Heterogeneous nucleation of Fe-containing intermetallic in Al alloys

Z. Que and Z. Fan

Introduction
The control of Fe-rich intermetallic compounds (IMCs) is a big challenge to improve the properties of recycled Al alloys. Therefore, this research is based on understanding the heterogeneous nucleation mechanisms of IMCs, and is focused on developing an approach to modify or refine them.

Summary of key results
In this study, heterogeneous nucleation of the Al_{15}(Fe,Mn)_{3}Si_{2} intermetallic phase in Al-Mg-Si alloys was investigated. The difficulty in nucleating IMCs, which requires large undercooling, was understood (Figure 1). A novel grain refiner which adsorbed the necessary alloying elements on the surface was developed. The heterogeneous nucleation of primary Al_{15}(Fe,Mn)_{3}Si_{2} phase with increased numbers and decreased size was greatly enhanced by the addition of 1000ppm novel grain refiner. The clear evidence of the atomic layering on the surface of the nucleus was observed by STEM (Figure 2). The effects of the alloying elements on the potential nucleus for the primary Al_{15}(Fe,Mn)_{3}Si_{2} phase in the alloy studied were investigated. A composition templating concept was developed to explain the heterogeneous nucleation mechanism of IMCs.

Impact
This research has presented the first report indicating clear evidence of heterogeneous nucleation of the Al_{15}(Fe,Mn)_{3}Si_{2} phase, and developed a novel grain refiner to enhance the nucleation. In addition, the large nucleation undercooling of IMCs was also measured, which has indicated nucleation difficulties. Furthermore, understanding of heterogeneous nucleation has been greatly improved by composition templating.

Future directions
Although this research has developed a more detailed understanding for nucleation of the Al_{15}(Fe,Mn)_{3}Si_{2} phase, the nucleation mechanism of other IMCs still needs to be studied in detail. This will include how to apply the new grain refiner in industry and study its associated applications.

Summary
The heterogeneous nucleation of primary Al_{15}(Fe,Mn)_{3}Si_{2} phase was studied and has become much clearer within this research. The key points of the difficulties (large undercooling) of controlling the nucleation of IMCs have been successfully understood.
A molecular dynamics study of the structural effect of substrates on heterogeneous nucleation

H. Men and Z. Fan

Introduction
The liquid at its interface with a substrate may exhibit pronounced atomic ordering even above the liquidus \( T_L \), and can play a critical role in heterogeneous nucleation on undercooling. This project intends to investigate effects of structural properties (misfit, \( f \)) of substrates on pre-nucleation (above \( T_L \)) and subsequent heterogeneous nucleation.

Summary of key results
This project reveals that the substrate lattice can induce 2D solid-like ordered structures in the liquid at the interface near \( T_L \), i.e., pre-nucleation (Figure 1a). The dislocations in the pre-nucleation structures largely eliminate the misfit of the initial systems. Simultaneously, the 2D solid-like structures provide a structural templating mechanism for formation of new solid phase during subsequent heterogeneous nucleation, as proposed in the Epitaxial model. The new phase then proceeds through a layer-by-layer mechanism during the heterogeneous nucleation, as shown in Figure 1b.

Impact
The achievement of this project is of significance to both industry and the academic community. We obtained reliable and fundamental knowledge of configurations of the liquid at the interface, where we found there exists 2D ordered structures even above \( T_L \). We have provided an in-depth understanding of the atomic mechanism of heterogeneous nucleation by proposing a structural templating mechanism. This research can shed new light on theories of heterogeneous nucleation, and should have an important impact in the field of solidification.

Future directions
The investigation of structural effects of the substrate on configurations of the liquid at the interface is far from complete, for instance, substrates with different crystal structures and orientation. The atomic mechanism of heterogeneous nucleation also remains far from clear, and we may have to reconsider the foundation of heterogeneous nucleation, based on the concept of pre-nucleation. This should provide us with a better understanding (modelling) of industrial practices for solidification.

