM alloys investigated (TM=transition metals).

7.5.1 Al-Cr-Si alloys

The compositions investigated in the Al-Cr-Si system do not fall on liquidus lines (Fig. 7.13). Nevertheless, two of the compositions showed a featureless zone at the as-cast wedge tip. The featureless zone in the $\text{Al}_{61.54}\text{Cr}_{7.69}\text{Si}_{30.76}$ alloy (Point 3 in Fig. 7.13) was up to 150 μm compared with that of 40 μm in the $\text{Al}_{63.63}\text{Cr}_{18.18}\text{Si}_{18.18}$ alloy (Point 2). Within the GFR of melt-spun ribbons, alloy 3 was closer than alloy 5 to the Al corner of the ternary phase diagram, which may possess a lower liquidus temperature. This indicates that, within the GFR of melt-spun ribbons, the

composition with the lower liquidus temperature may have a higher GFA. Alloy 2 has a featureless zone of $\sim 40\mu\text{m}$ in width that extended the GFR; compared with alloy 4, this alloy was closer to the liquidus line thus a lower liquidus temperature. Alloy 1 is far away from the optimal GFR and limited its propensity to form a glass. In these Al-Cr-Si alloys, the compositions with featureless zones indicated that the potential glass forming compositions are located at the edge of GFR with the lower liquidus temperature, which indicates that the driving force criterion is important in the search for potential glass formers in Al-based alloys.

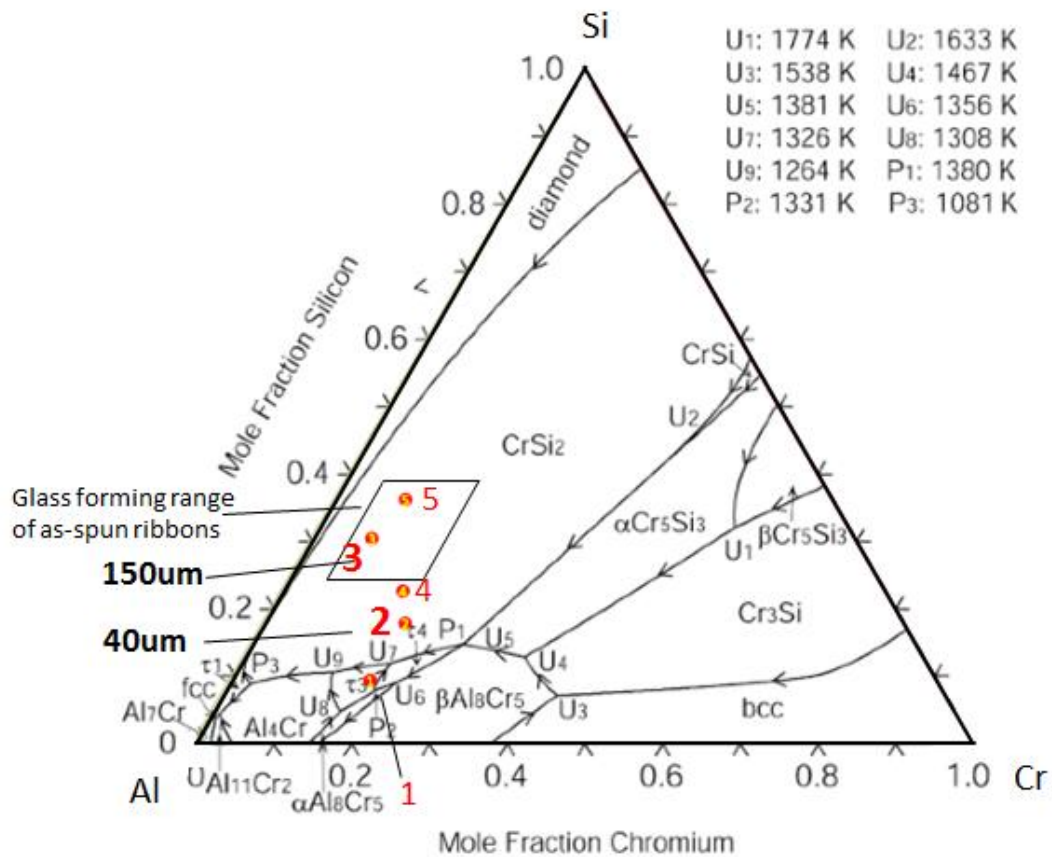


Fig. 7.13 Experimental Al-Cr-Si alloys studied in this thesis and the liquidus projection for this ternary system, after (Liang et al. 2009).

7.5.2 Al-Mo-Si alloys

As shown in Fig. 7.14, two compositions with a featureless zone at their wedge tip were $\text{Al}_{50}\text{Mo}_{31.25}\text{Si}_{18.75}$ (Point 4) and $\text{Al}_{54.54}\text{Mo}_{27.27}\text{Si}_{18.18}$ (Point 2). Based on the isothermal lines in this liquidus projection, the liquidus temperature of alloy 2 is $\sim 1600^\circ\text{C}$ and alloy 4 is $1600\text{--}1700^\circ\text{C}$. Hence, alloy 2 has a slightly lower driving

force for crystallization. This lower driving force correlates well with the observed featureless zone of $\sim 60\mu\text{m}$ and $44\mu\text{m}$ for alloy 2 and 4, respectively.

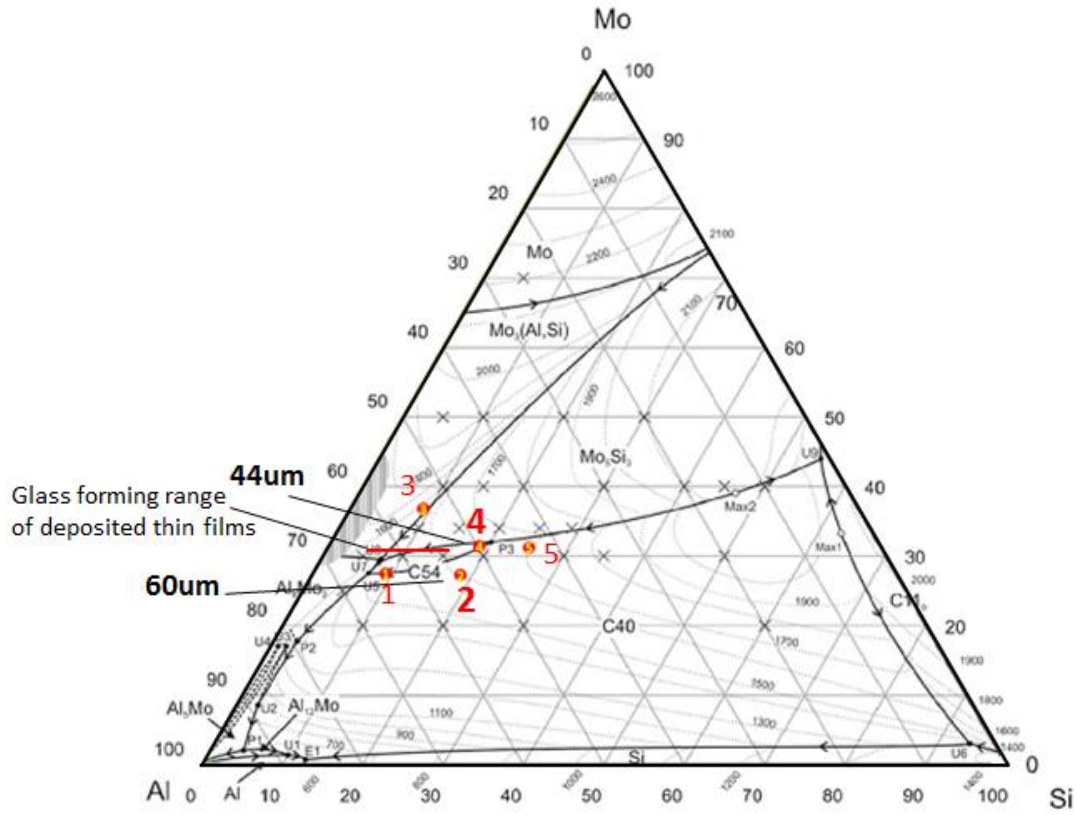


Fig. 7.14 Experimental Al-Mo-Si alloys studied in this thesis and the liquidus projection for this ternary system, after (Ponweiser et al. 2011).

