

Processing of Bulk Hierarchical Metal-Metal Composites



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Dedication

For my mother, Anne Brown.

Abstract

Spray forming with co-injection of a solid particulate phase to form a metal-metal composite has been studied as a new route for manufacture. Two Al-based matrices were investigated: Al-12Si for testing the feasibility of the new manufacturing route and Al-4Cu for providing better mechanical performance. For both composite types, Ti was chosen as the particulate phase and the processing-microstructure-property relationships then studied.

At Peak Werkstoff GmbH, Germany 12 wt%Ti particles were co-injected into an atomised Al alloy droplet spray and co-deposited to form a ~ 300 kg billet. The microstructure comprised refined equiaxed α -Al grains ($\sim 5\mu\text{m}$), spherical Si particles ($\sim 5\mu\text{m}$) and uniformly distributed Ti particles ($\sim 80\mu\text{m}$). Sections of the billet were extruded under a range of conditions into long strips 20mm wide and 6mm, 2.5mm and 1mm thickness. At high strains, the Ti particles were deformed into continuous fibres of a few microns in thickness. Accumulative roll bonding was then performed to higher total strains, while maintaining a constant cross-section, reducing the Ti fibres to sub-micron thickness. The fibres were studied by extraction after selective dissolution of the α -Al matrix. There was no interfacial reaction between α -Al and Ti or any measurable oxide formation, thus providing encouragement for the manufacture of metal-metal composites by co-spray forming.

A powder injection pump was successfully integrated and commissioned on the spray forming facility at Oxford University. The pump was calibrated to optimise powder flow rates. Three Al-4Cu+Ti composite billets were processed with each containing Ti powder with a different processing history. Up to 20vol%Ti was successfully incorporated, however due to the cooling effect from powder injection, porosity was significant. The quenching effect provided a finer Al-4Cu grain structure in the region of Ti injection, and also promoted precipitation of θ' -Al₂Cu precipitates. A Ti/Al-4Cu interfacial reaction was more prominent in the billet spray formed at

850°C than those spray formed at 750°C.

Angular Ti processed by a hydride-dehydride route had better deformation characteristics than spherical gas atomised Ti. Deformation processing by extrusion and rolling was investigated for Al-4Cu+20vol%Ti using SEM, EBSD and FIB. After extrusion to a strain of 5, the composite contained elongated reinforcing fibres characteristic of metal-metal composites. The microstructure studied by EBSD revealed equiaxed polygonal Al-4Cu matrix grains. Rolling was not as efficient as extrusion in producing elongated Ti fibres and was attributed to a lower deformation processing temperature. The rolled composites consisted of elongated Al-4Cu grains 1-5 μ m in thickness. An UTS of 339MPa at a strain of 3 was attributed to texture strengthening in the α -Al.

Preface

The work described in this thesis was carried out by the author in the Department of Materials, University of Oxford under the supervision of Prof. Patrick Grant.

No part of this thesis has been previously submitted for a degree at this or any other university. The work of others has been freely drawn upon and is duly acknowledged in the text.

Some of the work described in this thesis has been published in the following journals and conference proceedings:

1. A.J. Kelly, J. Mi, G.V. Sinha, P. Krug, F. Crosa, F. Audebert and P.S. Grant, *An Al-Si-Ti Hierarchical Metal-Metal Composite Manufactured by Co-Spray Forming*, Journal of Materials Processing Technology, 211(12), pp. 2045-2049, 2011.
2. A.J. Kelly, J. Mi, G.V. Sinha, P. Krug, F. Crosa, F. Audebert and P.S. Grant, *An Al Alloy-Ti Microfilament Composite Manufactured by Co-Spray Forming and Accumulative Deformation Processing*, Proceedings of the 12th International Conference on Aluminium Alloys, Yokohama, Japan, September 5-9 (2010), pp. 850-855.
3. J. Mi, A.J. Kelly, K. Jurkschat, G.V. Sinha, P. Krug and P.S. Grant, *An Al Based Hierarchical Metal-Metal Composite Manufactured by Co-Spray Forming*, Proceedings of the 4th International Conference on Spray Deposition and Melt Atomization, Bremen, Germany, Septemeber 7-9, 2009.
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Chapter 1

Introduction

Over the past two decades a new class of composite materials, where both the matrix and reinforcing phases are pure metals, has emerged. These materials have been manufactured typically by mixing the constituent metals via powder metallurgy (PM) or by co-melting two metals that are miscible as liquid but immiscible as solid so that complete phase separation occurs during solidification. Deformation of these ductile metal mixtures to very high strain levels produces a nano-scale fibrous structure in the minority phase. The materials show unusually high strengths that are much greater than predicted by the rule of mixtures. For example, an Al-20vol%Nb composite has been reported having an ultimate tensile strength (UTS) $>2\text{GPa}$ [3]. A key aspect of these materials is the combination of elements of different types of unit cell e.g. Al-Nb (fcc/bcc) and Al-Ti (fcc-hcp), and that dislocation motion is impeded at the very many interfaces between the dissimilar elements; however, toughness remains high because of the intrinsic ductility of the pure constituents.

Further development and exploitation of these alloys in industry has yet to take place, partly because of the embryonic state of the field and partly because of the difficulties in reproducibly scaling-up the conventional powder mixing approaches used to make feedstock billets and the attendant contamination of the constituents. This thesis investigates co-spray forming as a new route to manufacturing Al based

metal-metal composite feedstock ingots at a scale ($\sim 300\text{kg}$ per billet) significantly beyond previous powder metallurgy and immiscible alloy system approaches.

Spray forming was invented at the beginning of 1970s by Prof A.R.E. Singer at University College Swansea as an alternative way to produce ingots and strip, directly from the melt [13]. A few years later, the process was commercially developed by Osprey Metals Ltd for the manufacture of billet rather than strip, and subsequently became known as the Osprey process. The process is now successfully established in niche alloy production where it provides an opportunity to enhance alloy chemistry, microstructure, and properties by producing unrivalled micro- and macro- homogeneity. Co-injection has been practised previously for the manufacture of particulate reinforced metal-matrix composites for conventional alloys [14–23] and in co-injection of identical alloy powder obtained from overspray of previous production runs where the objective is to increase process yield. Pure solid particles of the minority phase will be co-injected into the atomised liquid spray of the matrix material and co-deposit to form a billet with a metallic majority matrix phase containing a homogeneous dispersion of a dissimilar minority metallic phase.

The overall objectives of this thesis are: (1) to manufacture bulk metal-metal composites by spray forming with co-injection, thus scaling-up material supply currently restricted to small scale powder metallurgy routes; (2) to severely deform the feedstock material by downstream processes such as extrusion and rolling into wire or sheet form producing an elongated filament morphology in the minority constituent; and (3) to examine the effect of primary (co-injection) and secondary (downstream) processing on the microstructure and mechanical behaviour of resultant composites.

To test the feasibility of the new manufacturing route Al-12Si was chosen as the matrix alloy due to its low melting point, high fluidity and the fact that it solidifies as pure Si and relatively dilute α -Al - so that the α -Al can withstand severe deformation processing. Once the new route was established, Al-4Cu was chosen as the matrix because it is an age hardenable alloy thus providing the composite with

better mechanical properties. In both cases Ti was chosen as the minority phase due to its high melting temperature that would inhibit the likelihood of a reaction from occurring with the molten alloy stream. In addition Ti has a high strength to weight ratio. Potential applications of metal-metal composites are ambient temperature, lightweight applications, in particular lightweight vehicle and personal armour which are of increasing importance in law and order and homeland security applications.

The thesis is arranged as follows:

Chapter 2 reviews the literature related to metal-metal composites, routes to manufacture (including co-spray forming and powder processing), and downstream processing; Chapter 3 describes the experimental procedure of co-spray forming, downstream processing, microstructural characterisation and mechanical testing; Chapter 4 presents the results and discussion of Al-12Si+Ti bulk MMC manufactured for the first time by co-spray forming at PEAK, Germany; Chapter 5 details the commissioning of a powder injection capability that allowed for bulk composite production on site at Oxford University, and discusses the results of three Al-4Cu+Ti MMC billets processed; Chapter 6 presents and discusses results from extruded and rolled Al-4Cu+Ti composites. Chapter 7 concludes with the significant findings of this work; and Chapter 8 gives suggestions of future work.

Chapter 2

Literature Review

2.1 Metal-metal composites (MMCs)

Metal-metal composites are dissimilar metal mixtures that can show remarkable strengthening at room or elevated temperatures following severe deformation. They most commonly comprise of a fcc matrix with a bcc minority phase such as Cu-Nb or Al-Nb, but other composite systems such as fcc/hcp, fcc/bct and fcc/fcc have been investigated. They differ from conventional metal matrix composites in that both the matrix and the “reinforcing” phase are ductile metals [24]. Metal-metal composites are manufactured typically either by mixing the constituent metals via powder metallurgy (PM) or by co-melting two metals that are miscible as liquid but immiscible as solid so that complete phase separation occurs during solidification. The PM or cast feedstock is then heavily deformed via a series of, or a repetitive process of extrusion, swaging, drawing and/or rolling into wire or sheet form producing an elongated filament morphology in the secondary phases as shown in Figure 2.1. Characteristic of these binary systems is the absence of intermetallic compounds. Initially and in the late 70’s, metal-metal composites were explored for the development of Cu-Nb₃Sn superconducting wires. By the mid-eighties, the focus of research had shifted to mechanical properties.

The objective of this project is to manufacture bulk metal-metal composites by spray forming and co-injection, and thus scale-up material supply currently restricted to small scale powder metallurgy routes. Solid particles of the minority phase will be co-injected into the atomised liquid spray of the matrix material and co-deposit to form a billet with a metallic majority matrix phase containing a homogeneous dispersion of a dissimilar minority metallic phase.

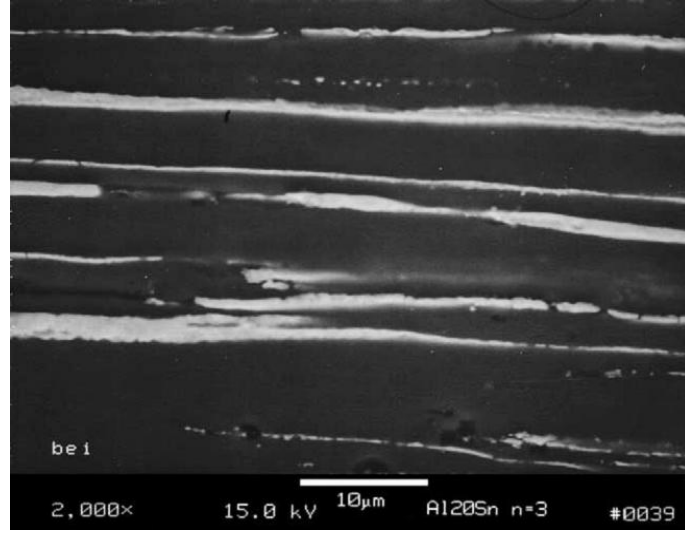


Figure 2.1: SEM micrograph of Al-20vol%Sn ($\eta = 3.2$). The Al matrix is dark gray and the Sn filaments are light gray [1].

2.1.1 MMC combination types

The most commonly studied MMC comprises a fcc matrix with a bcc minority phase such as Cu-Nb and studied for the first time by Bevk *et al.* [3]. Ultimate tensile strengths of 2200MPa at a deformation true strain of 11.5 were achieved, and sparked great interest in the field considering strengths were four times greater than those predicted by a “rule of mixtures”. In-situ Nb fibres were formed as the composite was drawn to a thin wire <0.5mm in diameter. During deformation the Nb developed a ribbon-like morphology as evidenced from a cross-sectional view of the wire, and the Nb was also forced to curl around the surrounding matrix that accommodated axi-symmetric flow during wire drawing [25]. Wire drawn bcc metals

generally assume a strong $\langle 110 \rangle$ fibre texture in which the $\langle 110 \rangle$ direction of the individual grains lies parallel to the drawing direction [26].

The extent of filament deformation depends on the degree of deformation and on the matrix properties: a harder matrix can accommodate deformation of the minority phase better than a softer matrix. A low modulus matrix will flow plastically around the harder minority phase and provide only limited strain transfer to the minority phase. An empirical rule, referred to as a “3-to-1 Rule”, suggested by investigators stated that if the flow stresses of two phases differ by more than a factor of 3, they are unlikely to co-deform [26]. Two phase alloys in which there is a large discrepancy between their flow stresses were termed “mechanically incompatible”. However, seemingly mechanically incompatible metals such as Ni and W with a large difference in room temperature hardness have been shown to co-deform [27]: Ni has a Brinell hardness of 700MPa whereas W has a hardness of 2570MPa. The ability of this composite mixture to co-deform was attributed to the single crystalline microstructure of the W powder that provided a lower flow stress [27]. In addition, the eutectic composition of the Ni-10vol%W that was fabricated by directional solidification provided an initially aligned fibrous microstructure [27], and both of these factors supported the co-deformation of the harder W phase.

In contrast to fcc/bcc MMCs, composites where both constituents were fcc, such as Cu-Ag, roughly cylindrical particles were produced instead of elongated fibres [28], because the texture of the fcc minority phase did not constrain Ag to deform in plane strain but allows multiple slip systems.

Xu *et al.* [1, 29] were the first to analyse an Al fcc matrix with bct β -Sn as the minority constituent. Axisymmetrically deformed Al commonly forms a $\langle 100 \rangle$ fibre texture [29], that results in equal probability of slip in all four members of $\{111\} \langle 110 \rangle$ slip system, and rapid strain hardening. The Sn filaments did not develop a strong orientation since Sn recovers and recrystallizes almost immediately after deformation at room temperature. It was therefore unusual that Sn developed

a filamentary morphology because the fibre texture of the Sn filaments oriented several slip systems which might be expected instead to give the cylindrical shaped particles, similar to that previously described for fcc/fcc composites. This called into question whether or not texture-induced plane strain deformation was the sole cause for the filamentary morphology of the second phase. The cause of the Sn behaviour was unknown but other factors of anisotropic interface energies acting between Al and Sn was tentatively suggested.

Russell *et al.* also explored a combination of fcc/hcp elements in powder processed Al-20vol%Ti [30]. The resulting sub-micron Ti filaments were textured with the hexagonal close packed $\langle 10\bar{1}0 \rangle$ direction parallel to the drawing direction, and confined the fibres to plane strain. A convoluted ribbon morphology was observed in a section transverse to the drawing direction. The elongated filamentary microstructure was similar to bcc minority phase morphology in Al-Nb composites [31] and Cu-Nb composites [3] [32] [33].