Summary
We are investigating the effects of \( f \) on atomic ordering of the liquid at the interface, with MD simulations. This project reveals that there is an ordered structure at the interface even above \( T_L \), i.e., pre-nucleation, and this pre-nucleation may dramatically facilitate heterogeneous nucleation. We have also proposed a new mechanism of structural templating for heterogeneous nucleation.
The effect of interfacial segregation on heterogeneous nucleation

Y. Wang, T. Hashimoto, X. Zhou, D.H. Maldonado, Q.M. Ramasse and Z. Fan

Introduction

As the most widely used grain refiner for Al alloys, Al–Ti–B master alloy provides TiB$_2$ particles which promote heterogeneous nucleation to achieve grain refinement. Although extensive research has been carried out since the introduction of grain refiners over 60 years ago, the mechanism underlying nucleation was not well understood. In our research, Cs-corrected electron microscopy was used to examine directly TiB$_2$/Al interfaces in order to understand the mechanisms of TiB$_2$ inoculation and the so-called Zr poisoning effect at the atomic scale.

Summary of key results

As shown in Figure 1a, Ti atoms were found to absorb on TiB$_2$ surfaces and the Ti-rich adsorption monolayer was responsible for heterogeneous nucleation of Al. This clarifies that an effective grain refiner for Al alloys contains necessarily excess Ti, such as the most commonly used Al-5Ti-1B and Al-3Ti-1B master alloys. Addition of a small amount of a Zr significantly reduced the grain refining efficiency of TiB$_2$. Advanced TEM/STEM revealed the presence of Zr-rich adsorption monolayer on the TiB$_2$ surface, as shown in Figure 1b. The Zr “poisoning effect” was attributed to the preferential adsorption of Zr over Ti, leading to poisoning. Segregation of Fe atoms was also observed on the boride surface, with the Fe atoms-coated borides being an effective refiner for Fe-rich intermetallics.

Impact

The mechanisms underlying TiB$_2$ inoculation for heterogeneous nucleation of Al and the Zr poisoning effect have been understood at the atomic scale for the first time. Based on the research results, manipulation of specific nucleation substrates can be achieved, so that more effective and cost efficient grain refiners for various alloy systems can be designed.

Future directions

Further extensive work will be focused on the universal adsorption phenomenon of alloying elements at interfaces and actual crystal structure of adsorption or segregation layers on the substrate surface. This will deepen our understanding of how such adsorption of alloying elements modifies the surface of nucleation substrates and its effect on nucleation potency.
Impact
One of the major tasks during recycling of Al- and Mg- alloys is to clean the alloy melts in order to reduce or eliminate the detrimental effects of oxides and other inclusions. However, our research demonstrates that oxides in Al- and Mg- alloy melts can be harnessed to mitigate their harmful effects and be deployed for grain refinement during a variety of casting processes.

Summary of key results
Significant grain refinement of Al- and Mg- alloys has been achieved by intensive melt shearing without addition of grain refiner. Inoculation by a large number of such native oxide particles, which had been dispersed by melt shearing, promotes heterogeneous nucleation and thus leads to grain refinement. MgAl$_2$O$_4$ particles in Al-Mg alloys are potent nucleation substrates for Al grains. MgO particles in pure Mg and AZ91D melts are faceted with (100) and (111) planes respectively. High resolution TEM revealed that, with well-defined orientation relationships (OR), both types of MgO particles act as the heterogeneous nucleation substrates for Mg. The images below show the oxide cubes and MgO/Mg interface, demonstrating that MgO nucleates Mg.

Future directions
Extensive investigation of growth behaviour of native oxides in Al- and Mg- alloys will be carried out. In particular, the effects of alloying elements on size and morphology will be studied with processing parameters being optimised in order to achieve appropriate morphology and size distribution required for heterogeneous nucleation. Advanced Cs-corrected TEM/STEM will be utilised to examine Al or Mg/oxide interfaces in order to understand the effects of adsorption and segregation of alloying elements and the resultant effect on nucleation.