7.5.3 Al-Fe-Si alloys

In Fig. 7.15, $\text{Al}_{63.63}\text{Fe}_{18.18}\text{Si}_{18.18}$ (Point 1) showed featureless zone of $20\mu\text{m}$ at wedge tip, whereas the other compositions studied had rod-shape crystals present at their tips. Among these compositions, $\text{Al}_{62.5}\text{Fe}_{12.5}\text{Si}_{25}$ (point 2) falls on a liquidus line and, hence, has the lowest driving force (it is located between the isothermal lines of 800°C and 850°C). However, this alloy also falls at the edge of the GFR of melt-spun ribbons (Inoue et al. 1988), which may limit its potential to form an amorphous tip by wedge casting. Alloy 1 falls in the GFR of Al-Fe-Si melt-spun ribbons (red boxed region) and, compared with alloys 3, 4, and 5, this alloy has a lower liquidus temperature of $\sim 900^\circ\text{C}$. As $\text{Al}_{63.63}\text{Fe}_{18.18}\text{Si}_{18.18}$ was the only alloy to generate a featureless zone at its wedge tip, this implies that within the GFR, the lower driving force for crystallization enhances the size of the featureless zone, but it also depends on the factors discussed in the previous sections.

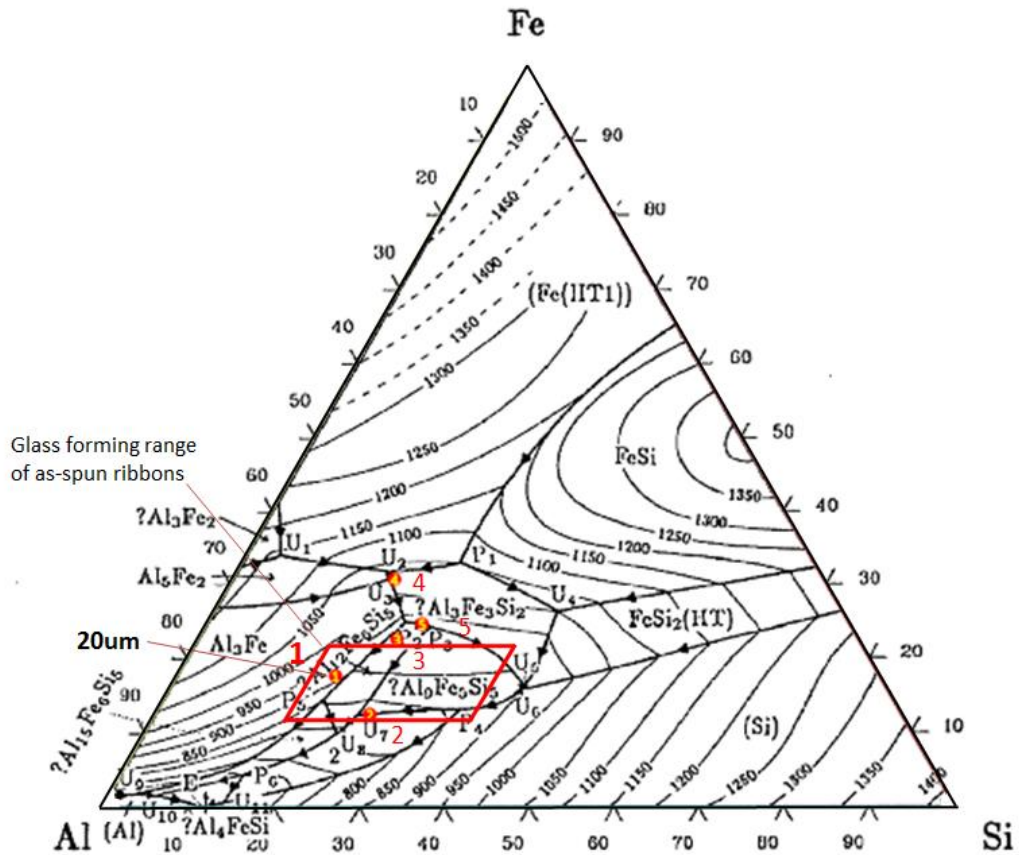


Fig. 7.15 Experimental Al-Fe-Si alloys studied in this thesis and the liquidus projection for this ternary system, after (Villars 1994).

7.5.4 Al-Co-Si alloys

In the Al-Co-Si system (Fig. 7.16), compositions with identifiable featureless zones were $\text{Al}_{74.18}\text{Co}_{7.64}\text{Si}_{18.18}$ (Point Y), $\text{Al}_{56.25}\text{Co}_{18.75}\text{Si}_{25}$ (Point 8), $\text{Al}_{75}\text{Co}_{12.5}\text{Si}_{12.5}$ (Point 1), and $\text{Al}_{63.63}\text{Co}_{9.09}\text{Si}_{27.27}$ (Point 4). Compared with the other seven compositions that were crystallised fully, these compositions are located in the Al-rich end of the ternary diagram and have lower liquidus temperatures. Among these four compositions, alloy Y (195 μm featureless zone) has the lowest liquidus temperature of 740°C, followed by alloy 8 (120 μm zone; liquidus temperature $\sim 900^\circ\text{C}$), alloy 1 (78 μm zone; liquidus temperature $\sim 885^\circ\text{C}$) and alloy 4 (75 μm zone; liquidus temperature $\sim 795^\circ\text{C}$). This analysis supports the other alloys in the previous sections, whereby a low driving force for crystallization substantially contributes to glass formation in the Al-Co-Si system.