2.1.2 Strengthening mechanisms

The anomalous strengthening of metal-metal composite arises with progressive deformation processing. Microstructural changes are induced in both phases. The matrix undergoes a deformation-recovery-recrystallisation cycle that permits further deformation [24]. As mentioned above, the minority phase forms thin ribbon-like filaments with large interfacial area. With progressive deformation processing, the filament thickness and inter-filament size decreases resulting in a rapid increase in strength because the filaments act as planar barriers to matrix dislocation motion. As a result, extensive dislocation pile-up and dislocation entanglement is assumed to occur. Dislocation sources are no longer able to operate as the expanding dislocation loops become pinned by grain boundaries. At this point, the strength increases further as the interfaces act as sinks, annihilating the dislocations such that their density diminishes in the filamentary phase. By using near pure elements in the

filamentary phase, the rate of recovery is equal to the rate of work hardening and consequently the filaments do not fracture at large deformations. A simple rule of mixtures shown in equation (2.1) usually fails to predict the strength of heavily deformed MMCs [1]:

$$\sigma_c = \sigma_f V_f + \sigma_m V_m \quad (2.1)$$

where σ_c , σ_f and σ_m are the ultimate tensile strength of the composite, filament and matrix respectively and V_m and V_f are the matrix and fibre volume fraction respectively.

The ultimate tensile strength of metal-metal composites was suggested to relate to the filament spacing via a Hall-Petch type relationship [34,35].

$$\sigma_y = \sigma_0 + \frac{K}{\sqrt{d}} \quad (2.2)$$

where K is a constant and d is the mean grain size, σ_y is the yield stress and σ_0 is the friction stress. The slope K in the Hall-Petch relationship of a two-phase alloy system is related to the shear moduli of the two phases by [36]:

$$K = \left[\frac{G_1}{G_2} \right]^{1/2} \quad (2.3)$$

where G_1 and G_2 are the shear modulus of the matrix and second phase respectively. The higher the filament modulus, the more effective the filaments act as barriers to dislocation motion [24]. Spitzig and Krotz [36] analysed the strengthening mechanisms in Cu-Ta and Cu-Nb metal-metal composites where the Cu-Ta composites were stronger than the Cu-Nb composites because of the higher modulus of Ta filaments. The ultimate tensile strength was most affected by the deformation true strain, followed by filament spacing and thirdly, the elastic modulus of the filaments. For example, increasing the strain from 5 to 10 increased the strength by 150%. The strength increased by 40% with a reduction in filament spacing from 6 - $3\mu\text{m}$, and

an increase in filament modulus to twice that of Cu increased the strength by 20%.

Recently a new model for strengthening of metal-metal composites was proposed by Morris *et al.* [2]. They challenged the accepted ideas of dislocation pile-up and interfacial area between the phases as controlling factors of strengthening in the composites. A study on Cu-5vol%Cr fabricated initially by casting was undertaken. The as-cast ingot was extruded at 800°C to a 20mm diameter bar that was then cold-rolled and drawn to a wire of diameter 4mm. The material was cold-worked to a strain of 3.5 resulting in Cr ribbons less than 50nm thick and a Cu sub-grain size of 100-150nm according to transmission electron microscopy images shown in Figure 2.2. Because there were no dislocations in the thinnest ribbons, the ribbons were claimed as strong as their ideal strength. For these composites with 10-20vol% of second phase material, the ribbon spacing was smaller than the sub-grain size of the Cu matrix and so it was suggested that the matrix could not support any significant dislocation pile-up, and that both the Cu matrix and the Cr ribbons were essentially free of any dislocation sub-structures. Consequently the Cu matrix was unable to work harden and since dislocation nucleation was too difficult in the Cr ribbons, they approached ideal (bond) strength. A new modified strengthening model was developed based on the ribbons having ideal strength in a sub-structure free matrix. This is a radical theory and requires support from further experimental evidence by other researchers.

The relationship between Al-20vol%Sn composite strength with deformation true strain, filament size and thickness was investigated [1]. As the deformation increased, there was an exponential decrease in filament thickness and spacing. Figure 2.3 shows a comparison of ultimate tensile strengths of four different Al based deformation processed metal-metal composites: Al-20vol%Sn [1], Al-20vol%Nb [37], Al-20vol%Ti [30] and Al-20vol%Mg [38]. At low deformation strains ($\eta < 7$), the ultimate tensile strength was similar for all alloys, although the Nb and Ti containing alloys were stronger than Sn. The source of strengthening came from the Al

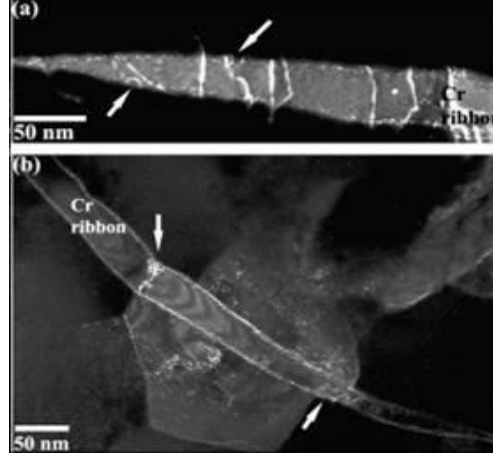


Figure 2.2: TEM images of Cu-5vol%Cr wires showing (a) dislocation sources activated at the ribbon-matrix interface and a subsequent dislocation segment movement along the ribbon width and (b) intense ribbon deformation where matrix boundaries impinge [2].

matrix that underwent work hardening and dislocation multiplication [1]. At higher deformation strains of $\eta > 7$, the finely dispersed second phases and the role of the large area inter-phase played a greater contribution to the strengthening, and the tensile strength differed for each composite combination.

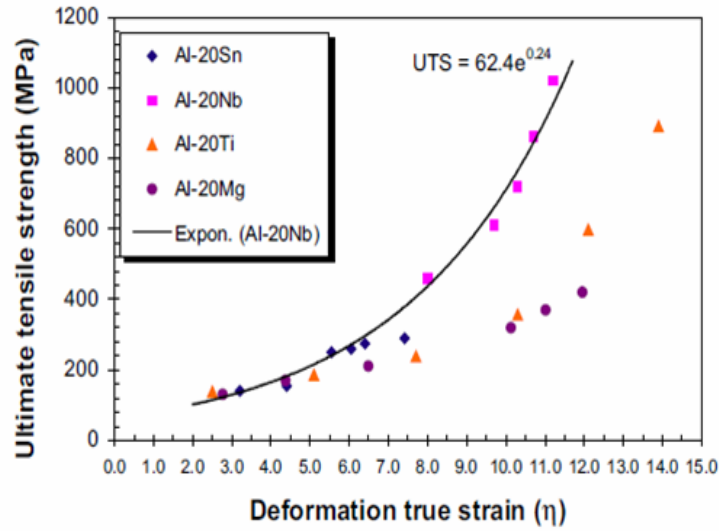


Figure 2.3: Ultimate tensile strength of Al-based MMCs at various deformation true strains [1].

Due to the similar hardnesses of Al and Sn (and presumably similar flow stresses), filaments were readily formed during deformation. However, Al-Sn is not a favourable MMC combination because after storage at room temperature (60% of the melting temperature of Sn), spheroidization of the Sn filaments occurred [29]. The strength

of Al and Sn in the fully strain hardened condition is 120MPa and 12MPa respectively. Sn recovers and recrystallizes almost immediately after deformation at room temperature preventing meaningful strain hardening. Therefore, strengthening of Al-20vol%Sn at higher strains (250MPa at $\eta \sim 7$) is accounted for primarily by the interface that acts as a barrier to dislocation motion.

The mode of fracture in the composites was also investigated as shown in Figure 2.4 [3]. Larger diameter two-phase wires, 50 μ m or above in diameter, showed evidence of necking, indicating ductile failure. However, smaller diameter wires below 50 μ m showed a fracture surface indicative of brittle fracture. The elongation to failure was 2.45% compared with 3.32% for larger diameter wires. No further explanation of the failure mechanism of the composite with a high density of immobile defects was provided, and it was difficult to analyse quantitatively the dependence of strength on filament size or interfilament spacing due to the irregular twisting and bending of the filaments.

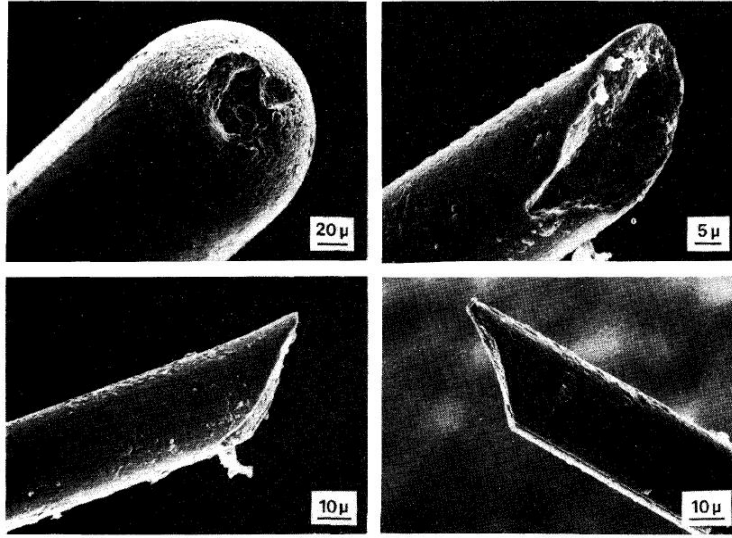


Figure 2.4: SEM images of fracture surfaces of (a) Cu-18vol%Nb alloy wire 130 μ m in diameter, (b) and (c) 24 μ m diameter wires and (d) same as (c) but tested at 77 K [3].

2.2 Routes for manufacture

MMCs are most commonly manufactured by powder processing and casting. Casting technique involves co-melting two metals that are miscible as liquids but once they turn to solids phase separation takes place. The starting Cu-Nb alloy processed by Bevk [3] was produced by rf levitation melting that employed electromagnetic stirring and strong convection. The resulting cylindrical ingots (7.5mm in diameter and 40mm long) showed a phase separation between near pure Cu and Nb as shown in Figure 2.5. Ingots were then swaged down to 2mm and cold drawn to a 99.9999% reduction. MMC manufacture by powder processing and spray forming is discussed in greater detail because MMCs are fabricated by this route in this work.

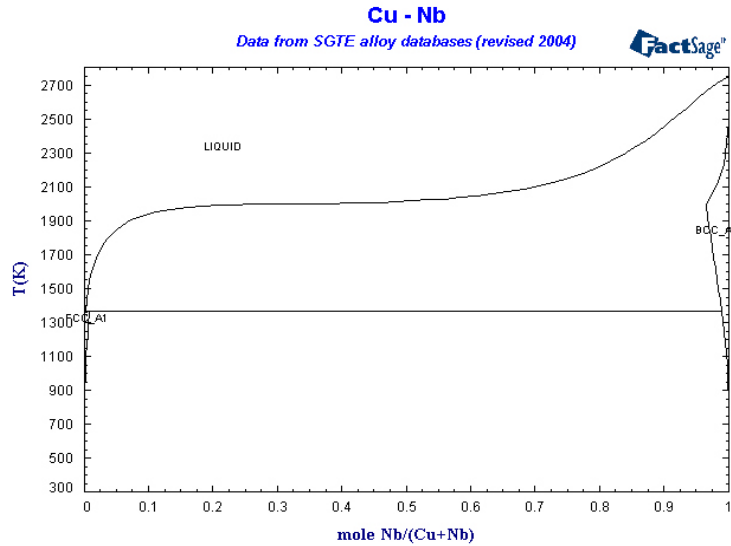


Figure 2.5: The Cu-Nb phase diagram showing phase separation of Cu and Nb when cooled from the melt to near pure Cu(Nb) and Nb(Cu) [4].

2.3 Powder processing

Powder metallurgy (PM) comprises the manufacture and consolidation of metallic powders to produce net shape components, which may in some cases also provide superior properties due to a refined and more uniform microstructure when compared with casting [39]. PM can be used for the processing of small particles, particularly

of complex alloys produced by atomisation from the melt. Since solidification occurs rapidly in these small diameter particles ($<100\mu\text{m}$), dendrite spacings are small ($1\text{-}5\mu\text{m}$) and inter-dendritic microsegregation is restricted to similar length scales. Furthermore, rapid cooling rates enhance supersaturation thus increasing the alloying potential in a variety of engineering alloy classes [39]. Larger precipitation hardening volume fractions may be achieved without the undesirable segregation effects that can occur in large ingots of the same composition. Another advantage of PM is the potential for the introduction of very fine ($\sim 1\mu\text{m}$) dispersions of inert particles such as ThO_2 that act as obstacles to dislocation motion [39]. These can be introduced on a fine scale to powder surfaces, for example by mechanical attrition. All powders require pressing and consolidating to full density for engineering applications where tensile load carrying capability is required. Invariably, this involves exposure to elevated temperatures, which in turn often leads to some loss of extended solid-solubility, microstructural coarsening, and dissolution of meta-stable phases formed during rapid solidification.

2.3.1 Powder production

Atomization is the most common and flexible method for producing metal powders for PM use [40]. Liquid metal is poured through a ceramic nozzle and then atomized using a high pressure inert gas to form droplets of $10\text{-}500\mu\text{m}$ diameter that are rapidly cooled by the relatively cold atomizing gas at quench rates of 1273K/s to 127300K/s . There are several variations of this method: centrifugal atomisation involves the use of a centrifugal force to break-up the liquid metal stream; ultrasonic atomization uses ultrasonic energy to break-up the stream; vacuum atomisation occurs in a vacuum; and the most common method of inert gas atomization [40]. Inert gas atomisation provides a high quality alloy feedstock with spherical powders and a wide size distribution. The greater the energy input at atomisation (gas pressure, flow rate), the finer the resulting powder. Particle diameters are typically

100 μ m.

Water atomization uses high pressure pumps to direct water jets onto the melt stream forcing disintegration and rapid solidification. Single jet, multiple jets or an annular ring may be used. A variation of water atomization uses a vaned rotating disc to disintegrate the water [40]. Unlike gas atomized powders, water atomization produces irregular, rough and oxidised powders in most liquid metals. Synthetic oils or other non-reactive liquids can be used to gain better control of particle shape and oxidation. The average particle diameter of water atomized powders is typically 150 μ m.

Mechanical alloying is another route to powder manufacture and involves ball milling at high speeds in a stirred ball-mill called an attritor, inside a conventional rotating ball mill, or in a shaker ball mill [41, 42]. Small amounts of organic surfactants are added to control the balance between welding and fracture of powder particles during milling. Due to the severe working of the powders during milling, very small grain sizes are obtainable and sub-structural strengthening occurs. One advantage of mechanical alloying is the effective superimposition of strengthening mechanisms including oxide and carbide dispersion, fine grain size, high dislocation density and solid-solution strengthening [39]. A major disadvantage is contamination, especially by oxidation and interaction with the milling balls or can. Powders can also be angular, difficult to flow, and are generally produced in a broad range of diameters.