Summary
Significant grain refinement of Al- and Mg-alloys was achieved by intensive melt shearing without addition of a grain refiner. Advanced high resolution TEM/STEM reveals that native oxides in alloy melts were dispersed by melt shearing and act as potent substrates to enhance nucleation, leading to grain refinement.
A new concept of solute growth restriction

F. Gao and Z. Fan

Introduction

The mechanisms of grain refinement in Al alloys have been widely investigated over the past decades, and solute growth restriction is considered to be one of the important factors for grain refinement. So far, how to quantify the solute growth restriction has been investigated but is still argued. The purpose of the presented work is to re-define a new parameter to quantify the solute growth restriction.

Summary of key results

A new concept of solute growth restriction coefficient is proposed as follows: \( \beta = \frac{C_0}{(k-1)\Delta T}, \) where \( C_0 \) is the solute content of the bulk liquid, \( m \) is the slope of liquidus, \( k \) is the partition coefficient and \( \Delta T \) is the undercooling. Figure 1 shows the relationship between growth restriction coefficient \( k \) and \( \beta \), showing \( k \) is a function of \( \beta \). From phase field simulation, the grain growth velocity can be expressed as a monotonic function of the growth restriction coefficient \( \beta \), as shown in Figure 2. From the blocking theory of CET (columnar to equiaxed transition), \( \beta \) can be used as the criterion for CET. This is shown in Figure 3: when \( \beta = 1.14 \), impingement just occurs and fully equiaxed grains form; when \( \beta < 1.14 \), the extended grains should overlap and columnar graphs form; when \( \beta > 1.14 \), impingement does not occur and fully equiaxed grains can further form.

Impact

This research is successfully combining thermodynamics and kinetics into solute growth restriction, which is helping us to correctly investigate the solute effect on grain growth.

Future directions

Further work is required to reveal the effect of \( \beta \) on grain size during solidification, which is helpful for understanding mechanism of grain refinement both in solidification science and industrial application.

Summary

A new concept \( \beta \) is proposed combining with thermodynamic parameters \( m(k-1) \) and kinetic parameters \( \Delta T \) from diffusion controlled spherical growth. Phase field simulation confirmed that \( \beta \) is an effective parameter to quantify the solute effect on grain growth. Meanwhile, a criterion based on blocking theory is proposed for CET.
Chemical bonding on pre-nucleation of Al: A first-principles study

C. Fang and Z. Fan

Introduction

Above its liquidus temperature, there exists ordering of liquid atoms on substrates. This pre-nucleation ordering plays a crucial role in the solidification processes of metals and alloys. Up to now, pioneering atomistic simulations have been performed but mainly for structural influences. Meanwhile, chemical effects of the substrate on pre–nucleation are largely unknown.

Summary of key results

Ab initio density-functional molecular dynamics (MD) simulations have been performed for liquid aluminum (Al) on metal (M) substrates of different chemical bonding to Al. A large hexagonal supercell with lattice parameters of $a = 14.57 \text{ Å}$ and $c = 49.95 \text{ Å}$ (525 atoms) were used. The temperature effects on the ordering of liquid metal have been simulated and analysed. The study showed that for an Al-affinitive substrate (Ag), the liquid Al has a shorter M-Al spacing, more ordered layers and higher in-plane ordering during the pre–nucleation processes (Figure 1a and 1c). Whereas the opposite phenomenon occurs for an Al-repulsive substrate (Cd) (Figure 1b and 1c).

Impact

The results obtained here are not only useful to understand the mechanism of pre nucleation of Al melts on different substrates, but are also helpful to gain insight into the related heterogeneous nucleation phenomena. These results obtained may help experimentalists to design new grain refiners and to prepare metals and alloys of desirable microstructures and related properties which meet the demands of industry.

Future directions

1) Further investigate the influences of substrate chemistry on Al (pre-) nucleation; 2) Study potential substrates, such as MB$_2$ (M= Mg, Al, transition metals), MgO, spinel, etc. on (pre-)nucleation of light metals, Mg and Al; 3) Develop new analysis methods for the partially ordered liquid metals on substrates.

Summary

Ab initio MD simulations have shown that during pre-nucleation processes there are strong chemical influences of substrate chemistry on the substrate-liquid spacing, atomic layering and in-plane ordering of liquid Al. Consequently such pre-nucleation ordering due to the chemical nature of the substrates impacts the subsequent solidification, and the final microstructures and properties of the products.
**Integrated cast-extrusion of light alloys**

Y. Huang, S. Khorsand and L. Zhou

**Introduction**

Metal casting and forming lie at the foundation of most manufacturing sectors. Although conventionally carried out separately, they are linked and can be integrated. Their integration has potential to improve energy efficiency and performance with reduced costs. This project focuses on the integration of casting and extrusion for light alloys.