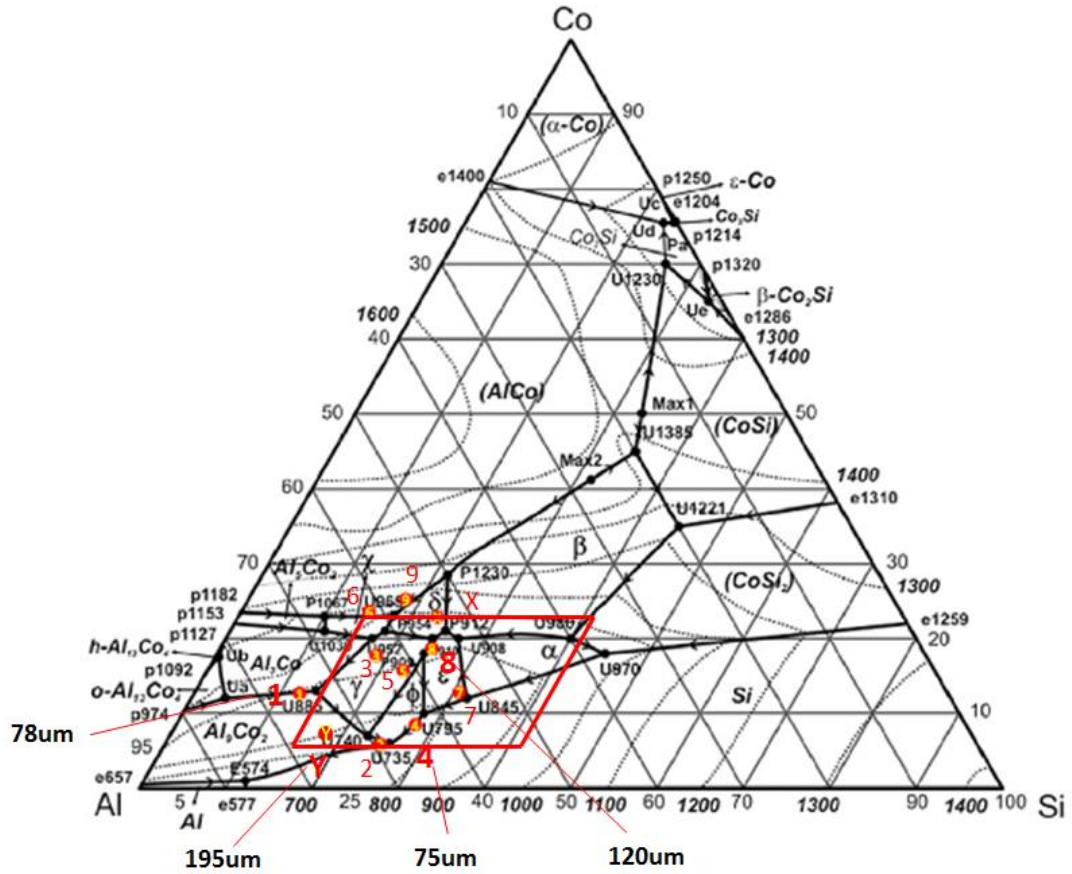


Fig. 7.16 Experimental Al-Co-Si alloys studied in this thesis and the liquidus projection for this ternary system, after (Huber et al. 2011).

7.5.5 Al-Ni-Si alloys

In the Al-Ni-Si system (Fig. 7.17), compositions with identifiable featureless zones were alloy a, c, 9, 1, 2 and 6. Similar to the Al-Co-Si system, the best glass formers are located at the Al-rich end in the phase diagram and have a lower liquidus temperature than the non-glass formers. Among these compositions, alloy c(400 μm featureless zone) has the lowest liquidus temperature of 700°C, followed by alloy 9 (160 μm zone; liquidus temperature 700-800°C), alloy 1 (108 μm zone; liquidus temperature $\sim$ 800°C), alloy 6 (90 μm zone; liquidus temperature $\sim$ 800°C), and alloy 2 (70 μm zone; liquidus temperature 800-900°C). These results are consistent with the other alloy systems in terms of the influence of driving force on the propensity for crystallization. However, while alloy a falls on the liquidus line of 700°C and extended the GFR of melt-spun ribbons (red boxed region), it has a relatively small featureless zone of 45 μm . The lower Si in this alloy composition limits the ability to form efficiently packed clusters (section 7.3) and is a very important factor contributing to glass formation.

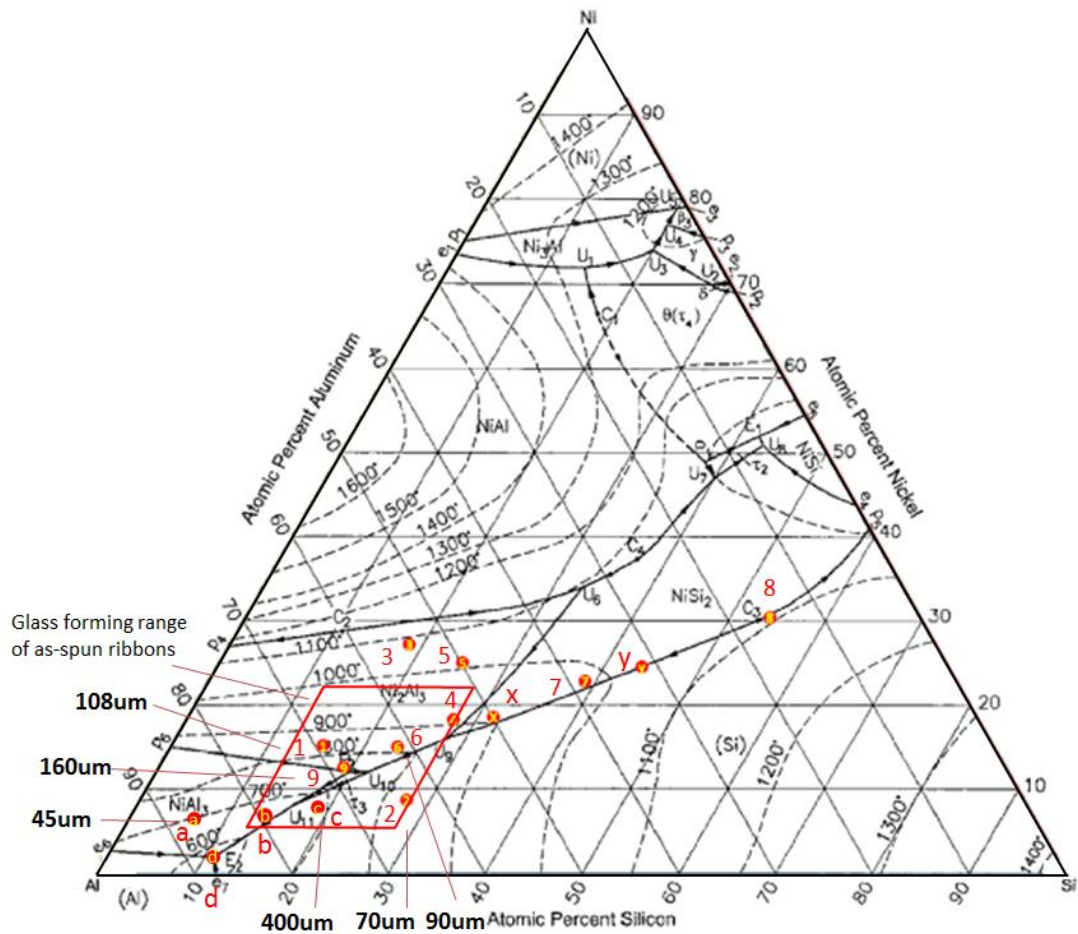


Fig. 7.17 Experimental Al-Ni-Si alloys studied in this thesis and the liquidus projection for this ternary system, after (Raghavan 2005).

7.5.6 Summary

The Al-based compositions with largest featureless zone at the tip of the as-cast wedges were generally located in the GFR of melt-spun ribbons and these compositions also have a low liquidus temperature, that is, the thermodynamic driving force for crystallization is low enough to circumvent crystallization on cooling of the melt at a reasonably rapid rate. Nevertheless, the other factors discussed in section 7.3 (atomic packing considerations) and 7.4 (chemical bonding) must also be taken into consideration in the design of glass forming Al-based alloys.

7.6 Reasons for Poor Glass-formation Al-LTM-Si-base Alloys

With the inclusion of this research, bulk glass formation in Al-based systems remains one of the major challenges of metallic glass research and alloy development. As mentioned previously, Al is considerably different to most other metals, residing in

Group 3A of the periodic table (electronic configuration: $[\text{Ne}]3s^23p^1$), and is hence trivalent. Essentially, by a flaw in nature, pure Al exhibits strong metallic characteristics as its pseudopotential is very shallow even though its bare Coulombic potential is quite deep (Hafner 1985). Indeed, the elements directly above and below Al in the periodic table (B & Ga) are poor metals. Therefore, when Al is alloyed, its true non-metallic nature is revealed (Li et al. 2009). This dualism of metal and non-metal characteristics tends to result in dramatic changes in bonding properties when Al is alloyed.