2.3.2 Powder de-gassing

It is essential in aluminium-based PM that the powders are de-gassed prior to mixing and consolidation. Aluminium and water vapour react to release hydrogen which may cause an explosion during consolidation. Hydroxyl groups from water vapour readily associate with the thin Al_2O_3 layer always present on Al powders. Powders should be de-gassed at a temperature equal to or greater than the temperature

reached during compaction in order to minimise porosity and surface blistering [39]. On the other hand, very high de-gassing temperatures may degrade powder microstructure and properties as previously described. Degassing can be performed under argon or in a vacuum, which is generally superior. Typical Al alloy degassing parameters are 340°C at 3×10^{-4} torr.

2.3.3 Powder consolidation

There are many methods of powder consolidation including direct powder forming, hot isostatic pressing (HIP), powder forging and dynamic compaction. The most common process for powder consolidation is of course sintering. However, this project focuses on Al alloys, and in the main, sintering other than in vacuum, is not relevant for the consolidation of Al powders since Al readily forms a thick Al_2O_3 covering on all powder surfaces that makes sintering very slow, and introduces deleterious oxide into the final component. This review therefore is restricted to consolidation processes that aim for full density in a controlled environment. No particular direct consolidation method demonstrates a definite superiority over the others [39].

Direct powder forming is the most cost effective route provided the powder has been sufficiently de-gassed so that blistering does not occur, and powders can be consolidated during hot-forming directly to a final product [43]. For extrusion at high extrusion ratios, a separate compaction step is not necessary [44]. Hot isostatic pressing involves de-gassing the powders in a can, placing them under vacuum and sealing, followed by hydrostatic pressures of typically 200MPa. Any oxide layer on the powder surface is not broken and can inhibit sintering so a further hot process that introduces a shear stress can sometimes be implemented to rupture oxide films in the hope of producing a more ductile and tougher material. Powder forging aims to remove the 10-20% of the pores normally produced in powder metallurgy [45]. The powders are heated to a temperature well below the sintering temperature of

the material and then forged in a closed die to produce a fully dense component. Allowances are made for thermal expansion and the draft angles on the forging tools so further minimal machining is necessary to achieve net shaped components.

Dynamic compaction is a high strain-rate technique that consolidates the powders using a shock wave from a high velocity projectile. The resulting friction between the particles generates heat that partially melts the surfaces so that they bond together. The melting region is highly localised and self-quenched by the interior of the powders, thus minimising thermal exposure and preventing coarsening [43]. However, this is a relatively small-scale and obscure process.

The most significant disadvantage of PM is the size constraints imposed on the volume of material that can be consolidated directly. The production of powders, tooling costs, presses and sintering furnaces contribute to a more expensive process than ingot metallurgy, despite its inherent conservation of material.

2.3.4 Problems with conventional processing routes

Metal-metal composites is a small research field but interest is growing. The main issue with these materials is from a practical point of view: large strains are required to reach high ultimate tensile strengths and this means large reductions in at least one dimension of the composites. A strain of 9 corresponds to a diameter reduction of 90 times [33]. Therefore it is difficult to produce engineering products unless one starts with larger diameter billet than possible by powder processing. Spray forming could potentially provide an interesting approach since it offers large billets of 300mm in diameter or more and 2m or more in length. Previous attempts at achieving high strain without using large billets involved a bundling technique where heavily deformation processed hexagonal wires were packed into a can and extruded again. However, temperatures as high as 760°C were necessary to get bonding between the individual wires leading to coarsened filaments and a subsequent degradation of mechanical properties [46]. Some other key issues regarding

strengthening mechanisms are yet to be resolved.

The focus of this thesis is the manufacture of scaled up metal-metal composites rather than elucidation of the mechanisms underpinning their mechanical behaviour.

2.4 Spray forming

2.4.1 Introduction

Spray forming was pioneered in the 1970's by Professor Singer at University College Swansea as an alternative way to produce ingots and strips directly from the melt [13]. Spray rolling was initially employed for the production of strip, however the process was incapable of controlling the thickness across the width of the strip exiting the rolls.

Spray forming was subsequently developed by Osprey Metals, Neath, Wales for the manufacture of billet rather than strip, and is since frequently referred to as the "Osprey Process". The process was developed for the metal-forming industry to reduce cost, to improve material utilisation, to improve structure and properties and to increase efficiency [47–50]. Discrete shaped preforms were produced using rotational or translational movements of a collector under the liquid/mushy droplet spray. The process combined atomisation and consolidation in a single step, and involved using the atomizing gas to extract all the superheat and latent heat from the atomised droplets partly during flight and partly after deposition from the large billet. Spray formed billets can consist of fine, uniform, equiaxed ($10\text{-}100\mu\text{m}$) grain structures, a very low oxide content and much reduced macro-segregation compared with cast ingots of the same size.

Spray forming has now become established in niche metal casting markets with applications in automotive, electronic and aerospace industries. PEAK, Germany produces Al-25Si-4Cu-Mg billets for Mercedes and Daewoo cylinder liners [51]. There have been five international conferences devoted to spray forming held ev-

ery three years and several review articles [52–54].

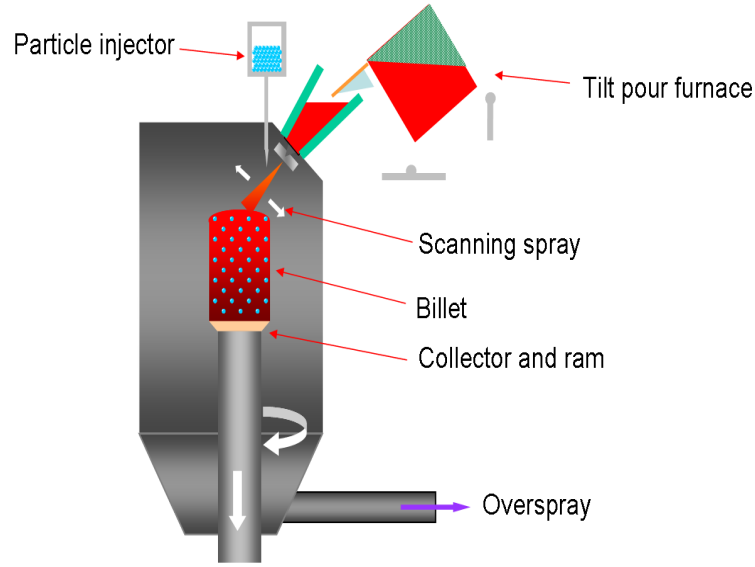


Figure 2.6: A schematic of the spray forming process for the manufacture of metal-metal composite billets [5].

The spray forming process, shown schematically in Figure 2.6, involves atomisation of a molten alloy stream, using high pressure and high flow rate inert gas (N_2 for Al alloys), into droplets with a mean diameter of $\sim 100\mu m$, that are then deposited onto a rotating substrate. Spray forming is a high flow rate casting process, unlike all other spray processes that are essentially low flow rate casting or coating processes. Typical liquid metal flow rates are $1\text{--}20\text{kg min}^{-1}$ [52]. By manoeuvring the substrate relative to the atomizer during deposition, preforms with different geometries can be obtained including billets, strips, tubes and rings. Droplets have a flight velocity of $50\text{--}100\text{ms}^{-1}$ due to the accelerating effect of the atomising gas. At the point of deposition, the droplet temperature and stage of solidification will depend on each droplet diameter [55]. Larger droplets may be liquid, whereas smaller droplets may be fully solidified. Thus, the liquid fraction in the spray at deposition must be sufficient to re-melt and break-up the semi-solid and solid particles for a homogeneous microstructure [55]. Overall, the spray is typically 50% solid at the point of deposition, and the residual liquid then solidifies within the billet to a density of up to 99%. The cooling rate of the residual liquid fraction in the spray

formed billet is relatively low ($0.1\text{-}10\text{Ks}^{-1}$).

2.4.2 Advantages of spray forming

Exceptionally homogeneous microstructures with fine equiaxed grains ($10\text{-}100\mu\text{m}$) are achievable because of the large number of solid and semi-solid particles in the depositing spray that provide an intrinsic grain refining effect, promoting high nucleation densities and fine scale polygonal grains as shown in Figure 2.7. If the average liquid fraction is too low, the individual particles retain their discrete microstructure; if the average liquid fraction is too high, a thick layer of liquid develops on the billet surface, trapping atomising gases and promoting macro-segregation. Under optimum conditions, the final structure of the billet is non-dendritic because of the remelting and extremely high heterogeneous nucleation density in the near surface region of the growing preform [56]. The characteristic spray formed microstructure comprises low levels of microsegregation in all areas of the billet.

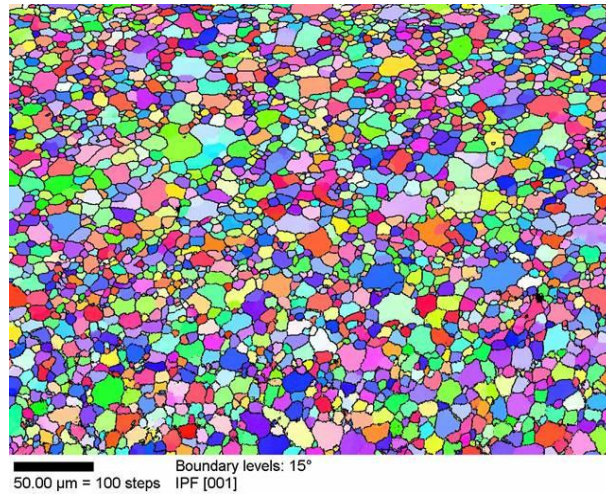


Figure 2.7: An electron back scatter diffraction map of a spray formed Al-Li-Mg-Zr alloy produced at Oxford University showing the typical spray formed polygonal microstructure [5].

2.4.3 Solidification in spray forming

Various mechanisms have been proposed to account for the formation of equiaxed grains in spray formed materials. Lavernia *et al.* [57, 58] and Annavarapu *et al.*

[59,60] suggested a semi-solid/semi-liquid layer forms on the deposition surface due to the interaction of solid, liquid and semi-liquid droplets. When solid or semi-solid droplets impinged on the deposition surface, dendrite arm fragments were generated that acted as nucleation sites for equiaxed grains. Nucleation and grain multiplication occurred as a result of mechanical fracture of dendrite arms in the semi-solid/semi-liquid layer as droplets were deposited at high velocity and with large strain rates. In addition, the grain growth (coarsening) in the mushy top surface was proposed to be constrained by the presence of porosity that restrained the migration of solid/liquid interfaces, contributing to the formation of equiaxed grains.

Grant [5] proposed in more detail how re-melting, grain multiplication, thermal and compositional equilibrium effects, and microstructural coarsening controlled the evolution of the refined, polygonal grains typical of spray formed microstructures. A numerical model for the spray formed grain size was produced describing the important solidification behaviour during spray forming. For example, the solid fraction of different droplet diameters (10, 50, 120 and 200 μm) created by atomisation as they moved away from the point of atomization were calculated in the case of an Al-4Cu alloy and are shown in Figure 2.8. The droplets were deposited at an assumed axial distance of 0.4m, and diameters less than 50 μm were solid; droplets greater than 200 μm were fully liquid; and droplets with intermediate diameters were mushy with a variation in droplet solid fraction dependent upon droplet diameter. Figure 2.9 shows the log-normal droplet diameter distribution that is typical of those produced experimentally. At the point of deposition the probability of mushy particles was greatest for intermediate droplet diameters. All modelling studies of droplet flight and solidification in spray forming showed a wide range of droplet thermal conditions at deposition [5]. Grant suggested that the large thermal mass of the larger droplets partially re-melted the solid fraction of the spray on deposition resulting in a mushy billet surface. In contrast to previous ideas, Grant

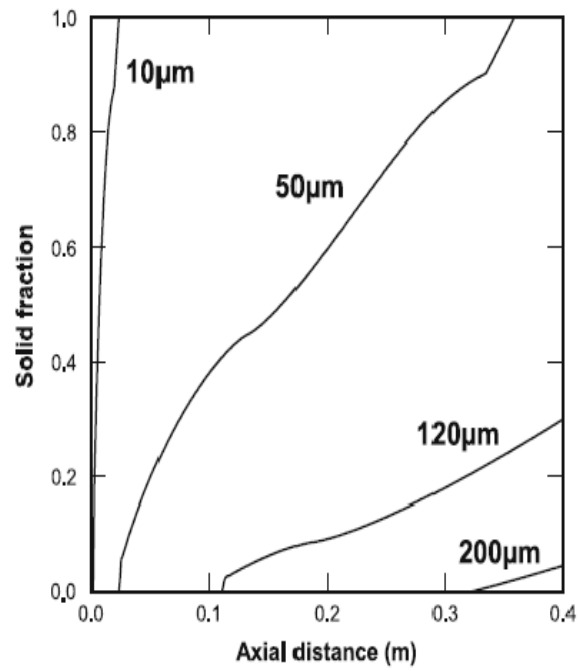


Figure 2.8: The droplet solid fraction of spray formed Al-Cu alloy as a function of droplet diameter and axial distance from the point of atomization [5].

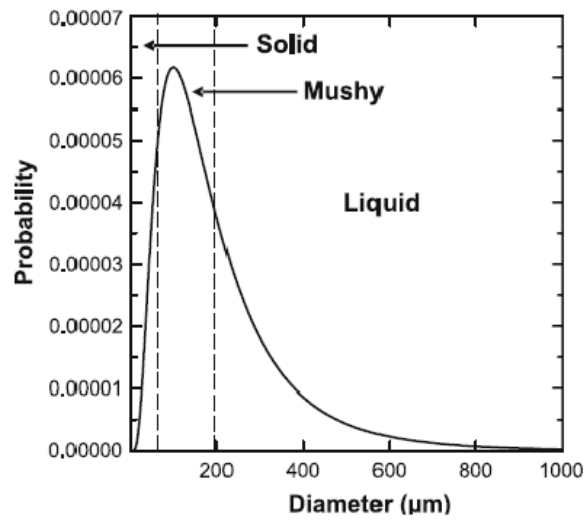


Figure 2.9: A typical log-normal droplet diameter probability density distribution on a mass or volume basis obtained by gas atomization showing typical fractions of solid, mushy and liquid droplets at deposition [5].

suggested that rapid re-melting and re-heating effects (thermal shock) were much more important than mechanical effects in the fragmentation of the solid and mushy dendritic microstructure, providing the grain multiplication effect. Rapid thermal and compositional equilibration was promoted by the small interdiffusion distances between the large number of small solid fragments in the mushy surface of the billet and also reduced microsegregation to lower levels than found in the solid droplets themselves.