**Summary of key results**

Integrated cast-extrusion has been successfully carried out, on a 100T hydraulic press and using a cylindrical casting mould/extrusion chamber of 60mm in diameter, for the production of AA6082 aluminium alloy rods of 10mm in diameter and AZ31 magnesium alloy tubes of 12mm in outer diameter and 2mm in wall thickness, at temperatures of 350-500°C. Material flow was uniform and microstructures were essentially free of casting defects. Both alloys showed microstructural and texture features similar to those of conventional extrusions. Selected samples were subjected to heat treatment and the hardnesses obtained were comparable to those of conventional extrusions of the same materials. Figure 1 shows typical microstructure and material flow pattern (a) and <111> direction dominated texture (b) for the AA6082 aluminium alloy rods.

**Impact**

This novel process makes full use of solidification heat and provides the shortest manufacturing route for metalworking. It offers energy, material and overall cost savings with improved recyclability. It can tailor products to meet specific needs, facilitating the ‘make to order’ approach. The integration will eliminate the boundaries between casting and wrought alloys, change the concept of material and product design and potentially lead to the merging of casting and forming into a single industrial sector with high energy resilience.

**Future directions**

Future research will combine critical thermal management analysis, computer simulation and physical experiments, to develop principles, strategies and novel processes for integrating casting with extrusion and a broader range of forming processes, aiming to achieve the highest possible energy efficiency without compromising the product performance. Comprehensive experimental studies will focus on the integrated cast-extrusion of fine magnesium tubes and wires.
Development of metallic biomaterials for orthopaedic applications

Y. Huang, M. Razavi and K. Burugapalli

Introduction
Novel metallic biomaterials including both biostable titanium alloys and biodegradable magnesium matrix nanocomposites have been developed for orthopaedic applications. The development involves new concept of material design and advanced technologies for materials processing and fabrication, aiming to provide orthopaedic implants with enhanced properties tailored to suit individual patient’s needs.

Summary of key results
A beta-type porous Ti-Nb-Ta titanium alloy was manufactured by powder metallurgy and coated with ZrO₂ by laser technology. The new alloy showed excellent biocompatibility and mechanical properties. Its low modulus has potential to effectively reduce the “stress shielding effect”, from which patients normally suffer with conventional titanium implants. Magnesium matrix hydroxyapatite (HA) reinforced nanocomposites were fabricated by a novel route combining high shear solidification and equal channel angular extrusion. The nanocomposites exhibited a fine microstructure and uniform hydroxyapatite particle distribution (Figure 1a and 1b), enhanced yield strength with good ductility (Figure 1c), and significantly improved corrosion resistance, which makes it possible to control the degradability of implants.

Impact
The beta-type Ti-Nb-Ta alloys with low modulus represent a new generation of titanium biomaterials for orthopaedic implants. A production line with an automatic, gas protected powder loading system is in construction at CNE Research and Innovation Centre Ltd (Cyprus) – one of our nine project partners (FP7-SME/606112), for industrial trials. The Mg/HA nanocomposite research offers a new concept of degradability control for magnesium biomaterials and a novel fabrication technology and has the potential to change the paradigm of biomaterial design and market structure of biodegradable biomaterials.

Future directions
Future research for this titanium alloy will focus on the enhancement of antibacterial performance, in addition to the control of porosity and coating structure. For Mg/HA nanocomposites, optimization of material design and fabrication process will be the focus, as well as the understanding of the degradation mechanism and kinetics. Collaboration with clinical experts and industries will be sought during these further developments.