Given the high outer shell electron density and high Fermi level, Al has a high ionization tendency and prefers to transfer electrons to transition metals (TMs), such as Ni, Co, Fe, Cr, and Mn, to form covalent bonds and a higher driving force to promote ordering i.e. to form intermetallic compounds. The strong electronic interaction between Al and TMs are also evidenced by bond shortening in Al-TM metallic glasses (Fourne ´e et al. 1999, Widom et al. 2000, Cheng et al. 2009). This is due to the high degree of sp-d electron orbital hybridization between Al and TMs, whereby the fewer electrons in the d-shell of the TM, the higher the degree of bond hybridisation and effective bond angle restriction which leads to a stronger ordering potential within the alloy. This is strongly evidenced in this thesis, whereby the degree of GFA found herein (i.e. the lack of structural ordering) increases across the periodic table (see Fig. 7.12) as the outermost d-shell of the TMs are progressively filled, hence we see the highest GFA with alloys that contain Ni, which can essentially maintain a full d-shell with a reduction valence state of 0.

It was hoped that the selection of Si as the major alloying addition to Al-based alloys for glass formation might reduce the ordering interaction between Al and TMs in the selected alloy systems due to the high ionizing potential associated with Si and the potential of establishing a chemical-short-range network-type structure within the glass to help promote glass formation. However, despite the deep eutectic reaction present in the binary Al-Si system, the interaction between Al and Si is largely repulsive, which may have hindered this effect somewhat.

Furthermore, given the relatively small atomic size of Si compared to the other alloy constituents and the experimental outcomes of this thesis, Si appears to have a relatively high diffusion rate within these alloys. On this note, it has also been

reported that the atomic size of constituents can also affect GFA, whereby it is known that alloys that contain larger atomic species generally have slower crystallisation kinetics (Egami 1997, Senkov et al. 2005) essentially due to larger diffusion distances required by an atom to establish crystalline lattice ordering from the liquid state. This is the likely reasoning behind the higher GFA observed in Al-LTM-RE alloys, where RE elements are considerably larger than Al and LTMs and greater than 1.6 times larger than Si.

High viscosity of an alloy melt is important when hindering diffusion and crystallisation kinetics. Here, both Al and Si are slightly disadvantaged with respect to glass formation, as it has been shown that their shear modulus to atomic radius ratio is relatively low which strongly affects alloy viscosity and atomic diffusion, which are clearly reduced for Al-Si alloys when compared to other base metals with high GFA such as Mg, Zr, La or Ca (Senkov et al. 2005).

With respect to phase equilibria, the ionizing nature of Al is also evident, where most alloy systems are dominated by high melting point intermetallics with few deep eutectic reactions, particularly at high solvent concentrations (higher chemical entropy assists with metallic glass formation). This affect strongly hinders the physical ability to undercool Al-based melts relative to cooling rates achievable by conventional copper mould casting methods, hence most Al-based metallic glasses with high GFA are very rich in aluminium (see section 2.4).

7.7 Means of Improving GFA of Al-Si-base Alloys

Due to the reasonably low cost elements in the ternary systems studied in this thesis, the large featureless zones at the wedge tips generated in some of the Al-Ni-Si and Al-Co-Si alloys is a promising starting point in the development of multi-element alloys systems with further improved GFA. The optimal alloy compositions in these systems were developed using a combination of the theory of efficiently packed clusters, chemical information such as the heat of mixing between the constituent elements and thermodynamic driving force considerations.

Based on the ideas brought forward in section 7.6, the addition of elements with larger atomic sizes such as RE elements of alkaline earth elements such as Mg or Ca may improve GFA in Al-Ni-Si alloys. These elements also exhibit a higher shear

modulus to atomic radius ratio which would prove beneficial. For example, it was shown that Al-Ni-Ca alloys can be wedge cast to generate featureless zones of up to 280 μm in width (Chen et al. 2012). Hence, Ca and similar elements may act as a suitable quaternary element addition to the Al-LTM-Si ternary system, although it is important to note that chemical and thermodynamic factors must also be taken into account.

Additions of large early transition metals such as Zr that can increase the thermal stability of the amorphous phase on heating may also improve GFA in the Al-Ni-Si-base system. The addition of multiple elements will also increase the entropy of the system which is also favourable for GFA, which proved effective for bulk glass formation in the Al-Co-Ni-La-Y quinary alloy system (Yang et al. 2009). Although quite expensive, the use of elements such as Pd and Pt, which exhibit a full outer electron d-shell and exceptional GFA in their own alloy systems, might be preferred to avoid the strong bonding interactions observed between Al and TMs with vacated d-shell electron sites.

Concluding Summary

Based on the previous criteria and results, a systematic approach was carried out in the current thesis to investigate the glass-forming ability (GFA) in a wide range of Al-Si-based alloys not containing rare earth (RE) elements, such that the heat-of-mixing rule is applied in the element selection, the driving force criterion introduced for the phase region inspection, and the efficient cluster packing model adopted for optimizing the composition. Based on these concepts, the following cast alloy systems were investigated by copper mould wedge casting:

- (i) **Al-ETM-Si/Ge** ternary and quaternary alloy systems (ETM = Mn, Cr, Mo);
- (ii) **Al-LTM-Si** ternary alloy systems (LTM = Fe, Co), and
- (iii) **Al-LTM-Si** and **Al-LTM₁-LTM₂-Si** ternary and quaternary alloy systems (LTM₁ = Ni; LTM₂ = Co).

The thickest featureless zones were found in the Al-Ni-Si and Al-Co-Si systems, followed by the Al-Cr-Si and Al-Mo-Si systems, with poor to no GFA observed in the Al-Mn-Si and Al-Fe-Si systems. This systematic decrease in the propensity for glass formation correlates well with the observation made in section 7.6, which relates to the progressive filling of outer d-shell by electrons in late transition metals and the associated ionic bonding potential of Al with these elements. Interestingly, the Al-Cr-Si and Al-Mo-Si systems, where Cr and Mo come from the same group in the periodic table with a half filled d-shell, exhibit moderate GFA, which could relate to specific interactions with Al.

Similarly, the featureless zone thickness was found to increase in alloy systems with more negative values of the heat of mixing between atomic constituents, in particular the Al-TM pairs. This again is specifically related to the chemical bonding between these pairs - an observation that has been long-known in the metallic glass community and essential for metallic glass formation, including Al-Si based alloys. The attractive interaction between Al-TM and Si-TM may have promoted short-range ordering that is favourable for glass-formation and appears to have restricted atomic mobility/crystallization kinetics to enough of an extent to enable glass formation in the systems studied here.

It was also revealed in the results of this thesis the important role of the crystallization driving force. Local compositional regions with depressed liquidus temperatures are an indicator of a lower driving force for crystallization and higher liquid stability, particularly near liquidus lines, peritectic or eutectic reactions. This has been highlighted previously in other known systems that exhibit high GFA such as Mg-Cu-Y, Cu-Zr-Al, La-Ni-Al and Pd-Cu-Si. The systems studied in this thesis that displayed the lowest liquidus temperatures in the Al-rich region, i.e. Al-Ni-Si and Al-Co-Si, tended to show the highest GFA and broadest glass-forming composition ranges. The best glass-forming alloy compositions within a given system were found in close proximity to liquidus lines and peritectic reactions, e.g. the $\text{Al}_{68.25}\text{Ni}_{12.5}\text{Si}_{18.75}$ and $\text{Al}_{74.13}\text{Ni}_{7.69}\text{Si}_{18.18}$ alloy compositions. This seems to be the case so long as there is a large enough quantity of each element to constitute an atomic cluster, as the $\text{Al}_{87}\text{Ni}_2\text{Si}_{11}$ ternary eutectic composition did not yield an observable glass, which highlights the important role of topology and entropy.