Grant [5] presented a simple model relating the distribution of droplet diameters and solid fraction at deposition to the embryonic grain diameter in the surface region of the billet. The number of solid particles per unit volume $N_{V,i}$ in the droplet diameter interval Δd_i with midpoint d_i is given by:

$$N_{V,i} = \frac{6}{\pi} \frac{P_i \Delta d_i}{d_i^3} \text{ for } f_i > 0 \quad (2.4)$$

where f_i is the droplet solid fraction with probability density P_i . Integrating Equation (1.3) over the full droplet diameter distribution, such as that shown in Figure 2.9 which has an integrated area of unity, the total number of solid and mushy particles per unit volume N_V is given by:

$$N_V = \sum_{i=1}^n N_{V,i} \quad (2.5)$$

The average embryonic grain diameter in the billet top surface $\overline{d_0}$ was then estimated based on two assumptions: (i) immediately after deposition each mushy or solid particle becomes an “embryonic” grain; (ii) little nucleation occurs in the liquid fraction of the surface because of little or no undercooling and an excess of nuclei arising from the deposition of many mushy and solid particles. Therefore, the embryonic grain diameter was given by:

$$\overline{d_0} \approx \left[\frac{f_s}{N_V} \right]^{1/3} \quad (2.6)$$

where f_s is the equilibrated solid fraction in the billet top surface. According to this model, embryonic grain diameters of 11 to $58\mu\text{m}$ were calculated, which agreed well with experimental measurements of final grain diameters in a range of alloys.

2.4.4 Disadvantages of spray forming

Disadvantages of spray forming include the loss of materials from the overspray droplets that are not incorporated into the billet, which can account for up to 30% of the feedstock material, the high cost of inert gases for atomization and poor process reproducibility. A further disadvantage of spray forming is the unavoidable formation of porosity in the billet. Hence, the as-sprayed billets are usually consolidated to full density by extrusion, hot/cold rolling or hot isostatic pressing. When this is done, the billets have properties superior to conventionally cast materials and generally are comparable or better than powder metallurgy equivalents. In particular, spray formed Al-based materials have much lower levels of oxidation and superior fatigue performance to PM materials [52].

2.4.5 Commercial development

The advantages of spray forming provide an opportunity to produce new engineering alloys that cannot be manufactured by conventional processing. Many companies took Osprey licenses in the 1980's and 1990's to investigate a variety of new products or cost-reduction strategies. Spray forming was used by Swissmetal to process Cu alloyed billets up to 2.5m in length which were then extruded, drawn or rolled to produce thin rods and wires or narrow strips [61]. They produced Cu alloys that could not be fabricated by ingot metallurgy such as spinodal Cu-Ni-Sn alloys, machinable bronzes with high concentrations of Sn for superconductivity applications [62]. Danspray produces 4 tonne spray formed steel billets at its plant in Taastrup, Denmark [63], including tool steels and high speed steels, where spray forming is a competitor to powder metallurgy.

A typical spray formed Al-Si billet produced by PEAK, Germany for Mercedes and Daewoo cylinder liners, is shown in Figure 2.10 (a). The hyper-eutectic Si

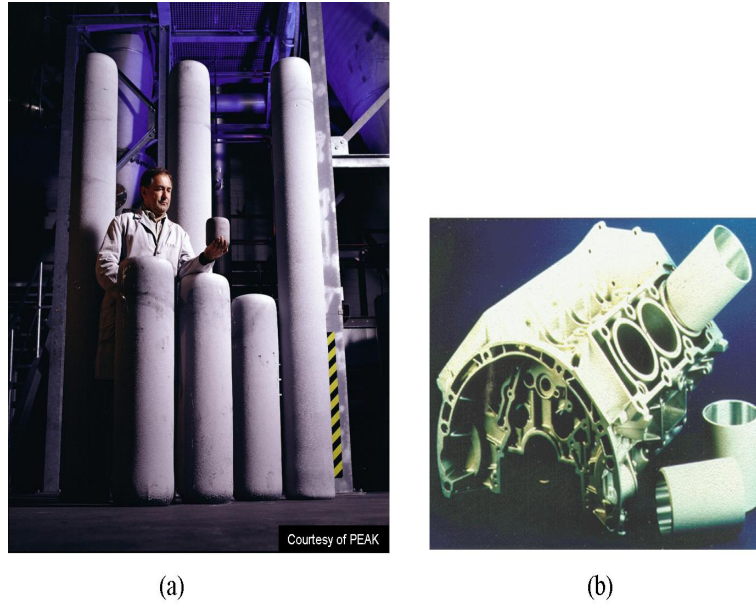


Figure 2.10: (a) An Al-Si spray-formed billet (0.3m diameter x 2.5m long); (b) cylinder liners in an automotive engine (courtesy of Peak).

concentration of up to 25-wt% means they cannot be processed by casting, and the high Si concentration confers good wear resistance and comparatively low thermal expansion. Seamless tube extrusion, rotary swaging and sectioning are used to manufacture the cylinder liners as shown in Figure 2.10 (b). Overall the cylinder liners save weight over the cast iron liners (reduced petrol consumption), an increase in engine power and efficiency, and a reduction in friction leading to lower piston wear [61].

Kobelco, Japan spray form Al-Nd alloys to be used subsequently as sputtering targets for coating thin wires used in over 70% of the world's thin-film transistor screens [64]. The refinement and homogeneity of the Nd distribution in the microstructure is superior to any casting process. The average grain size of the spray formed billet is extraordinarily small at $\sim 2\mu\text{m}$, and the size of Al-Nd intermetallics is $\sim 1\mu\text{m}$. Consequently, the target material is less susceptible to splashing during sputtering.

Spray forming of conventional Al alloys has also been investigated extensively. Spray formed 2xxx [65] and 7xxx [66] series have been studied to exploit the refined microstructure produced by spray forming as well as the greater scope for alloying elements, particularly Li, Zr and Zn.

2.5 Spray forming with co-injection

The objective of this project is to manufacture bulk metal-metal composites by spray forming and co-injection, and thus to scale-up material supply currently restricted to small scale powder metallurgy routes. Solid particles of the minority phase will be co-injected into the atomised liquid spray of the matrix material and co-deposit to form a billet with a metallic majority matrix phase containing a homogeneous dispersion of a dissimilar minority metallic phase. Co-injection has been practised previously for the manufacture of particulate reinforced metal-matrix composites for conventional alloys [14–19, 22, 23] and in intermetallic matrix composites [20, 21].

Metal-matrix composites produced by spray forming comprise a metallic matrix, usually an Al-based alloy and ceramic particulates, usually SiC or Al₂O₃ of typical diameter 3 to 15 μm , and intended to improve specific stiffness. The solidification behaviour of the molten matrix is affected by the injected ceramic particulate because the injected cold, ceramic (SiC, Al₂O₃) phase increases the rate of heat loss from the atomized spray and thereby promotes the retention of alloying elements in solid solution in the matrix [17] but requires re-optimisation of the spray forming process. The incorporation of the ceramic reinforcements gives rise to changes in the microstructure including increased dislocations densities, refined grain size and enhanced precipitation kinetics [67].

A fundamental issue concerning particulate injection in spray forming is achieving a homogeneous distribution of the co-injected phase in the matrix phase. Early studies showed severe agglomeration or even “banding” of the injected phases in

which the particulate bands into regions of high concentration parallel to the billet surface and may be related to the scanning action of the spray and the rotation of the billet. Another concern is the interaction between the matrix material and the ceramic particles.

2.5.1 Mechanism of incorporation during co-injection

Careful control of both the atomizing conditions and the particulate feeding conditions is essential for a homogeneous distribution of the particulate in the final microstructure. The incorporation of a solid phase into the liquid phase can occur at three different regions: in the region of atomisation; during flight of droplets/particulate to the billet; or at the point of deposition. Lavernia *et al.* carried out extensive modelling and experimental studies on the injection of SiC particles (3-15 μ m) into a range of aluminium alloys [6, 23, 67–70]. Two jets positioned at 180° to each other were employed to co-inject the reinforcing phase in the region of flight where the spray consisted of solid, liquid and partially solid droplets. Their primary aim was to prevent any interfacial reactions between the particles and the liquid metal droplets. The injection distance and substrate position from the point of atomisation was 20cm and 40cm respectively and was selected on the basis of their numerical analysis of the temperature and solid fraction of the atomized droplets. They suggested that a reduction in the average spray enthalpy of 40% was desirable, in order to reduce contact time and thermal exposure of the SiC particulates to the reactive liquid Al matrix.

Two mechanisms were proposed to describe particulate incorporation: co-injection into the droplet interior, or attachment to droplets and then entrapment after impact at deposition. Lavernia *et al.* [67] incorporated up to 20vol% of SiC particulates into an aluminium-lithium matrix, but it was not clear by which mechanism the particulate was introduced.

In order for particulate to penetrate droplets, the kinetic energy of the impact

must be sufficient to overcome surface tension/wetting forces and viscous forces. In flight, the chances of particle-droplet interaction is small because of the vast volumes of atomising gas used; whereas at deposition, injected particle velocities are much slower and the billet surface is substantially solid. Therefore, incorporation is proposed to be most efficient at atomisation, and in commercial injection systems, the particulate phase is introduced via the primary atomiser [71]. In this region, and especially where the much higher pressure (10 bar) high flow rate secondary atomising gas impacts the relatively low pressure (4 bar) low flow rate liquid metal stream, particulates are rapidly accelerated and forced into the liquid stream and droplets as they are formed by atomisation. A schematic of the co-injection process is shown in Figure 2.11.

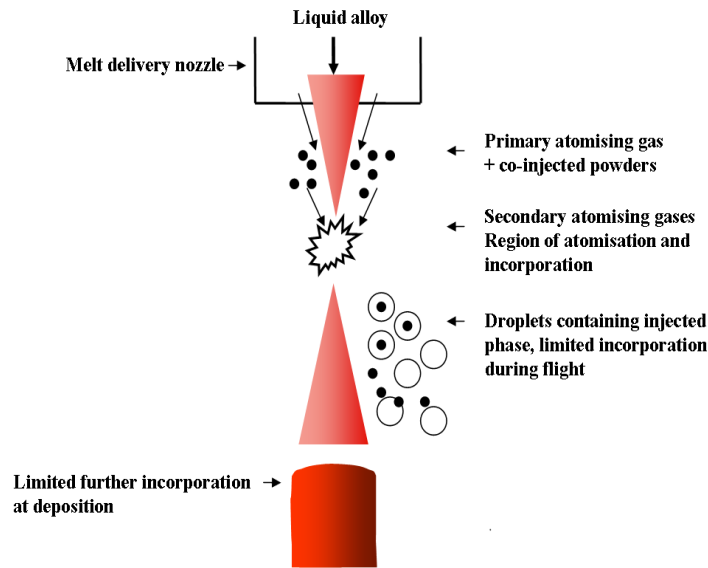


Figure 2.11: Schematic diagram showing the incorporation of a solid particulate phase into the liquid matrix phase during spray forming [6].

The primary grain size of alloys reinforced with ceramic particulate decreases with an increase in the reinforcement content [19] because of two factors: the cooling effect of the room temperature particulate, and possibly a direct increase in the number of nucleants per unit volume (see Equation (1.5)). The injected particulate which is usually at room temperature, cools the atomized melt and the billets leading to shorter overall solidification times and reduced time for microstructural

coarsening. Particulate may also “pin” migrating liquid films at grain boundaries in the final stages of solidification. The nucleation effect may be direct where the co-injected phase is a nucleant itself, however ceramic particulates used to reinforce Al alloys such as SiC are not known to be potent nucleants for α -Al; the nucleation effect may be indirect in which the particulate incorporation enhances dendrite fragmentation some way, as depicted in Figure 2.12. The liquid droplet starts to solidify and forms a dendritic structure. A co-injected particle impacts at high velocity and the temperature is drastically decreased at the droplet-particulate interface. The effect has been termed “thermal shock” effect [7]. A large thermal gradient is induced and the growing fine scale dendrites roots become unstable in the suddenly changed thermal environment; they are the most soluble part of the dendrite due to their curvature, re-melt and cause dendrite fragmentation. Alternatively, the cold injected particle may induce heterogeneous nucleation directly by chilling and undercooling liquid droplets. After $\sim 1\mu\text{s}$ the thermal shock effect disappears as the temperature of the droplet and particulate decreases relatively slowly, through convective heat transfer to the surrounding environment. The droplet now contains the co-injected particle and a larger number of nucleation sites or embryonic grains, leading to a small grain size in the final composite billet [7].

In addition to the velocity and mass of the co-injected particle, particle-droplet wettability and the difference in density between the particle and droplet are factors which determine the engulfment of a particle into atomized droplets. For example Lawley *et al.* [72] suggested that the diameter of solid particles must be greater than $3\mu\text{m}$ for engulfment to occur.

The nucleation behaviour depends not only on the thermal shock effect but also the critical wetting angle [7]. By varying the wetting angle between matrix material and ceramic reinforcements from non-wetting (180°) to complete wetting (0°), the nucleation free energy barrier is reduced. This is because the heterogeneous nucleation temperature increases and less undercooling is needed for nucleation. In

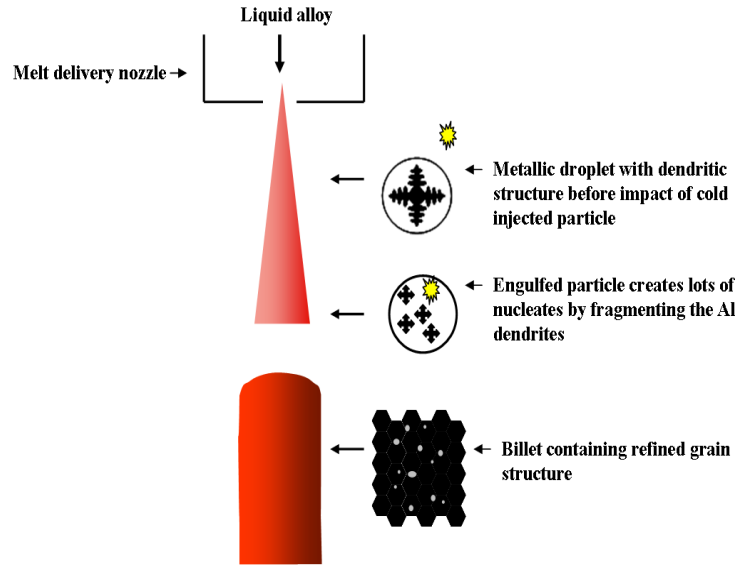


Figure 2.12: Schematic diagram showing the indirect nucleation effect resulting from the incorporation of the ceramic particulate into the melt stream during spray forming [6].

general, ceramics are non-wetting materials with regard to metallic matrices and therefore seldom initiate nucleation of primary phases.