Summary
Our research addresses the core issues that underpin wider applications of metallic biomaterials by introducing a new concept of material design and innovation in material processing and fabrication, with support from EC Research Council, The Royal Society and EPSRC. The research outcomes have been published in high impact journals and prestigious international conferences as invited/key note presentations.
**Al-Mg compound castings**

K. Schneider, B. McKay and H.B. Nadendla

**Introduction**
Aluminum-magnesium compound castings have been identified as a promising approach to meet the increasing requirements in terms of cost and performance in the automotive industry. These types of compound casting consist of a solid aluminum shape upon which liquid magnesium is cast, creating a reaction zone at the interface between the two metals.

**Summary of key results**
Soundness and properties of the interface are crucial for any actual application of Al-Mg compound castings. Therefore, the influence of alloying elements such as zinc and silicon on interfacial reaction were investigated within this research. The obtained interface followed the relevant ternary phase diagrams. Adding silicon resulted in the formation of numerous Mg$_2$Si particles within the interface, leading to increased interfacial brittleness and as such limiting any possible applications. With the addition of zinc the zinc-rich phases $\tau_1$ and $\varphi$ were found. While the $\tau_1$ displayed indications for brittleness the $\varphi$-phase was found to display lower brittleness while retaining a high level of hardness.

**Impact**
Being able to control to the interface formation in Al-Mg compound castings would lead to a number of benefits. It would allow for the construction of even more lightweight parts, as magnesium is approximately 1/3 lighter than aluminum. Furthermore, compound castings are thought to possess a high degree of function integration. Therefore, it would be possible to replace several separate components with one compound casting and reduce manufacturing, machining and joining costs.

**Future directions**
The metallurgical process taking place during interface formation is not fully understood so far. Therefore, the next step will be the acquisition of a more profound understanding of interface formation and the influence of zinc upon it.

**Summary**
Al-Mg compound castings are an interesting approach to meet the increasing requirements in the automotive industry as they possess a number of benefits. So far little is known about how to actively influence the interface of such structures. The work undertaken so far shows that the addition of zinc may result in improved mechanical properties and beneficial interface. However, interface formation in such structures is still not fully understood and requires further research in this area.
Specialised thimbles for offshore renewable marine energy (STORM)

O. Adole, T. Minton, L. Anguilano and B. McKay

Introduction

The goal of this research is the development of a lightweight, multi-material hybrid connector for use in mooring systems which are crucial for all offshore floating renewable energy devices. The study investigates the potential of employing a nylon/aluminium-basalt hybrid composite which offers high strength, low coefficient of friction and improved corrosion resistance.

Summary of key results

Using 5 wt.% basalt whiskers as a reinforcement, an aluminium-basalt composite (used to form the core of the proposed connector) was developed via stir casting and ultrasonic cavitation. Tensile specimens were obtained and test results show improved mechanical property performance over the reference Al matrix alloy (Figure 1a). Preliminary studies also show improved corrosion resistance over conventional connector material, mild steel (~3µm/year vs. ~170µm/year for mild steel). This improvement in mechanical properties may be due to the formation of an iron-rich intermetallic phase around the fibres which appears to maintain the integrity and strength of the fibres structural core (Figure 1b).

Impact

Currently, there are no known hybrid connectors on the market while aluminium-basalt composites have never been commercially produced. Our novel composite shows a very high degree of versatility with a high potential for different types of application from inland wind turbines to offshore wave energy harvesters. If successful, this novel connector would contribute to the reduction of levelised cost of electricity (LCOE) through the overall reduced deployment/operating costs for offshore renewable energy devices.

Future directions

This research is focused on the process optimisation for the best commercial manufacturing route for the aluminium-basalt composite. Once this is realised, the next phase will investigate the combination of the composite with a next-generation nylon material, Oilon, which would ensure a superior low friction component is developed. Testing of industrial prototypes will then be conducted in preparation for possible commercial exploitation. This phase will be led by our industrial partners, TTI, EMEC and Nylacast.

Summary

Our study aims to establish an optimal process for the development of a light-weight, high performance aluminium-basalt composite using novel processing techniques. A full understanding of the mechanism behind its improved mechanical properties over its reference alloy will be achieved through the microstructure characterization of the composite and the matrix-reinforcement interfacial reactions.
Improving properties of high Fe containing Al-Si alloy by treating β-phase

C.B. Basak and H. Nadendla

Introduction
High iron impurity affects castability and tensile properties of recycled aluminium alloys. This ongoing research focuses on tackling the unfavourable effects of iron impurity. In Al-Si cast alloys Fe is contained within β-phase; β-phase can be controlled by gravitational segregation, morphological change or by destabilizing it.