Furthermore, a lower liquidus temperature allows for ease in undercooling the alloy melt during copper mould casting, being much closer to the ambient temperature and physically reducing the amount of heat that needs to be removed from the melt by the copper mould. This could also be the reason why Al-Mo-Si alloys showed relatively low GFA, given their considerably high melting points.

The final compositions explored in this thesis within the known GFRs were determined using the efficient cluster packing model about all three possible atomic centres. Generally, it was observed that GFA occurred when efficient packing was maintained around the solute elements, either Si or the TM centres with coordination

numbers of $N=10$ and $N=12$, respectively. The widest featureless zone was found for a composition that simultaneously provided efficient packing about both solutes in the $\text{Al}_{74.13}\text{Ni}_{7.69}\text{Si}_{18.18}$ composition where $N=10$ Si-centred and $N=12$ Ni-centred clusters are both efficiently packed. This efficiently-packed bi-cluster method theoretically provides improved so-called ‘global packing efficiency’ for this alloy, suggesting a higher melt viscosity leading to the improved GFA of this particular alloy compared to nearby compositions. Hence, a higher degree of packing efficiency is thought to promote glass formation and the efficient packing concepts outlined in this thesis are also a viable tool for predicting compositions with a higher propensity for glass formation.

The microstructure of Al-Si-based alloys showed that the featureless zones were present in compositions with larger negative mixing heat, lower crystallization driving force, and higher global packing efficiency. The combination of these criteria was used to synthesize and investigate the GFA of Al-TM-Si alloys. The width of featureless zones formed in the wedges followed the order: $\text{Al-Ni-Si} > \text{Al-Co-Si} > \text{Al-Cr-Si} > \text{Al-Mo-Si} > \text{Al-Mn-Si} > \text{Al-Fe-Si}$. The widest featureless zone up to $400\mu\text{m}$ in width was found for the $\text{Al}_{74.13}\text{Ni}_{7.69}\text{Si}_{18.18}$ composition, which is thus far the largest ternary glass-forming composition discovered in Al-metalloid alloys.

By utilizing specific alloy design concepts, optimizing alloy synthesis techniques, and intensive structural characterization, the GFA of a wide range of Al-Si-based alloys was explored. The results and analysis of this exploratory study may hence provide a sound fundamental background for future development of multi-element Al-based alloys with high GFA without RE elements.

Chapter 9

References

- Aburada T., Ünlü N., Fitz-Gerald J. M., Shiflet G. J. and Scully J. R. (2008). *Scripta Materialia* 58(8): 623-626.
- Ahmed E. M. (2008). *Materials Letters* 62(6-7): 960-963.
- Aliaga L. C. R., Danez G. P., Kiminami C. S., Bolfarini C. and Botta W. J. (2011). *Journal of Alloys and Compounds* 509, Supplement 1(0): S141-S144.
- Audebert F., Sirkin H. and Escorial A. G. (1997). *Scripta Materialia* 36(4): 405-410.
- Audebert F., Colaço R., Vilar R. and Sirkin H. (2003). *Scripta Materialia* 48(3): 281-286.
- Becker J. S. (2002). *Spectrochimica Acta Part B: Atomic Spectroscopy* 57(12): 1805-1820.
- Bendersky L. A. and Momprou F. (2012). *Journal of Alloys and Compounds* 536, Supplement 1(0): S171-S174.
- Bo H., Wang J., Jin S., Qi H. Y., Yuan X. L., Liu L. B. and Jin Z. P. (2010). *Intermetallics* 18(12): 2322-2327.
- Boyde A., Switsur V. R. and Fearnhead R. W. (1961). *Journal of Ultrastructure Research* 5(3): 201-207.
- Busch R., Schroers J. and Wang W. H. (2007). *MRS Bulletin* 32: 620-623.
- Chapman K. W., Chupas P. J., Long G. G., Bendersky L. A., Levine L. E., Momprou F., Stalick J. K. and Cahn J. W. (2014). *Acta Materialia* 62(0): 58-68.
- Chen H. S. (1974). *Acta Metallurgica* 22(12): 1505-1511.
- Chen F.-K. and Tsai J.-W. (2006). *Journal of Materials Processing Technology* 177(1-3): 146-149.
- Chen B., Li Y., Li R., Pang S., Cai Y., Wang H. and Zhang T. (2011). *Journal of Materials Research* 26(20): 2642-2652.

- Chen Z. P., Gao J. E., Wu Y., Li H. X., Wang H. and Lu Z. P. (2012). *Journal of Alloys and Compounds* 513(0): 387-392.
- Cheng Y., Ma E., and Sheng H. (2009). *Physical Review Letter* 102: 245501.
- Cini E., Vinet B. and Desre P. J. (2000). *Philosophical Magazine A: Physics of Condensed Matter, Structure, Defects and Mechanical Properties* 80: 955-966.
- Dunlap R. A. and Dini K. (1986). *J. Phys. F: Met. Phys.* 16: 11-16.
- Dunlap R. A., McHenry M. E., Srinivas V., Bahadur D. and O'Handley R. C. (1989). *Physical Review B* 39(7): 4808.
- Egami T. and Waseda Y. (1984). *Journal of Non-Crystalline Solids* 64(1-2): 113-134.
- Egami T. (1997). *Materials Science and Engineering: A* 226-228(0): 261-267.
- Fecht H. J. (1995). *Materials Transactions, JIM* 36: 777-793.
- Feller-Kniepmeier M. and Uhlig H. H. (1961). *Geochimica et Cosmochimica Acta* 21(3-4): 257-IN213.
- Fourne ´ e V., Mazin I., Papaconstantopoulos D.A., and Belin-Ferre ´ E. (1999). *Philosophical Magazine B* 79: 205.
- Gaidarova V. (2007). *Vacuum* 81(9): 1082-1087.
- G ögebakan M. and Okumus M. (2009). *Materials Science- Poland* 27(1): 79-87.
- Gu X., Shiflet G. J., Guo F. Q. and Poon S. J. (2005). *Journal of Materials Research* 20(8): 1935-1938.
- Guo F. Q., Poon S. J. and Shiflet G. J. (2000). *Scripta Materialia* 43(12): 1089-1095.
- Guo F. Q., Enouf S. J., Poon S. J. and Shiflet G. J. (2001). *Philosophical Magazine Letters* 81(3): 203-211.
- Habazaki H., Takahiro K., Yamaguchi S., Hashimoto K., Dabek J., Mrowec S. and Danielewski M. (1994). *Materials Science and Engineering: A* 181-182(0): 1099-1103.
- Hafner, J. (1985). *MRS Proceedings* 63: 73-84.
- Hafner J. and Krajčí M. (1998). *Physical Review B* 57(5): 2849.
- Han G., Qiang J., Li F., Yuan L., Quan S., Wang Q., Wang Y., Dong C. and Häussler P. (2011). *ActaMaterialia* 59(15): 5917-5923.
- Hauser J. J., Chen H. S. and Waszczak J. V. (1986). *Physical Review B* 33(5): 3577.
- He Y., Poon S. J. and Shiflet G. J. (1988a). *Science* 241(4873): 1640-1642.
- He Y., Poon S. J. and Shiflet G. J. (1988b). *Scripta Metallurgica* 22(11): 1813-1816.