Figure 2.13 shows the combined influence of assumed wetting angle and thermal shock effect on nucleation behaviour for different particulate sizes. The average droplet temperature was 933 K and the average particulate temperature was 300 K. Each temperature-wetting angle curve (A, B, C) is divided into two separate regions. Below a critical angle for each case, the curve is flat and the temperature remains around the melting temperature. Thermal shock induced nucleation occurs. Above the critical wetting angle, the temperature curve resembles that of nucleation curves in the absence of thermal shock such as curve D. When the particulate diameter was increased to $7\mu\text{m}$ (curve A), the thermal shock effect increases and the critical wetting angle increases accordingly.

Results from Gupta *et al.* [73] confirmed that co-injection promoted a finer microstructure with a 67% reduction in grain size of deposited Al-Li-SiC_p relative to the unreinforced Al-Li matrix.

Grant [5] spray formed a Si-30Al alloy with co-injected Si-30Al particles in order to provide experimental support for the qualitative grain size model presented earlier

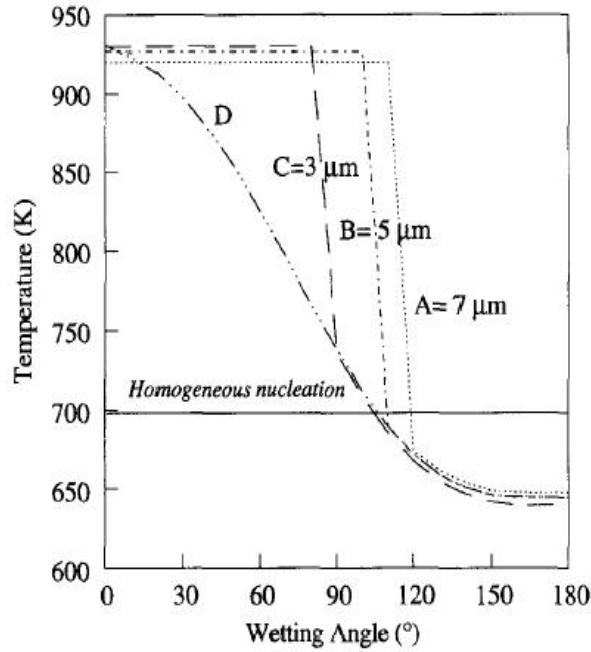


Figure 2.13: A comparison of the combined influence of assumed wetting-angle and thermal-shock on the nucleation behaviour, for various ceramic particulate sizes. Curve D represents heterogeneous nucleation without thermal shock. The solid line is homogeneous nucleation [7].

in Equations 1.3-1.5. The ratio of particle mass flow rate to liquid alloy mass flow rate was varied. Figure 2.14 shows the inverse of the α -Al/Si interface length per unit area as a function of the flow rate ratio. The α -Al/Si interface length per unit area was calculated by quantitative image analysis of the optical micrographs taken from the billet centres. An increase in the co-injected particle mass flow rate caused a reduction in the inverse of interface length per unit area i.e. the microstructure became finer as more particulate was injected. Because the injected and atomised phases were identical and because some attempt was made to keep the billet temperature the same in each experiment, this refinement was attributed directly to nucleation effects rather than microstructural coarsening because of billet cooling.

Spray forming with co-deposition of over-sprayed material from previous experiments of the same composition has become standard commercial practise to improve spray forming process yield and productivity [74]. Tan *et al.* [75] spray formed an Al-8.5Fe-1.3V-1.7Si alloy with co-injection of the solid powder of the same alloy.

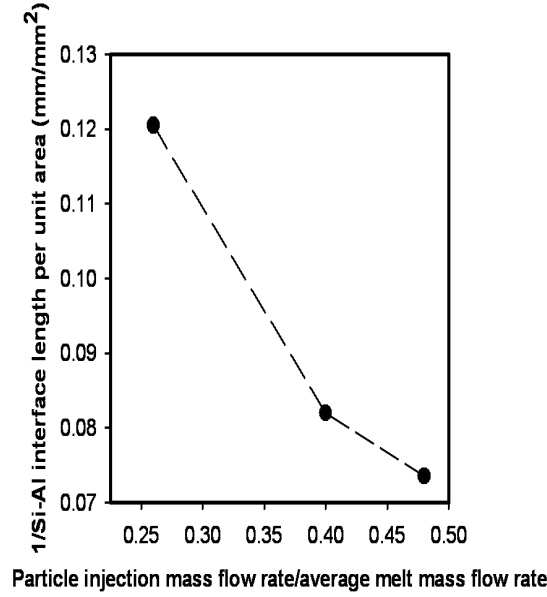


Figure 2.14: The inverse of the Si- α -Al interface length per unit area as a function of the ratio of co-injected Si-30Al particulate flow rate to liquid Si-30Al flow rate [5].

To obtain fine precipitates of $\text{Al}_{12}(\text{Fe,V})_3\text{Si}$, a high cooling rate of $>10^4 \text{ Ks}^{-1}$ was suggested to be necessary, and usually this alloy was produced by planar flow casting. They attempted to increase the cooling rate, which they suggested was 10^2 - 10^4 Ks^{-1} for a spray formed billet, by co-injection of the over-sprayed material into the region of atomisation. During atomization, small powders were completely remelted and larger particles were partially remelted. A section of the resulting billet was hot extruded at 400°C at an extrusion ratio of 11:1. The tensile strength increased from 204MPa to 343MPa by the addition of 10% over-sprayed powders. A further increase of over-sprayed powders resulted in a gradual decrease in the tensile strength. The elongation also increased from 7.3 to 10.7% and then decreased gradually with further addition of over-sprayed powders. Most over-sprayed powders contained a thin oxide layer and it was suggested that the addition of more than 10% of over-sprayed powders, increased the level of oxidation in the billet to such an extent that the cooling effect of the over-sprayed powders no longer dominated properties, and increased oxide fraction lead to a deterioration of mechanical properties.

Tang *et al.* [8] spray formed an Al-8.5Fe-1.3V-1.7Si alloy with co-deposition of

overspray powders that were prescreened into different diameter ranges of $\leq 43\mu\text{m}$ and $43\text{--}74\mu\text{m}$. The powders were injected into the region of atomisation. The billets were then hot extruded at $450\text{ }^{\circ}\text{C}$ using an extrusion ratio of 16:1. The addition of over-spray powder enhanced the mechanical properties: the smaller diameter co-injected powders increased the ultimate tensile strength from 360MPa to 433MPa and to 392MPa with diameters of $43\text{--}74\mu\text{m}$. The greater surface area of the smaller particles in contact with the melt increased the thermal shock effect, leading to increased nucleation site densities as outlined above, providing a more refined microstructure. However in the study above by Zhang *et al.* [7], a larger particulate diameter gave rise to an increased thermal shock effect and is perhaps more plausible than Tang's explanation. In the study by Tang *et al.*, most of the overspray particulate interacted with the droplets during deposition. Some powders retained their morphologies in the matrix as shown in Figure 2.15 (a), while Figure 2.15 (b) shows some powders that were cracked due to the effects of rapid heat expansion on incorporation. In Figure 2.15 (c), the over spray particulate kept its original morphology (arrow a), or the powder cracked (arrow b) or partially remelted (arrow c). The powder has sufficiently re-melted in Figure 2.15 (d) to almost lose its prior morphology and microstructure. If co-injection is to be successful to increase spray forming yield, then it cannot produce any deleterious effect on properties. This can only be achieved if substantial re-melting of the particulate phase occurs. The optimum microstructure is that where no remnant of the particulate microstructure remains, and by definition a micrograph of this cannot be shown. Fundamentally, this condition is only that which occurs in spray forming under optimum conditions anyway since the depositing spray without co-injection already contains many solid particles of which no trace remains in the microstructure.

Overall, co-injection has been used successfully for the introduction of (i) a strongly dissimilar particulate into an alloy matrix e.g. SiC in an Al alloy to produce composites of up to 20vol% where the critical aspect is homogeneity of the particu-

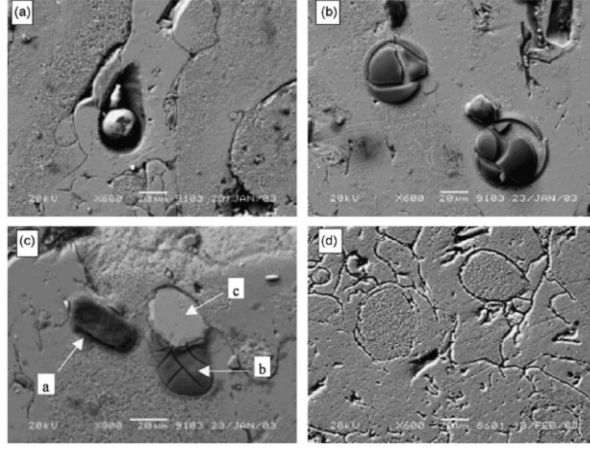


Figure 2.15: SEM morphologies of over-sprayed powders in a Al-Fe-V-Si alloy [8].

late phase; and (ii) the identical alloy powder obtained from overspray of previous production runs where the objective is to increase process yield and to ensure no remnant of the overspray microstructure remains.

2.6 Deformation processing

2.6.1 Extrusion

As previously described, once a homogeneous distribution of the metal phases has been achieved, either by casting, powder processing, or in the future possibly by spray forming, the minority phase requires extensive deformation to achieve the unusual and desirable mechanical strengthening effects. Deformation can be exerted through extruding, swaging, drawing, rolling or equal-channel angular pressing (ECAP). In extrusion the material is forced through a die of desired cross-section. Hot extrusion followed by cold swaging or drawing is the most commonly used processing approach [9]. Hot extrusion reduces the alloy flow stress and may reduce work hardening through dynamic recovery or recrystallization, allowing easier movement of the alloy through the extrusion die. Cold extrusion causes less oxidation, requires higher forces and can lead to higher strengths through work hardening of the majority phase.

The mode of deformation processing in powder processed Al-20vol%Ti composites was accumulative extrusion bonding, also known as repetitive extrusion processing [30]. Extrusion followed by swagging provided rods 2.5mm diameter which were then cut to 90mm lengths and bundled into a can for a second extrusion. Subsequent SEM analysis showed incomplete bonding between rods. The resultant 2.5mm diameter wire was then swagged and wire drawn to 1mm diameter wire providing a total strain of 13.9. An attempt was made to repeat the extrusion for a third time, but the procedure failed. The ultimate tensile strength of the composite was 890MPa which is higher than any precipitation-hardened commercial Al alloy which had a maximum strength of ~ 700 MPa.

2.6.2 Rolling

Chen *et al.* [9], studied the mechanical properties of Al-20vol%Nb metal-metal composites fabricated by powder processing and cold rolling. The powders were mechanically blended and uniaxially compacted at room temperature. The green preform was hot extruded into a composite plate of cross-section 8mm x 10mm, which was then rolled into sheet. The cold rolling reduction per pass was less than 10% in order to avoid side and surface cracking. Scanning electron microscopy images of the microstructure of 90% cold rolled composite are shown in Figure 2.16. No shape change took place in the Nb particles after a slight amount of cold rolling reduction as shown in Figure 2.16 (a). After a severe cold rolling reduction of 90%, the thickness of the Nb filaments decreased and they began to develop a ribbon-shaped morphology as shown in Figure 2.16 (b).

The ultimate tensile strength of 90% cold rolled Al20vol%Nb was 210MPa which was approximately double the strength before cold rolling reduction. The dependence of tensile properties on the annealing temperature was also investigated and compared with pure Al sheet processed under the same conditions. As expected, properties were significantly reduced in the Al sheet because of static recrystal-

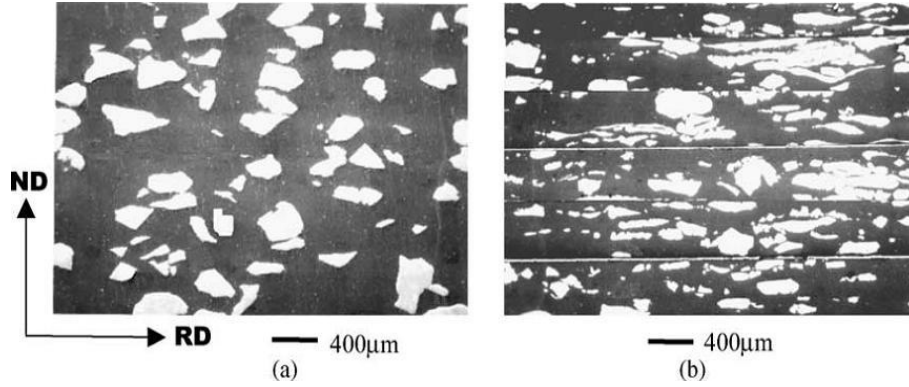


Figure 2.16: SEM microstructures of (a) extruded Al20vol%Nb and (b) 90% cold rolled Al20vol%Nb. RD = rolling direction, ND = normal direction to the rolling plane [9].

lization whereas the alloy retained substantial strength because the annealing temperature was too low to recrystallise the Nb. At 700K, the UTS of Al-20vol%Nb remained rather high at ~ 150 MPa.

Trybus *et al.* processed Cu-20vol%Nb composites by rolling to a true strain of 6.9 [76]. The minority Nb phase was deformed into planar ribbons elongated in both the longitudinal and transverse directions. This resulted in equivalent strengths in both directions. The Cu matrix underwent a deformation - dynamic recovery - recrystallisation cycle. The strength of the composite did not show a Hall-Petch type behaviour in that the strength was not dependent on filament spacing to the same extent as observed in axisymmetrically deformed composites. This is because the planar filaments do not provide effective barriers to dislocation motion in all directions as the filaments that curl around the centreline axis would [76]. Strengths were in line with those predicted by a rule of mixtures, which is generally the case for composites processed to strains < 7 [37].

2.7 Bulk nanostructured materials

Initial studies used inert gas condensation to fabricate nanostructured materials with grain sizes of ~ 10 nm [77]. This process approach has limitations, most notably the size of the sample that can be produced comprising a maximum of 10mm in diameter

and 1mm in thickness. A more recent approach to fabricating bulk nanostructured metals is being developed, involving refining the microstructure using severe plastic deformation (SPD). This approach applies large shear under a high imposed pressure without any significant change in the overall dimensions of the solid [78]. The use of heavy deformation in metal processing can be traced back to early metal-working of ancient China [79], the blacksmith's manufacture of high-quality Damascus steel in the Middle East [80] and the fabrication of the legendary Wootz steel in ancient India [81]. From a more modern perspective, interest in SPD was first stimulated 50 years ago by Bridgman in the United States [82] who subjected metals to large deformation under high applied pressures and to concurrent torsional straining using a methodology that would now be regarded as a classic SPD procedure. However, the applied pressure was generally insufficient to produce strongly attractive improvements in properties. In the last few years, fabrication of nanostructured materials by SPD has been one of the most active areas in nanomaterials research [83, 84]. There are many different SPD techniques, including equal-channel angular pressing (ECAP), high pressure torsion (HPT), multi-directional forging and accumulative roll-bonding (ARB).