Summary of key results
Detailed thermodynamic calculations were carried out to understand the compositional dependency of β phase formation and it was found that below approximately 0.5wt% Si, β-phase cannot be formed irrespective of the Fe concentration. Elimination of Fe via gravity segregation of β-phase is an ideal method for high-Si content alloy. On the other hand, morphological change of β-phase is the preferred choice to counteract the detrimental effect of Fe content in low-Si high-Fe content recyclable Al-Si alloy. It was observed that partial spheroidization of β-phase takes place when heated at 570°C for 12 hours or more.

Impact
Change in morphology of β-phase is strongly dependent on the heat-treatment temperature. Aging above the eutectic temperature (575.7°C) causes faster growth of β-phase (in thickness) due to the faster diffusion in the liquid phase; whereas below 575.7°C, it was observed that the growth process is slow and fragmentation across the length. Morphology of Si particles is also greatly dependent on the heat-treatment temperature. Such morphological change in β-phase and Si particles improves the ductility of the recycled Al-Si alloys.

Future directions
Though spheroidization treatment improves the ductility, Al-Si cast alloys exhibit slightly lower yield strength due to the grain growth during heat-treatment. To restrict the grain growth, incorporation of Nb and/or Ni in the alloy, which can form intermetallic phases for effective grain boundary pinning could be considered. Also, addition of Cu is another avenue to compensate the lost strength by subsequent aging treatment of the nano-sized coherent or semi-coherent Al2Cu (θ) intermetallic phase. Both of these routes are being explored.

Summary
To make recycled Al-Si alloys more tolerant towards Fe content several methodologies have been explored which essentially targets the Fe-containing β-phase. Spheroidizing treatment of β-phase shows improvement in ductility. Gravitational segregation of β-phase in high Si containing Al-Si alloy is industrially more amenable.
Nucleation and growth of intermetallic compounds (IMCs) in Mg-alloys

G. Zeng and C.M. Gourlay

Introduction

Impurities such as Fe, Ni and Cu are damaging to the corrosion performance of Mg-alloys. This research investigates the nucleation and growth of $\text{Al}_8\text{Mn}_5$ and the mechanisms by which Mn acts as a getter for impurity Fe in Mg-9Al-0.7Zn-0.15Mn-0.004Fe (wt.%) (AZ91D).

Summary of key results

$\text{Al}_8\text{(Mn,Fe)}_5$ formed as a primary and a eutectic phase in Mg-9Al-0.7Zn-0.15Mn-0.004Fe. Primary $\text{Al}_8\text{(Mn,Fe)}_5$ often nucleated from Fe-rich particles and enveloped them (Figure 1a), and tended to grow as small <10 µm equiaxed faceted particles with a variety of non-uniform morphologies (Figure 1b). The numerous facets can be understood as combinations of {100}, {110} and {112} surfaces when considering primary $\text{Al}_8\text{Mn}_5$ as a pseudo-cubic body centred rhombohedral cell (Figure 1c). Eutectic $\text{Al}_8\text{Mn}_5$ grew from primary $\text{Al}_8\text{Mn}_5$ with a complex faceted morphology ranging from rod, to sheet, and folded plate-like.

Impact

The findings are an initial step towards a deeper understanding of how Mn additions ameliorate the negative effects of Fe in Mg-Al-based alloys, which may enable similar approaches to be applied to other impurities.

Future directions

Future research aims to (i) perform quantitative synchrotron imaging studies on IMC formation sequences in Mg alloy solidification; (ii) control the nucleation and growth of $\text{Al}_8\text{Mn}_5$ to achieve optimum getterer and settling behaviour; (iii) control the nucleation and growth of IMCs to prevent the formation of IMCs that are most harmful to corrosion performance; (iv) identify potential IMCs that can dissolve impurity Cu and Ni to assist in the development of impurity-tolerant recycled Mg alloys.