- He Y., Dougherty G. M., Shiflet G. J. and Poon S. J. (1993). *Acta Metallurgica et Materialia* 41(2): 337-343.
- Hippert F., Audier M., Klein H., Bellissent R. and Boursier D. (1996). *Physical Review Letters* 76(1): 54.
- Hong S. J., Warren P. J. and Chun B. S. (2001). *Materials Science and Engineering: A* 304–306(0): 362-366.
- Huang Z. H., Li J. F., Rao Q. L. and Zhou Y. H. (2008). *Intermetallics* 16(5): 727-731.
- Huber B., Kodentsov A. and Richter K. W. (2011). *Intermetallics* 19(3): 307-320.
- Inoue A., Yamamoto M., Kimura H. M. and Masumoto T. (1987). *Journal of Materials Science Letters* 6(2): 194-196.
- Inoue A., Bizen Y., Kimura H. M., Masumoto T. and Sakamoto M. (1988a). *Journal of Materials Science* 23(10): 3640-3647.
- Inoue A., Bizen Y. and Masumoto T. (1988b). *Metallurgical and Materials Transactions A* 19(2): 383-385.
- Inoue A., Matsumoto N. and T. (1990). *JIM, Materials Transactions* 31: 493-500
- Inoue A., Zhang T. and Masumoto T. (1991). *Materials Science and Engineering: A* 134(0): 1125-1128.
- Inoue A., Zhang T. and Masumoto T. (1993). *Journal of Non-Crystalline Solids* 156–158, Part 2(0): 473-480.
- Inoue A., Nishiyama N., Hatakeyama K. and Masumoto T. (1994a). *Materials Transactions, JIM* 35(4): 282-285.
- Inoue A., Onoue K. and Masumoto T. (1994b). *Materials Transactions, JIM* 35(11): 808-813.
- Inoue A. (1995). *Materials Transactions, JIM* 36(7): 866-875.
- Inoue A. (1997). *Materials Science and Engineering: A* 226–228(0): 357-363.
- Inoue A., Takeuchi A. and Zhang T. (1998). *Metallurgical and Materials Transactions A* 29(7): 1779-1793.
- Inoue A. (2000). *Acta Materialia* 48(1): 279-306.
- Inoue A. and Takeuchi A. (2011). *Acta Materialia* 59(6): 2243-2267.
- Johnson W. L. (1986). *Progress in Materials Science* 30(2): 81-134.
- Kalay Y. E., Chumbley L. S., Kramer M. J. and Anderson I. E. (2010). *Intermetallics* 18(8): 1676-1682.
- Kiliçaslan M. F., Yilmaz F., Ergen S., Hong S. J. and Uzun O. (2013). *Materials Characterization* 77: 15-22.

- Kim D., Lee B. J. and Kim N. J. (2004). *Intermetallics* 12(10-11): 1103-1107.
- Kim D., Lee B. J. and Kim N. J. (2005). *Scripta Materialia* 52(10): 969-972.
- Kimura H. M., Inoue A., Bizen Y., Masumoto T. and Chen H. S. (1988). *Materials Science and Engineering* 99(1-2): 449-452.
- Klement W., Willens R. H. and Duwez P. (1960). *Nature* 187(4740): 869-870.
- Krendelsberger N., Weitzer F. and Schuster J. (2002). *Metallurgical and Materials Transactions A* 33(11): 3311-3319.
- Kuzmin O. V., Pei Y. T. and De Hosson J. T. M. (2012). *Scripta Materialia* 67(4): 344-347.
- Legresy J. M., Audier M., Simon J. P. and Guyot P. (1986). *Acta Metallurgica* 34(9): 1759-1769.
- Legresy J. M., Audier M. and Guyot P. (1988). *Materials Science and Engineering* 97(0): 385-390.
- Laws K. J., Gun B. and Ferry M. (2008). *Materials Science and Engineering: A* 475(1-2): 348-354.
- Laws K. J., Shamlaye K. F., Gun B. and Ferry M. (2009). *Journal of Alloys and Compounds* 486(1-2): L27-L29.
- Laws K., Shamlaye K., Wong K., Gun B. and Ferry M. (2010). *Metallurgical and Materials Transactions A* 41(7): 1699-1705.
- Laws K. J., Cao J. D., Reddy C., Shamlaye K. F., Gun B. and Ferry M. (2014). *Scripta Materialia* 88(1): 37-40.
- Li C., Li J.C., Zhao M., and Jiang Q. (2009). *Journal of Alloys and Compounds* 475: 752.
- Li X. P., Yan M., Yang B. J., Wang J. Q., Schaffer G. B. and Qian M. (2011). *Materials Science and Engineering: A* 530(0): 432-439.
- Li X. P., Yan M., Imai H., Kondoh K., Wang J. Q., Schaffer G. B. and Qian M. (2013). *Materials Science and Engineering: A* 568(1): 155-159.
- Liang Y., Guo C., Li C. and Du Z. (2009). *Journal of Phase Equilibria and Diffusion* 30(5): 462-479.
- Lu Y. J. (2011). *Philosophical Magazine Letters*: 1-11.
- Maret M., Chieux P., Dubois J. M. and Pasturel A. (1991). *Journal of Physics: Condensed Matter* 3(16): 2801.
- McHenry M. E., Dunlap R. A., Srinivas V., Bahadur D. and O'Handley R. C. (1990). *Physical Review B* 41(10): 6933.
- Miracle D. B., Sanders W. S. and Senkov O. N. (2003). *Philosophical Magazine* 83(20): 2409-2428.

- Miracle D. B. (2004a). *Nature Materials* 3(10): 697-702.
- Miracle D. B. (2004b). *Journal of Non-Crystalline Solids* 342(1–3): 89-96.
- Miracle D. B., Lord E. A. and Ranganathan S. (2006). *Materials Transactions* 47(7): 1737-1742.
- Ovun M., Kramer M. J. and Kalay Y. E. (2014). *Journal of Non-Crystalline Solids* 405(0): 27-32.
- Perepezko J. H. and Hildal K. (2008). *Materials Science and Engineering: B* 148(1-3): 171-178.
- Perepezko J. H. and Imhoff S. D. (2010). *Journal of Alloys and Compounds* 504, Supplement 1(0): S222-S225.
- Ponweiser N., Paschinger W., Ritscher A., Schuster J. C. and Richter K. W. (2011). *Intermetallics* 19(3): 409-418.
- Raghavan V. (2005). *Journal of Phase Equilibria and Diffusion* 26(3): 262-267.
- Roy D. and Raghuvanshi H. (2011). *Journal of Non-Crystalline Solids* 357(7): 1701-1704.
- Salehi M., Shabestari S. G. and Boutorabi S. M. A. (2013). *Materials Science and Engineering: A* 586(0): 407-412.
- Sanders W. S., Warner J. S. and Miracle D. B. (2006). *Intermetallics* 14(3): 348-351.
- Schroers J., Nguyen T., O’Keeffe S. and Desai A. (2007). *Materials Science and Engineering: A* 449–451(1): 898-902.
- Schroers J. (2010). *Adv. Mater.* 22: 1566-1597.
- Schumacher P. and Greer A. L. (1994a). *Materials Science and Engineering: A* 181–182(0): 1335-1339.
- Schumacher P. and Greer A. L. (1994b). *Materials Science and Engineering: A* 178(1–2): 309-313.
- Schumacher P. and Greer A. L. (1997). *Materials Science and Engineering: A* 226–228(0): 794-798.
- Senkov O.N., Miracle D.B., Mullens H.M. (2005). *Journal of Applied Physics* 97: 103502.
- Sheng H. W., Liu H. Z., Cheng Y. Q., Wen J., Lee P. L., Luo W. K., Shastri S. D. and Ma E. (2007). *Nat Mater* 6(3): 192-197.
- Sheng H. W., Cheng Y. Q., Lee P. L., Shastri S. D. and Ma E. (2008). *Acta Materialia* 56(20): 6264-6272.
- Song K., Bian X., Guo J., Wang S., Sun B. A., Li X. and Wang C. (2007). *Journal of Alloys and Compounds* 440(1–2): L8-L12.