The strength of a material can be related to the grain size through the Hall-Petch equation (Equation 2.2). Smaller grain sizes give increased strengths leading to an ever growing interest in processing nanostructured materials. Huge amounts of strain will introduce a high density of dislocations that may then configure into arrays of grain boundaries, providing the material with ultra fine grains, and the mechanical response suggested by Hall and Petch.

2.7.1 Accumulative roll bonding (ARB)

Accumulative roll bonding (ARB) is a cyclic severe deformation processing technique used to induce ultra high strains in sheet materials. A schematic of the rolling procedure is shown in Figure 2.17. Samples for bonding are passed through a roller

that may have heating capabilities. The bonded sheets are cut in half and surfaces to be bonded are prepared. The sheets are stacked together and bonding is repeated. In principle, the accumulated strain is unlimited since repetitions of ARB cycles are endless, although cracks generated along the edges are a practically limiting factor. Sample preparation of the bonded surfaces is critical to achieving good bonding [85].

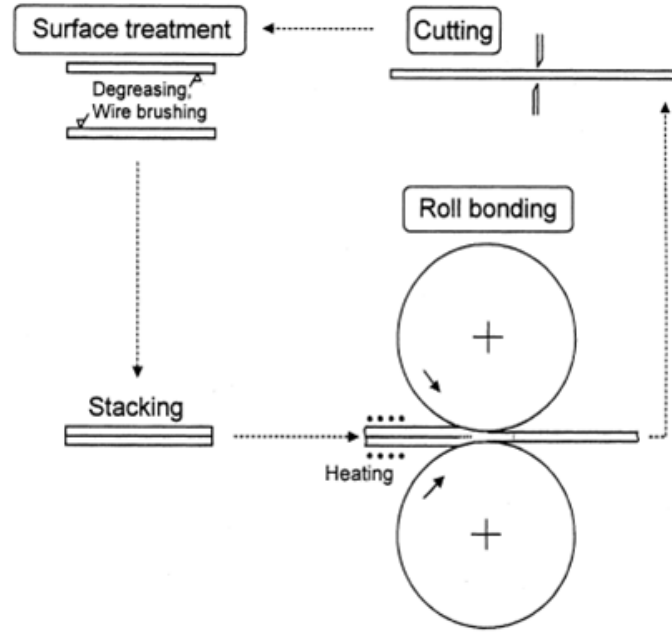


Figure 2.17: A schematic showing the principle of the ARB process [10].

ARB was invented in 1998 by Saito *et al.* who showed that severe plastic strain can be induced in a material without any geometrical change in thickness provided reduction is kept at 50% per pass [10]. The materials investigated were commercial Al, Al-Mg alloy, and steel and after processing to ~ 7 ARB cycles, sub-micron grains and high UTS were obtained.

Considering ultra-fine grained (UFG) materials have significant grain boundary density, it was expected that this would affect the precipitation behaviour and therefore a study was conducted on solution treated Al-2wt%Cu alloy processed by ARB [86]. After ARB to a strain of 4.8, a lamellar structure was observed with mean intervals of 67nm between boundaries. The fine lamellar structure was attributed to solute atoms that retarded recovery during ARB because 99%Al subjected to ARB

had coarser grains. The precipitation behaviour of ARB solution treated Al-2Cu was different from conventional coarse grained alloy. Equilibrium θ phase preferentially appeared whereas in coarser grained material θ' phase precipitated. The precipitation kinetics occurred more quickly in UFG materials due to the increase in grain boundaries that acted as nucleation sites. Consequently, the hardness decreased after ageing as the strengthening phase (θ') was not precipitated.

Ultra-fine grained bulk Al with an average grain size of 670nm was obtained by ARB [87]. After 6 cycles of ARB the commercially pure Al had a tensile strength of 300MPa. Thus, ARB has proved successful in producing bulk nanostructured Al with high tensile strengths. In this work, ARB is explored as a downstream processing route for the manufacture of bulk hierarchical metal-metal composites.

Chapter 3

Experimental programme

Two routes to manufacturing metal-metal composites were investigated in this work: co-spray forming to produce near-industrial scale billets; and conventional powder mixing followed by solid-state consolidation route for smaller scale investigations. Downstream processing experiments included extrusion and rolling to deform the spray formed billet and to induce the characteristic filamentary morphology in the minority phase. The materials were characterised at each processing stage and the final composites with maximum deformation were tested mechanically.

3.1 Alloy selection

The powder processing route was used primarily to investigate different metal-metal composite mixtures as a way of exploring more combinations of materials than were possible by spray forming and to try to isolate the effect of particular microstructural variables e.g. particle morphology.

Table 3.1 outlines the major factors that were taken into consideration when choosing optimum metal-metal combinations. An important factor in determining the deformation behaviour of the minority phase is strain compatibility between the matrix and minority phase. It has been suggested that the flow stresses of both phases should not differ by more than a factor of 3 for co-deformation to occur [26].

If the minority phase has a high flow stress, the majority matrix will tend to flow plastically around it until it ruptures [26]. In addition, the minority phase should also have a dissimilar crystal structure to the matrix phase for enhanced strengthening to come into effect by dislocation pile up at the interface. Since the focus of the thesis is on Al, the matrix phase was not altered. Optimum combinations for Al-based deformation processed metal-metal composites include Al-Mg, Al-La, Al-Zn, since each minority phase has a similar hardness to Al. However, for spray formed metal-metal composites another important parameter in choosing suitable phase combinations is the relative melting temperatures of the phases. To avoid an interfacial reaction from occurring the minority solid injected phase should have a high melting temperature compared with the matrix, and ideally few low temperature intermetallic phase possibilities. Therefore Mg and Zn are unsuitable because their melting temperatures are 650°C and 420°C respectively, lower than the temperature of Al at 660°C. La has a higher melting temperature of 920°C, but has high density of 6.1g/cm³, and is prohibitively expensive for structural applications. Thus, Ti is considered a good candidate and with a lightly alloyed Al matrix phase, the flow stresses should be within closer agreement. Therefore, the primary factors for choosing suitable MMC systems to spray form were crystal structure, hardness, melting temperature and density.

Aluminium based MMCs investigated by previous researchers include Al-Ti [88] Al-Nb [31, 89]. Al-Sn [90, 91] and Al-Mg [38, 90]. In this work, powder processed Al-Ti and Al-Nb were selected because both Ti and Nb have a high elastic modulus, are inherently stronger than Sn and Mg and can be expected to have better overall mechanical properties. For example, at a deformation true strain of ~ 11 , Al-20vol%Nb had an ultimate tensile strength of 1020MPa [31]; at a deformation true strain of 14, Al-20vol%Ti had an ultimate tensile strength of 900MPa [88]. According to powder processing experiments in this work, Ti undergoes deformation into filaments more readily than Nb, due to closer matching flow stresses between

	Crystal structure	Melting temperature (°C)	Hardness (MPa)	Density (g/cm ³)
Al	FCC	660	245	2.7
Ni	FCC	1453	700	9
Cu	FCC	1000	874	8.9
Fe	FCC	1500	600	8
Ag	FCC	961	24	10.5
Cr	BCC	1900	1120	7
V	BCC	1910	628	6
W	BCC	3422	2570	19
Nb	BCC	2477	736	8.5
Mo	BCC	2623	1500	10
Mg	HCP	650	260	1.7
Ti	HCP	1660	716	4.5
Zn	HCP	420	412	7
Re	HCP	3186	1320	21
Ta	HCP	3017	800	16.7
Sc	HCP	1541	750	2.9
Zr	HCP	1855	650	6.5
La	HCP	920	363	6.1
Be	HCP	1287	600	1.9
Sn	BCT	230	51	7.3

Table 3.1: Properties of metals for MMC combination assessment (Data taken from Wikipedia).

Al and Ti compared to Al and Nb. Powder processed experiments focused on Al-Ti composites since this combination was investigated by spray forming.

3.1.1 Al-12Si+Ti

Having selected Al-Ti as a candidate system for spray forming, a near eutectic composition of Al-12wt%Si might be an attractive candidate for the matrix alloy, for the following reasons: (1) It has a low melting point of 577°C that would help to restrict any possible exothermic runaway reactions between the injected Ti powder and the Al matrix; (2) it has high fluidity, relatively low reactivity and the group had experience with this alloy by spray forming.

Spray formed Al-Si alloy billets for cylinder liners are commercially produced for Daimler-Mercedes and Daewoo by PEAK, Germany, based on Al-25Si-4Cu-Mg(wt%). The hyper-eutectic Si concentration of these alloys cannot be processed by casting and offers high wear resistance, high temperature operation and low ther-

mal expansion [52]. Al-Si based alloys also have good friction resistance and good machinability. Spray formed Al-12wt%Si solidifies with a divorced eutectic reaction at 577 °C, involving essentially pure Si faceted plates and α -Al with limited solubility of Si. The Al-Si equilibrium phase diagram is shown in Figure 3.1 [4]. Hence, the Al-12Si+Ti system was not expected to produce the high tensile strengths reported for powder processed Al-Ti composites because of the high fraction of brittle Si expected, but provided an acceptable starting point that minimised risk from which to explore the feasibility of spray forming metal-metal composites.

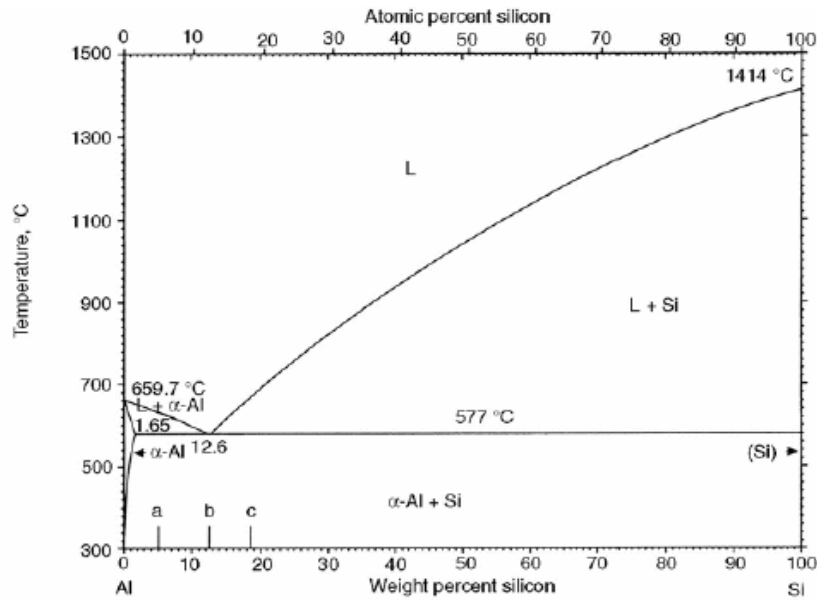


Figure 3.1: The binary Al-Si phase diagram showing a divorced eutectic reaction at $\sim 12\text{wt}\%\text{Si}$ at 577°C [4]

3.1.2 Al-4Cu+Ti

In order to achieve better mechanical properties and building on the encouragement provided by Al-12Si+Ti, a matrix alloy of Al-4wt%Cu was subsequently investigated, again with co-injected Ti. The binary phase diagram of Al-Cu at low Cu concentrations is shown in Figure 3.2, and Al-4Cu has a much higher liquidus temperature of $\sim 650^\circ\text{C}$ than Al-12Si. According to the “3-to-1 rule”, if the flow stress of two phases differ by more than a factor of three they are unlikely to co-deform

into a filamentary MMC [26]. Al-4wt%Cu has a flow stress of 80MPa at 675K at a strain rate of 0.01/s [92], and Ti has a flow stress of 125MPa under the same conditions [93] - although this will be expected to be sensitive to the Ti oxygen concentration. Therefore it was hoped that a Al-4Cu+Ti composite might exhibit very good co-deformation behaviour since the flow stresses are within a factor of three. Al-4Cu is also a heat treatable alloy and the basis for many commercial Al-based alloys used in aerospace applications, including struts and panels, making use of the high specific strength. Heat treatment involves a high temperature solution treatment, quenching and then ageing, and it was envisaged that the ability to vary the matrix alloy flow stress by heat treatment (unlike the Al-12Si) would add an extra degree of flexibility in the processing.

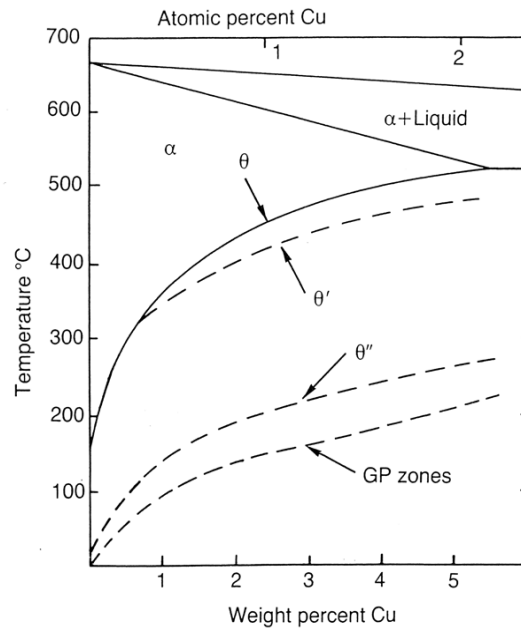


Figure 3.2: The binary Al-Cu phase diagram at low Cu concentrations showing the metastable precipitates that form during age hardening [11].

	Al	Si	Ti	Fe	Cu	Mn	Zn	Mg	V
Composition	86.9	12.12	0.74	0.18	0.01	Mn	0.03	0.01	0.02

Table 3.2: The chemical composition (wt%) of Al-12Si powder.

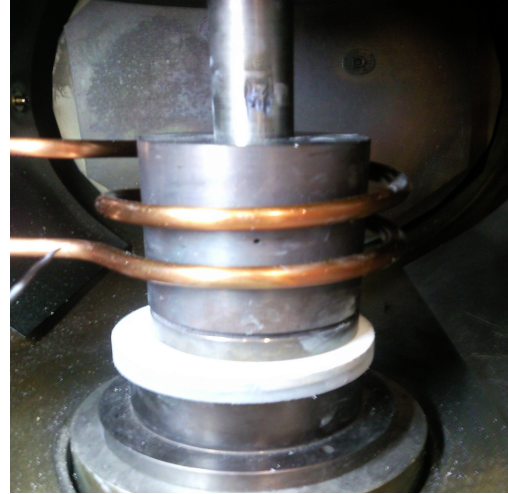
3.2 Powder processing

The powders studied were: Ti, Nb, Al, Al-12Si and stainless steel. Al-12Si powder was sourced from Sulzer Metco with a size of $d_{50}=25\mu\text{m}$ according to laser diffraction measurements. The chemical composition of Al-12Si powder is shown in Table 3.2 and was analysed using induction coupled plasma-optical emission spectrometry (ICP-OES) at London and Scandinavian Metallurgical Co. Ltd. UK. The Si content was close to the 12wt% target at 12.12wt% and the Si particles were roughly spherical according to microscopy studies. The remaining powders were from Beijing Haoyun Industry Co. Ltd. and were 99% pure, according to the supplier, with a size of $d_{50} \sim 26\mu\text{m}$ according to laser diffraction measurements. The majority of powder processing work was concerned with Ti and therefore only Ti powder is analyzed in detail (section 6.2).