Primary $\text{Al}_8\text{(Mn,Fe)}_5$ nucleate on Fe-rich particles and envelope them. Subsequent growth of $\text{Al}_8\text{(Mn,Fe)}_5$ results in small (<10 µm) equiaxed particles, even at cooling rates of 1 K/s. The growth facets can be understood as {100}, {110} and {112} surfaces when considering $\text{Al}_8\text{Mn}_5$ as a pseudo-cubic crystal.

Summary

FIGURE 1. (a) Typical primary $\text{Al}_8\text{Mn}_5$ particle in Mg-9Al-0.7Zn-0.15Mn-0.004Fe cooled at ~ 1 K/s. (b) Identification of an Fe-rich core by EDS line scanning and mapping. (c) Indexing of primary $\text{Al}_8\text{Mn}_5$ growth facets by combined 2D-EBSD and FIB-tomography.
X-ray imaging studies of the solidification of Al alloys

E. Liotti and P.S. Grant

Introduction
This presented research focuses on the use of X-ray imaging techniques for the study of solidification phenomena in Al alloys to help understanding of solidification science, including the inter-relationships between the use of grain refiners, alloy composition including tramp impurities, and cooling rate. The effect of a pulsed magnetic field on microstructural evolution during solidification is also being studied.

Summary of key results
The solidification of Al-Cu alloy samples grain refined with TiB₂ particles was captured in-situ using synchrotron X-ray radiography under a wide range of experimental conditions. The videos were then automatically analysed using a state-of-the-art computer vision algorithm that was trained to measure time resolved solidification parameters, such as grain density and nucleation rate, which then related to experimental conditions. Figure 1a shows a radiographic image of a mushy sample, representative of the type of experiment in which the grains were detected and tracked by the computer vision algorithm, while Figure 1b shows an example of the quantified data available from the algorithm, in this case the measured grain density as a function of time.

Impact
There is an impact to improve the understanding of how grain refiners work in realistic conditions and the possibility to improve industrial practice. The measurement methodology can also be applied to other phenomena such as second phase nucleation and the role of impurities on the efficacy of grain refiners.

Future directions
We are combining this methodology with multi-elemental mapping to move beyond model binary alloys and to investigate more realistic alloys with more than two elements. We also aim to use the computer vision algorithm on other groups’ radiographic data to promote wider impact.

Summary
These synchrotron X-ray imaging approach has been combined with a new computer vision algorithm to quantify automatically critical and time-varying microstructural parameters during solidification, such as nucleation rate, grain size and grain movement.
Real-time studies of nucleation and growth of Fe-rich intermetallics during solidification of aluminium alloys

S. Feng, E. Liotti, A. Lui and P.S. Grant

Introduction
This research focuses on real-time synchrotron X-ray studies of solidification to understand and mitigate harmful needle-like intermetallic compounds (IMCs) through manipulations in alloy chemistry and conditions.

Summary of key results
X-ray radiography is being used to measure the length, growth velocity, tip temperature and phase selection of secondary needle-like Fe-rich IMCs in model Al-Cu-Fe alloys at different Fe-concentrations and cooling rates. Figure 1a shows IMC tip temperature as a function of cooling rate for Al-10Cu-1.5Fe (wt.%), based on over 200 measurements. The morphology of Fe-rich IMCs was controlled by the primary Al microstructure and was therefore influenced by addition of primary Al grain refiners, but these grain refiner additions also changed the relative population of the different Fe-rich IMCs, which grew at different IMC tip temperatures. To image primary IMC nucleation and growth more easily, a model Pt-containing alloy has been developed, which also promotes optimum X-ray imaging contrast (Figure 1b) so that a pixelated spectrometer can be used for multi-element imaging.

Impact
Understanding of IMCs has been gained from post-solidification microscopy, calorimetry and other measurements. We can augment these data and extend understanding using in-situ X-ray imaging to contrive solidification conditions and compositions that either suppress or promote certain IMCs (Figure 1a). This may help to eliminate or reduce current post-solidification heat treatments used to manipulate IMC populations.

Future directions
As well as pursuing further synchrotron X-ray measurements, opportunities for complementary laboratory-based X-ray imaging arrangements are being developed.