- Stadnik Z. M. and Stroink G. (1991). *Physical Review B* 43(1): 894.
- Stojanova L., Russew K., Fazakas E. and Varga L. K. (2012). *Journal of Alloys and Compounds* 540(0): 192-197.
- Takeuchi A. and Inoue A. (2005). *Materials Transactions* 46(12): 2817-2829.
- Tsai A. P., Inoue A. and Masumoto T. (1988a). *Metallurgical Transactions A* 19(2): 391-393.
- Tsai, A. P., Inoue A. and Masumoto T. (1988b). *Metallurgical transactions. A, Physical metallurgy and materials science* 19: 1369-1371.
- Tsai A. P., Inoue A., Masumoto T. and Kataoka N. (1988c). *Japanese Journal of Applied Physics, Part 1: Regular Papers and Short Notes and Review Papers* 27: 2252-2255.
- Tsai A. P., Inoue A., Bizen Y. and Masumoto T. (1989). *Acta Metallurgica* 37(5): 1443-1449.
- Uzun O., Karaaslan T., Gogebakan M. and Keskin M. (2004). *Journal of Alloys and Compounds* 376(1-2): 149-157.
- van Dooren A. A. and Müller B. W. (1984). *International Journal of Pharmaceutics* 20(3): 217-233.
- Vernon-Parry K. D. and Wright A. C. (2001). *III-Vs Review* 14(1): 48-51.
- Villars P. (1994). *Handbook of ternary alloy phase diagrams*. Materials Park, OH, Materials Park, OH: ASM International.
- Walaszek D., Senn M., Faller M., Philippe L., Wagner B., Bulska E. and Ulrich A. (2013). *Spectrochimica Acta Part B: Atomic Spectroscopy* 79–80(1): 17-30.
- Wang J. Q., Zhang H. W., Gu X. J., Lu K., Sommer F. and Mittemeijer E. J. (2004a). *Materials Science and Engineering: A* 375–377(1): 980-984.
- Wang W. H., Dong C. and Shek C. H. (2004b). *Materials Science and Engineering: R: Reports* 44(2-3): 45-89.
- Wang Q., Qiang J. B., Xia J. H., Wu J., Wang Y. M. and Dong C. (2007). *Intermetallics* 15(5–6): 711-715.
- Wang J. Q., Dong P., Hou W. L., Chang X. C. and Quan M. X. (2013). *Journal of Alloys and Compounds* 554(1): 419-425.
- Widom M., Al-Lehyani I., and Moriarty J.A. (2000). *Physical Review B* 62: 3648.
- Wilde G., Sieber H. and Perepezko J. H. (1999). *Scripta Materialia* 40(7): 779-783.
- Xu D., Lohwongwatana B., Duan G., Johnson W. L. and Garland C. (2004). *Acta Materialia* 52(9): 2621-2624.
- Yang B. J., Yao J. H., Zhang J., Yang H. W., Wang J. Q. and Ma E. (2009). *Scripta Materialia* 61(4): 423-426.

- Yang B. J., Yao J. H., Chao Y. S., Wang J. Q. and Ma E. (2010). *Philosophical Magazine* 90(23): 3215-3231.
- Yang H. W., Tan M. J. and Ramanujan R. V. (2012). *Scripta Materialia* 66(6): 382-385.
- Zhang, Z., W. Zhou, X. Z. Xiong, L. T. Kong and J. F. Li (2012). *Intermetallics* 24: 1-6.
- Zhuo L. C., Pang S. J., Wang H. and Zhang T. (2009). *Chinese Physics Letters* 26(6): 066402.

Appendix A

The Efficiently Packed Cluster Model

A.1 Introduction

The efficiently packed cluster model is based on the observation of increased density in metallic glasses compared to their crystalline counterparts (Miracle et al. 2003). Miracle's model introduced the sphere-packing scheme, i.e., the dense packing of atomic clusters (Miracle 2004). This model predicted the number of the first shell atoms according to the critical radius ratio of the solute atom and the solvent atom; the relationship between the critical radius ratio (R) and the coordination number (N) of the cluster is listed by the equation below. This offered a way to predict glass-forming compositions in a range of alloy systems (Laws et al. 2009, Laws et al. 2010, Laws et al. 2012, and Laws et al. 2014).

$$N = \frac{4\pi}{\pi(2 - q) + 2q \cos^{-1} \left\{ \left(\sin \frac{\pi}{q} \right) \left(1 - \frac{1}{(R+1)^2} \right)^{1/2} \right\}}$$

Equation A.1 The relationship between the coordination number and the critical radius ratio.

Here, N is the coordination number, indicating the number of atoms in the first shell; R is the critical radius ratio of solute and solvent atoms; q is the surface coordination number. Based on the calculation, Miracle's model generated the list of coordination numbers for each critical radius ratio. Later, Wang et al. (2007) proposed the cluster line criteria, which used the average radius of the first shell atoms r_1 to calculate the radius ratio of solute and solvent atoms $R_{0/1}$; the packing efficiency is then represented by the percentage deviation Δ from the critical radius ratio R :

$$R_{0/1} = \frac{r_0}{r_1}$$

$$\Delta = \frac{(R_{0/1} - R)}{R} \times 100\% = \left(\frac{R_{0/1}}{R} - 1 \right) \times 100\%$$

Equation A.2 The packing efficiency, represented by the percentage of deviation of radius ratio from the critical radius ratio.

Here, $R_{0/1}$ is the radius ratio of solute and solvent atoms, R the critical radius ratio, and Δ the packing efficiency.

A.2 Example Calculation for Efficiently Packed Clusters

The determination of efficiently packed clusters is based on the calculated packing efficiency. The packing efficiency is represented by the percentage deviation between the average radius ratio and the critical radius ratio. For each coordination number, there is a unique critical radius ratio. As most glass-forming systems have clusters with coordination numbers between 9 and 17, the following procedure is used for the calculation of efficiently packed clusters.

1. Select the constitutive elements for the ternary system and list their radii.
2. Choose one element, such as nickel, to be the centre atom of the cluster, and start building the cluster with $N=9$.
3. List all possible combinations of the first shell atoms and calculate the average radius of first shell atoms r_1 .
4. Calculate the radius ratio of the centre and first shell atoms $R_{0/1}$, and then the percentage of deviation Δ from the critical radius ratio R for this cluster.
5. Repeat the procedure for Al-centred and Si-centred clusters with $N=9$, and then calculate for clusters with $N=10$ to 17.

Taking the Al-Ni-Si cluster with $N=12$ as an example, the atomic radii are $r_{Al}=143.0\text{pm}$, $r_{Ni}=124.6\text{pm}$, and $r_{Si}=115.3\text{pm}$. The critical radius ratio for the cluster of $N=12$ is 0.902. Taking Point 1 in Al-Ni-Si alloys as an example, the Ni-centred cluster has the centre atom of Ni, and first shell atoms of 1 Ni, 2 Si, and 9 Al. The packing efficiency is calculated as follows:

$$R_{0/1} = \frac{r_0}{r_1} = \frac{124.6}{\left[\frac{(124.6 \times 1) + (115.3 \times 2) + (143 \times 9)}{12} \right]} = 0.910$$

$$\Delta = \left(\frac{R_{0/1}}{R} - 1 \right) \times 100\% = \left(\frac{0.91042}{0.902} - 1 \right) \times 100\% = 0.93\%$$

Equation A.3 The packing efficiency, calculated for the location 1 in the phase diagram of Al-Ni-Si in Al-rich end ($\text{Al}_9\text{Ni}_1\text{Si}_2$).