In order to produce mixed metallic powders for subsequent consolidations, the following procedure was adopted: powders were weighed and combined usually according to 80:20 volume percent and were placed into glass jars. A rubber bung with a hole drilled through its center was used for a lid. During degassing in a low vacuum chamber, the hole allowed for only slow release of air from the jar so that powders did not escape. Powders were degassed for a few hours and until a vacuum of 10^{-2}bar was achieved. The powder processing chamber was back-filled with Ar to eliminate oxygen for safer mixing and once the chamber was opened a screw was quickly inserted into the hole in the rubber bung at the top of the jar to seal in the Ar. The jars of powders were securely placed in a Turbula Shaker Mixer shown in Figure 3.3 (a) and mixed for 10 hours at a rotation frequency of 40rpm.



(a)



(b)



(c)

Figure 3.3: (a) The Turbula Shaker-Mixer used to blend powders; (b) die used for hot pressing of powders; and (c) the diffusion bonding press used for its low vacuum chamber in degassing of powders and for hot pressing of mixed powders.

The mixed metal powders were then poured into a cylindrical stainless steel BH13 die as shown in Figure 3.3 (b) and hot compacted using the hydraulic press shown in (c). Al foil was used to protect the inner surface of the die that was also coated with a boron nitride spray. A copper washer was used as a solid lubricant and placed between the powders and the ram to facilitate compaction. Due to a limited ram travel distance, the powders were compacted in two stages: firstly a pre-compaction at ~ 5 tonne at 150°C under vacuum so that 19mm of ram travel was reached and then spacers were then added to facilitate the travel limitation; and secondly a vacuum of 3×10^{-2} bar was acquired again and the temperature was gradually increased to allow for further outgassing. At 300°C the powders were hot pressed and held as follows: 5 tonnes for 2 minutes; 10 tonnes for 2 minutes; 15 tonnes for 2 minutes; and 20 tonnes for 5 minutes. The 30mm diameter “green” preform was removed and ready for hot extrusion.

3.3 Spray forming

Co-spray forming was carried out at PEAK Werkstoff GmbH, Germany for Al-12Si+Ti and at Oxford University for Al-4Cu+Ti. The spray forming rig and procedure at PEAK are essentially identical to that at Oxford (except the melt capacity is ~ 6 times greater at PEAK), therefore details of the Oxford unit only are presented.

3.3.1 Operation principle of co-injection pump

Prior to this project, no co-injection work had been performed at Oxford. Therefore a major step in the experimental work was to introduce this capability to the Oxford equipment. This presented several major challenges: (1) safe integration of the powder injection equipment recognising that safety protocols mandate the elimination of oxygen from the spray forming system, and the avoidance of all potential

ignition sources; (2) remote operation since similarly the safety protocols mandate the entire spray forming operation takes place without the presence of people close to the equipment; (3) the powder injection system must be able to deliver metal powders at a mass flow rate consistent with $\sim 20\text{vol}\%$ of injected powder in the final billet and this value depended on the metal flow rate of the matrix alloy; (4) the powder must be injected into the atomisation/spray in a chamber in a manner to ensure its efficient incorporation into the final billet.



Figure 3.4: DACS co-injection pump and yellow hopper.

A DACS powder injection pump, initially designed and commissioned by PEAK, was transferred to Oxford and installed on the spray forming unit. The pump was commissioned by Robin Vincent and the author. The pump was positioned a few meters away from the spray forming chamber due to space restrictions and is shown in Figure 3.4. The yellow hopper was manufactured at Oxford according to designs provided by Osprey that provided a fluidised system. An incoming pipe at the base fed nitrogen gas to purge the powders. An outlet pipe was installed at the top of the hopper on its lid, to relieve the build-up of nitrogen gas. The hopper was over 1m height to minimise the volume of powder that might escape through the release

pipe at the top and in addition, a filter was placed at the exit.

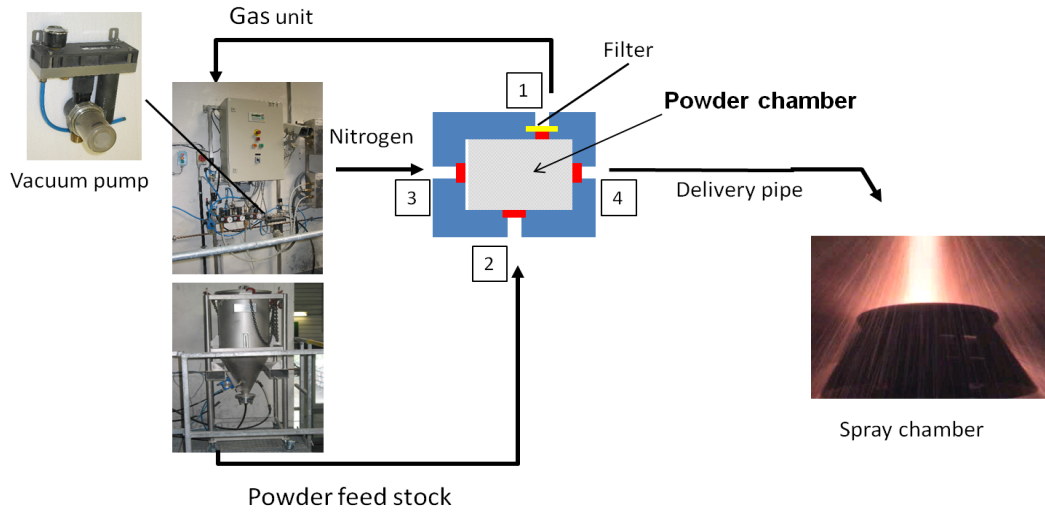


Figure 3.5: The principle of operation of the powder injection pump.

The pump was operated remotely from the control room and was interlocked such that the whole system would shut down if any oxygen entered the unit via the co-injection pump. The operating principle of the powder pump is illustrated in Figure 3.5. The key to this pump technology is the “powder chamber” that contained four valves operating in succession.

The first valve 1 opened to withdraw gas from the powder chamber using a vacuum pump. This valve then closed. Valve 2 connected to a hopper containing the feedstock powder opened next and the low pressure of the vacuum sucked in a burst of powder. This valve then closed. Valve 3 connected to a nitrogen supply then opened to fluidise the powder. Finally, the outlet valve 4 opened to release the metered quantity of powder through a 5m delivery pipe connected to the atomiser of the spray forming unit, and valves 3 and 4 then closed. This cycle was repeated. The pump had three modules of this type that operated in rapid sequence to maintain a near constant flow. All pipes involved in the operation were anti-static and grounding leads were attached to the hopper, pump and atomiser.

The frequency of cycle of powder bursts ranged from 2Hz to 11Hz and the powder flow rate was also adjusted by changing the volume of the powder chamber itself.

To ensure that the powder feedstock did not adhere to the walls of the hopper or get blocked at the pipe exit, a vibratory mechanical transducer was fixed to the outside of the hopper cone. The hopper was placed on a balance and a camera recorded the display of the balance so that powder flow rates could be calculated. The powder was injected into the melt stream via the primary gas. The primary gas is used in spray forming to constrain the metal stream close to melt delivery nozzle exit, and to stabilise it during a drop of $\sim 15\text{cm}$ to point of atomisation provided by the secondary atomiser, operating at high gas pressure and flow rate.

3.3.2 Pump installation

Figure 3.6 illustrates the co-injection principle relative to the actual co-injection unit. The powder exits the hopper through three outlet pipes at the base of the fluidised funnel shown in Figure 3.6 (a). The pipes are connected to the three modules that lead to the powder chamber shown in Figure 3.6 (b) and are mixed with nitrogen and delivered to the primary atomiser of the spray forming unit shown in Figure 3.6 (c).

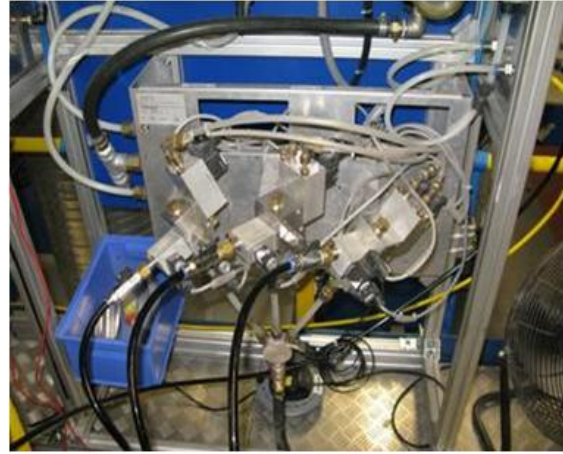
A number of challenges were faced during installation of the co-injection pump. To begin with the pump control panel was in German and translations were required to fully comprehend the software. The nitrogen supply for the pump was initially sourced from nitrogen cylinders but the supply was always exhausted before experiments were completed and so the pump was connected to the large external cryogenic nitrogen supply.

3.3.3 Co-injection pump set-up

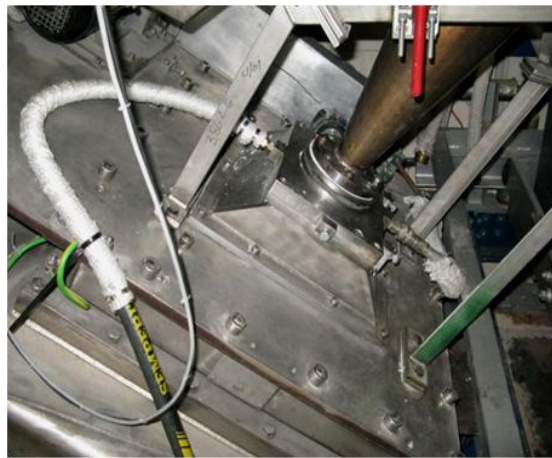
A number of precautionary measures were taken during the set-up procedure for powder flow calibrations. The pump was serviced between each run using a pneumatic vacuum cleaner connected to the spray forming chamber. A lamp was placed in the hopper for a few hours to ensure it was completely dry. Before loading the



(a)



(b)



(c)

Figure 3.6: Co-injection process begins at (a) hopper with 3 exit pipes that are fed into (b) the powder chamber where powders are mixed with nitrogen and delivered into the atomiser at (c).

hopper, fluidisation gas was turned on for two minutes to purge the feed pipes and hopper. A respiratory gas mask was used during powder handling. The hopper, powder trays, scoop and metal powder delivery tube were earthed before use to avoid risks associated with static build-up.

Powders were dried in the oven at 50°C for 24 hours. Before loading powder, the vacuum of the powder chamber in each of the three modules was tested with the pump set to run mode. Once the powders were in the hopper, the lid was tightly fastened and the pressure outlet pipe was connected and fluidisation was turned on at 0.2bar. A grounding lead was attached to the delivery pipe and to the hopper.

The powder feed regulator was set to zero pressure before turning the power on. The powder feed gas was set to 2.5bar. The extraction system for the spray forming unit was turned on so that nitrogen could be safely released from powder pump. For the powder calibration runs, the pump was operated manually. Instead of running powder through the delivery pipe and into the spray forming chamber, the powder was collected so that delivered powder weight could be recorded. The collector had an inlet for the incoming powder and an outlet at the lid to release the nitrogen gas safely into the spray forming unit. The collector rested on a balance so that incoming powder flow rates could be recorded.

The pump was turned on for operation in standby mode to purge the delivery pipe and powders for at least 20mins prior to spraying. During this time the oxygen analyser was calibrated and once it reached 100ppm oxygen there was one hour for experiments to be completed before the oxygen check and calibration would need to be repeated. Ti powder was injected via the primary atomiser into the melt stream close to the point of atomisation.

3.3.4 Optimising the powder flow rate

To achieve the required powder mass flow rate, a series of calibration trials were carried out. In these experiments, powders were delivered to the collector rather

than the spray forming chamber. Many parameters were investigated for their effect on powder flow rate including frequency, pressure of the carrier gas, morphology of powders, length of delivery pipe and effect of hopper vibration. A variety of powders were tested including stainless steel (comparatively low cost), spherical Ti-6Al-4V that was injected into a Al-10Si billet, and commercial purity, near spherical Ti powder that was injected into a Al-4Cu billet.

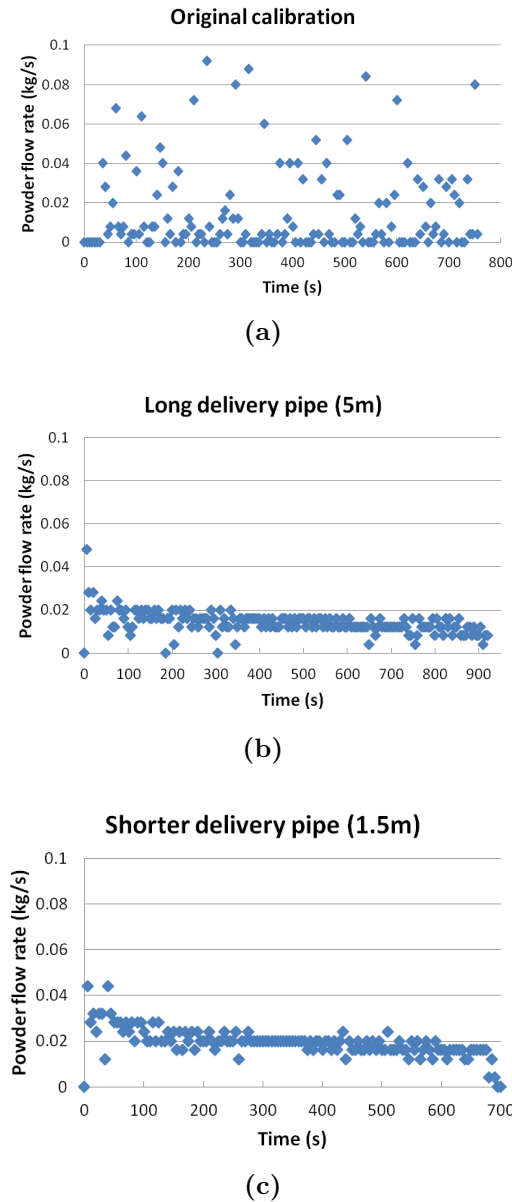


Figure 3.7: Calibrating Ti-6Al-4V powder mass flow rate at frequency of 7Hz under the same conditions.