Summary
Preliminary data from in-situ X-ray imaging and post-solidification microscopy, together with new imaging modalities, is helping to understand the selection of IMC type during the solidification of Al alloys.
Effect of interfacial segregation on heterogeneous nucleation

T. Hashimoto, Y. Wang, Y. Zhou and J. Lim

Introduction
In order to advance the understanding of the heterogeneous nucleation mechanism, the elemental adsorption and atomic arrangement at the solid/substrate interface were investigated using high resolution transmission electron microscopy, with particular focus on the surface of inclusions commonly present in recycled alloys, and the competition for nucleation between different inclusion particles.

Summary of key results
As an example, aluminium with the addition of 0.2 wt.% Al-5Ti-1B grain refiner poisoned by 500ppm Zr was characterized using HRTEM and high spatial and energy resolution EELS and EDS with the aim of understanding the mechanism of the so-called Zr “poisoning” effect (Figure 1a). It is found that the adsorption of Zr atoms on the surface of TiB₂ particles occurs, in the form of an atomic monolayer, which results in the decrease in nucleation efficiency of TiB₂ inoculation.

Impact
The knowledge created in this presented study will advance the understanding of the heterogeneous nucleation mechanism and be exploited for high performance alloy development for closed-loop recycling and resource efficient manufacturing technologies (Figure 1b).

Future directions
Future research will focus on correlating the structural nature of the solid/substrate interface with the heterogeneous nucleation mechanism.

Summary
HRTEM, together with the unique specimen preparation techniques, is successfully employed to characterize the solid/substrate interface. The atomic arrangement at the interface is visualized by Z-contrast and high spatial and energy resolution EELS and EDS, revealing the relationship between the solid and the substrate.
Microstructure characterization of twin roll cast AZ31 Mg alloy

S. Pawar, X. Zhou, G.E. Thompson, G.M. Scamans and Z. Fan

Introduction
To meet the challenges of light-weighting, especially relevant in transportation, it is necessary to improve the castability of light alloys to enhance grain refinement in monolithic alloys. This research project is focused on microstructure characterization of twin roll cast Mg alloys, aimed at explaining the relationship between nucleation and distribution of intermetallics formed during solidification, which directly influence the mechanical and electrochemical properties.

Summary of key results
The twin roll cast alloy reveals a dendritic microstructure with a wide range of grain sizes (~600 µm) and crystal orientations (Figure 1). Faceted Fe-particles with sizes less than 100 nm were observed enclosed within the Al₈Mn₅ particles, which display rosette, flower and dendritic morphologies (Figure 2), with a sub-micron particle size, and located at the grain centres, grain boundaries and the interdendritic regions. The rejected solute at the interdendritic and grain boundaries reveal two types of Mg-Al-Zn intermetallics, namely Mg₁₇(Al,Zn)₁₂ and MgZn₂, coupled together. Cuboidal, nano-crystalline Mg₂Si phase was observed at the interdendritic boundaries, mostly associated with the MgZn₂ phase (Figure 3).

Impact
The complex processing conditions have a direct influence on solidification and the resultant microstructure. The relatively high cooling rates, ranging from 10⁶ to 10⁷ K/s allow a narrow temperature range/solidification interval, which affects the formation as well as distribution of intricate intermetallics. Furthermore, the rapid solidification affects the formation of β-phase, which promotes excess rejection of Zn towards the boundaries leading to formation of Mg-Al-Zn type intermetallics in the twin roll cast AZ31 Mg alloy, which is usually reported to be Mg₁₇Al₁₂ type β-phase. These research findings have been disseminated to industrial collaborators and widely to the scientific community through publications.

Future directions
The discreet understanding of the twin roll cast AZ31 Mg alloy microstructure performed in the current investigation provides the fundamental impetus to improve and tailor mechanical and corrosion properties.

Summary
The investigation reveals the distribution of Al₈Mn₅ and Mg₂Si intermetallics associated with their formation during the solidification of twin roll cast AZ31 Mg alloy. At the same time, some new facts regarding the formation of Mg-Al-Zn type β-phase have emerged which significantly affect the alloy properties.