The composition for this cluster can then be calculated based on how many atoms of each element are present in the centre atom position and in the first shell.

$$at. \% (Ni) = \left(\frac{2}{13} \right) \times 100\% = 15.38\%$$

$$at. \% (Si) = \left(\frac{2}{13} \right) \times 100\% = 15.38\%$$

$$at. \% (Al) = \left(\frac{9}{13} \right) \times 100\% = 69.23\%$$

Equation A.4 The atomic percentage of each element in this calculated cluster.

The composition of this cluster is calculated as $\text{Al}_{69.23}\text{Ni}_{15.38}\text{Si}_{15.38}$. The rest of the Ni-centred cluster with N=12 is shown in Table A.1, and the highlighted part is the cluster calculated in the example.

Table A.1: The packing efficiency calculated for Ni-centred clusters with N=12 and their corresponding compositions.

Ni-Centred Clusters								
Atom Number			Atomic Packing Efficiency			Atom%		
Ni	Si	Al	R _{av} (nm)	R	Δ (%)	Al	Si	Ni
1	12	0	0.115	1.081	19.80	0	92.31	7.69
1	11	1	0.118	1.059	17.45	7.69	84.62	7.69
1	10	2	0.120	1.039	15.19	15.38	76.92	7.69
1	9	3	0.122	1.019	13.01	23.08	69.23	7.69
1	8	4	0.125	1.000	10.92	30.77	61.54	7.69
1	7	5	0.127	0.982	8.90	38.46	53.85	7.69
1	6	6	0.129	0.965	6.95	46.15	46.15	7.69
1	5	7	0.131	0.948	5.07	53.85	38.46	7.69
1	4	8	0.134	0.931	3.26	61.54	30.77	7.69
1	3	9	0.136	0.916	1.51	69.23	23.08	7.69
1	2	10	0.138	0.900	-0.19	76.92	15.38	7.69
1	1	11	0.141	0.886	-1.82	84.62	7.69	7.69
1	0	12	0.143	0.871	-3.41	92.31	0	7.69
2	11	0	0.116	1.073	19.00	0	84.62	15.38
2	10	1	0.118	1.052	16.68	7.69	76.92	15.38
2	9	2	0.121	1.032	14.45	15.38	69.23	15.38
2	8	3	0.123	1.013	12.30	23.08	61.54	15.38
2	7	4	0.125	0.994	10.23	30.77	53.85	15.38
2	6	5	0.128	0.976	8.24	38.46	46.15	15.38
2	5	6	0.130	0.959	6.31	46.15	38.46	15.38
2	4	7	0.132	0.942	4.46	53.85	30.77	15.38
2	3	8	0.135	0.926	2.67	61.54	23.08	15.38
2	2	9	0.137	0.910	0.93	69.23	15.38	15.38
2	1	10	0.139	0.895	-0.74	76.92	7.69	15.38
2	0	11	0.141	0.881	-2.36	84.62	0	15.38
3	10	0	0.117	1.066	18.21	0	76.92	23.08
3	9	1	0.119	1.046	15.92	7.69	69.23	23.08
3	8	2	0.121	1.026	13.72	15.38	61.54	23.08
3	7	3	0.124	1.007	11.60	23.08	53.85	23.08
3	6	4	0.126	0.988	9.55	30.77	46.15	23.08
3	5	5	0.128	0.970	7.58	38.46	38.46	23.08
3	4	6	0.131	0.953	5.68	46.15	30.77	23.08
3	3	7	0.133	0.937	3.85	53.85	23.08	23.08
3	2	8	0.135	0.921	2.08	61.54	15.38	23.08
3	1	9	0.138	0.905	0.37	69.23	7.69	23.08
3	0	10	0.140	0.890	-1.29	76.92	0	23.08
4	9	0	0.118	1.059	17.43	0	69.23	30.77
4	8	1	0.120	1.039	15.17	7.69	61.54	30.77
4	7	2	0.122	1.019	13.00	15.38	53.85	30.77
4	6	3	0.125	1.000	10.90	23.08	46.15	30.77
4	5	4	0.127	0.982	8.88	30.77	38.46	30.77
4	4	5	0.129	0.965	6.94	38.46	30.77	30.77
4	3	6	0.131	0.948	5.06	46.15	23.08	30.77

4	2	7	0.134	0.931	3.25	53.85	15.38	30.77
4	1	8	0.136	0.916	1.50	61.54	7.69	30.77
4	0	9	0.138	0.900	-0.20	69.23	0	30.77
5	8	0	0.118	1.052	16.66	0	61.54	38.46
5	7	1	0.121	1.032	14.43	7.69	53.85	38.46
5	6	2	0.123	1.013	12.29	15.38	46.15	38.46
5	5	3	0.125	0.994	10.22	23.08	38.46	38.46
5	4	4	0.128	0.976	8.22	30.77	30.77	38.46
5	3	5	0.130	0.959	6.30	38.46	23.08	38.46
5	2	6	0.132	0.942	4.45	46.15	15.38	38.46
5	1	7	0.135	0.926	2.65	53.85	7.69	38.46
5	0	8	0.137	0.910	0.92	61.54	0	38.46
6	7	0	0.119	1.045	15.91	0	53.85	46.15
6	6	1	0.121	1.026	13.70	7.69	46.15	46.15
6	5	2	0.124	1.006	11.58	15.38	38.46	46.15
6	4	3	0.126	0.988	9.54	23.08	30.77	46.15
6	3	4	0.128	0.970	7.57	30.77	23.08	46.15
6	2	5	0.131	0.953	5.67	38.46	15.38	46.15
6	1	6	0.133	0.937	3.84	46.15	7.69	46.15
6	0	7	0.135	0.921	2.07	53.85	0	46.15
7	6	0	0.120	1.039	15.16	0	46.15	53.85
7	5	1	0.122	1.019	12.98	7.69	38.46	53.85
7	4	2	0.125	1.000	10.89	15.38	30.77	53.85
7	3	3	0.127	0.982	8.87	23.08	23.08	53.85
7	2	4	0.129	0.964	6.93	30.77	15.38	53.85
7	1	5	0.131	0.948	5.05	38.46	7.69	53.85
7	0	6	0.134	0.931	3.24	46.15	0	53.85
8	5	0	0.121	1.032	14.42	0	38.46	61.54
8	4	1	0.123	1.013	12.27	7.69	30.77	61.54
8	3	2	0.125	0.994	10.21	15.38	23.08	61.54
8	2	3	0.128	0.976	8.21	23.08	15.38	61.54
8	1	4	0.130	0.959	6.29	30.77	7.69	61.54
8	0	5	0.132	0.942	4.43	38.46	0	61.54
9	4	0	0.121	1.025	13.69	0	30.77	69.23
9	3	1	0.124	1.006	11.57	7.69	23.08	69.23
9	2	2	0.126	0.988	9.53	15.38	15.38	69.23
9	1	3	0.128	0.970	7.56	23.08	7.69	69.23
9	0	4	0.131	0.953	5.66	30.77	0	69.23
10	3	0	0.122	1.019	12.97	0	23.08	76.92
10	2	1	0.125	1.000	10.88	7.69	15.38	76.92
10	1	2	0.127	0.982	8.86	15.38	7.69	76.92
10	0	3	0.129	0.964	6.92	23.08	0	76.92
11	2	0	0.123	1.013	12.26	0	15.38	84.62
11	1	1	0.125	0.994	10.19	7.69	7.69	84.62
11	0	2	0.128	0.976	8.20	15.38	0	84.62
12	1	0	0.124	1.006	11.56	0	7.69	92.31
12	0	1	0.126	0.988	9.52	7.69	0	92.31
13	0	0	0.125	1.000	10.86	0	0	100