Initially the delivery rate of powder to the collector was sporadic. Figure 3.7

(a) shows that occasionally there was no recorded change in powder mass and this was usually followed by a large mass of delivered powder in subsequent intervals. Figure 3.7 (a) is a preliminary calibration carried out when the pump operation and various settings were not fully optimised. Figure 3.7 (b) shows a more steady and consistent flow rate was obtained after further trials were carried out although, the mass feed rate was low and gradually declined with time. The delivery pipe was then shortened from 5m to 1.5m and Figure 3.7 (c) shows a shorter travel distance had little effect on increasing powder flow rates, and the initial drop-off in flow rate was a consistent feature for the preliminary calibrations. Once the pump operation was optimised the flow rate was reasonably constant for the complete experiment as shown in subsequent chapters.

3.3.5 Spray forming with co-injection

The spray forming and co-injection process was shown schematically in Figure 2.1. The spray forming plant at Oxford, shown in Figure 3.8, was designed and commissioned by Sandvik-Osprey and involves a 50kg tilt-pour induction furnace, a two stage scanning atomiser using N_2 and a manually controlled ram withdrawal rate.



Figure 3.8: The spray forming plant at the Begbroke Science Park, Oxford. The spray forming chamber is shown to the left, the induction furnace is shown in the center and the DACS co-injection powder pump is shown to the right.

In preparation for spray forming, master alloy ingots were pre-heated overnight at

150 °C to remove any moisture. The crucible, thermocouples and foundry tools were coated with a BN refractory furnace wash. The powders for injection were dried for 24 hours at 50 °C prior to co-injection. The co-injection pump was cleaned, serviced and the vacuum of the three powder chambers was checked. Warm powders were loaded into the hopper through a tall funnel that gently guided the powders. The lid was tightly fastened and an outlet pipe leading to the spray forming chamber was connected to the lid to release N₂ once fluidisation was turned on. A vibratory device was attached to the base of the hopper and the frequency and pressure of the delivery gas was set. The hopper was purged for at least 30 minutes prior to co-injection. The pump was then switched to remote operation mode so that injection and vibration could be initiated from the remote control room.

The spray forming chamber was purged with N₂ to <150ppm of O₂. The spray forming software that runs the spray forming experiments from the remote control room provided an interlock to prevent any molten metal from being poured into the chamber should the O₂ concentration reach 150ppm. In the unlikely event of an explosion due to rapid exothermic oxidation of Al powders, the back wall of the chamber comprised a 1m x 1m explosion relief panel that faced onto an external secure compound.

The first co-spray formed composite billet processed at Oxford was Al-10Si with injected Ti-6Al-4V powder. Al-10Si provided a wider freezing range than eutectic Al-12Si, and alloyed Ti powder was preferred over the more reactive pure Ti powder. The Al-10Si spray formed billet with co-injected Ti-6Al-4V is shown in Figure 3.9 (a). The billet was cut in half along the axial direction as shown in Figure 3.9 (b), for macrostructural investigation of the region of co-injected phase and microstructural examination. Downstream processing was carried out on sections taken from the monolithic alloy and the co-injected region of each of the billets.

Following from this “trial billet”, three co-spray formed billets of Al-4Cu with injected commercially pure Ti powder were subsequently manufactured at Oxford

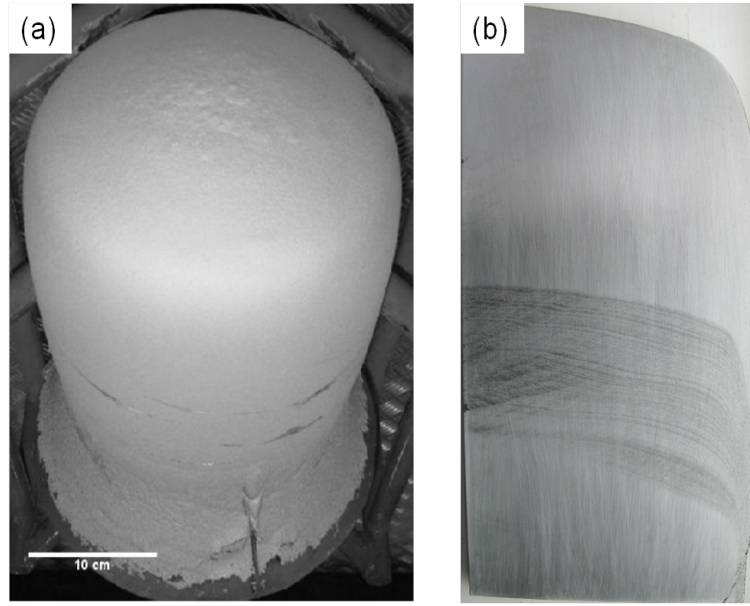


Figure 3.9: (a) Co-spray formed Al-10Si+Ti_{alloy} billet; (b) the interior of the billet showing the region of injected powder.

and are referred to as AlCuTi1, AlCuTi2 and AlCuTi3. Each billet contained Ti powder manufactured by a different route: mechanical milling; gas atomisation; and the hydride-de-hydride process respectively.

Melting of either the Al-10wt%Si or Al-4wt%Cu alloys was carried out in a rammed refractory crucible induction heated by an Inductotherm power-trak VIP-75R rated to 75kW. The Al-10Si 50kg charge was melted and heated to 860°C, representing a superheat of 283°C. For Al-4wt%Cu a 50kg charge of 47.5kg of high purity Al and 2.5kg of Al-80wt%Cu to provide Al-4wt%Cu was heated to 1100°C with a soak time of 20 minutes, representing a superheat of 450°C. The melt was poured at a lower temperature (750°C-850°C) by remote operation from the control room, through a pre-heated ceramic fibre tundish at a flow rate of $\sim 5\text{-}9\text{kg/min}$ into a ZrO₂ nozzle, and into the atomiser. The atomiser scanning at $\pm 5^\circ$ and 16 Hz produced atomised droplets that were intercepted by a rotating stainless steel substrate in the deposition chamber. The ram withdrawal rate was set to 30-40mm/min to maintain a constant height of $\sim 700\text{mm}$ between the top of the billet and the end of the melt delivery nozzle. Overspray powder that was not incorporated

	AlCuTi1	AlCuTi2	AlCuTi3
Melt temperature (°C)	750	750	850
Metal flow rate (kg/min)	8.7	7.6	5.78
Melt delivery nozzle	ZrO ₂	ZrO ₂	ZrO ₂
Nozzle size (mm)	5.8	5.7	5.0
Spray distance (mm)	680	680	680
Spray time (s)	325	343	512
Scan frequency (Hz)	16.6	16.6	16.6
Primary pressure (bar)	2	2	2
Secondary pressure (bar)	6.5	6.5	6
Gas to melt ratio	2.17	1.83	1.79
Ti type	Mechanically milled	Gas atomised	Hydride-dehydride
Target Ti volume fraction (%)	14	14	20
Amount of Ti injected (kg)	3.8	4.64	10.1
Target Ti flow rate (kg/min)	2.5	2.5	2.5
Actual Ti injection rate (kg/min)	-	2.4	2.2
Yield	68.5	70.1	72.5
Preform diameter (mm)	270	240	230

Table 3.3: The experimental parameters used during spray forming of AlCuTi1, AlCuTi2 and AlCuTi3.

	Al	Cu	Fe	Si	Mn	Zn	Mg	Li	V
AlCuTi1	95.31	4.49	0.06	0.10	0.01	<0.01	0.01	<0.0005	0.01
AlCuTi2	95.84	4.05	0.04	0.02	<0.01	<0.01	<0.01	<0.0005	<0.01
AlCuTi3	95.73	4.14	0.02	0.04	<0.01	0.05	<0.01	<0.0005	<0.01

Table 3.4: The chemical composition (wt%) of spray formed Al-4Cu in AlCuTi1, AlCuTi2 and AlCuTi3.

into the billet was continuously removed by the extractor fan into a wet scrubber system outside of the building. Further details of Al-4Cu spray forming parameters are shown in Table 3.3.

The chemical composition of spray formed Al-4Cu for each of the 3 billets is shown in Table 3.4 and was analysed using induction coupled plasma-optical emission spectrometry (ICP-OES) at London and Scandinavian Metallurgical Co. Ltd. UK. The sample for analysis was taken from the co-injected section of the billet that contained Ti. To assess the matrix alloy only, the Ti weight was subtracted from the total composition and each element weight was taken as a percentage of the total weight excluding Ti.

3.4 Downstream processing

Downstream processing is a crucial step to achieving the fibrillar microstructure characteristic of this type of metal-metal composites, and both extrusion and rolling processes were investigated. Extrusions were carried out in the Department, while rolling was carried out at the University of Buenos Aires, Argentina and the University of Warwick, UK.

3.4.1 Extrusion

Extrusion was carried out on metal-metal composite preforms processed by both the powder route and co-spray forming. Sections from the powder co-injection region of the co-spray formed billets were machined to 30mm diameter and 30mm length bars. Preforms were extruded at various extrusion ratios to circular, square and rectangular cross-sections using appropriate dies. Boron nitride was sprayed around the inside of the extrusion chamber, the ram and on the preform to provide lubrication. Preforms were heated in the extruder that is shown in Figure 3.10 at temperatures between 350 and 500°C depending on the material and the extrusion ratio. The extrusion temperature was measured using a thermocouple that was inserted into 2mm hole at the base of the preform. Heating was carried out for a further 30mins once the appropriate temperature was reached and the thermocouple was removed prior to extrusion. Extrusion speeds were in the range 1 to 600mm/min and extrusion forces were 400 to 720kN depending on the composition, temperature and extrusion ratio.

3.4.2 Accumulative extrusion bonding

Given that the literature shows that increases in tensile properties require very significant deformations of true strains >10 , strategies were explored to increase deformation strains beyond that achievable in a single extrusion (~ 5) (in all cases

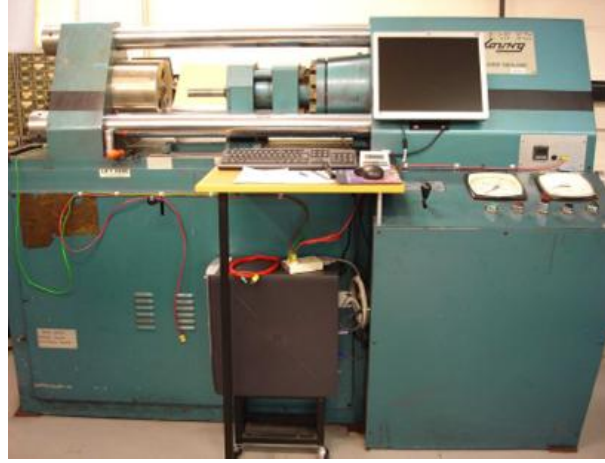


Figure 3.10: Extruder at Oxford University with a maximum force of 720kN.

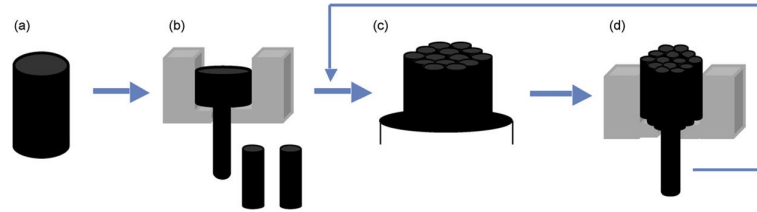


Figure 3.11: (a) Green preform (30mm dia), (b) hot extrusion to cylindrical rods, (c) rods cut from the extrusion and stacked prior to next extrusion pass (d).

strains are given as true strains). The principle of accumulative extrusion bonding is shown in Figure 3.11 and was explored using the in-house extruder. It was difficult to obtain good bonding between rods, and although wire was used to tighten the bundle it appeared to have little effect in prevented rods from moving sideways. Thus a square holder was constructed of the same material as the rods to hold them in place as shown in Figure 3.12. A 3.5mm² rectangular rod was extruded and cut into 25 pieces of 20mm length and packed tightly into container. The container was 30mm in diameter, with a 17mm x 17mm square hole. The packed preform was extruded through a square die at 415 °C at an extrusion force of 720kN. The process was repeated a second time on the resulting extruded bar. However there was little improvement in the mechanical properties after multiple passes.

Multiple extrusion of Al-4Mg-1Zr was carried out previously by Garcia [94]. The method worked relatively well in refining the grain structure and led to improved mechanical properties but the effect lessened after the first two passes. Following

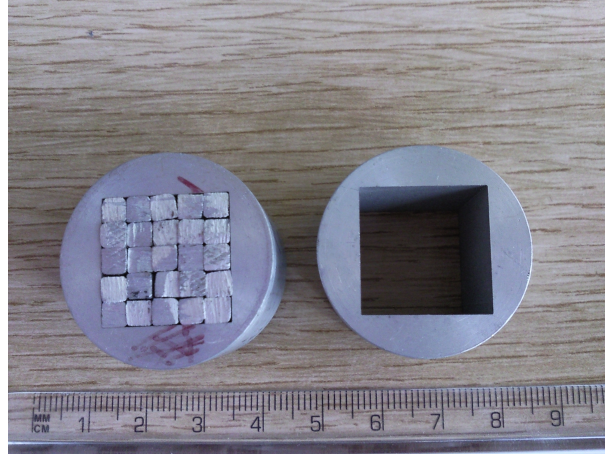


Figure 3.12: Stacked rods of extruded Al-12Si+Ti packed into Al-10Si spray formed holder for carrying out accumulative extrusion bonding.

from their experience it was attempted to use a lower extrusion temperature after the first extrusion to prevent recrystallisation but this was not possible due to the force limitations of the equipment already reached after the first extrusion.

3.4.3 Accumulative roll bonding

Rolling was carried out at the University of Buenos Aires with the help of Mr Crosa and the University of Warwick with the help of Mr. Keyte. At the University of Buenos Aires the rolling mill was similar to the Farmer Norton mill shown in Figure 3.13. The speed of the mill ranged from 3 to 10m/min and the roll diameter was 239mm. The samples investigated by rolling were powder processed Al-12wt%Ti and spray formed PEAK Al-12Si+Ti materials. Two 1mm thick, 20mm wide and 150mm long strips were degreased in acetone, and faces to be bonded were wire brushed to remove oxides. 2mm holes were drilled at both ends of the strips and they were tied tightly together with wire. The material was rolled at room temperature at a speed of 1m/min. The material already at a strain of 6, was rolled at 50% reduction. Three ARB cycles were conducted to provide a total strain of 8.4 in the spray formed material.

A Farmer Norton rolling mill was used at the University of Warwick and is shown in Figure 3.13. The speed of the mill ranged from 0 to 23m/min and the

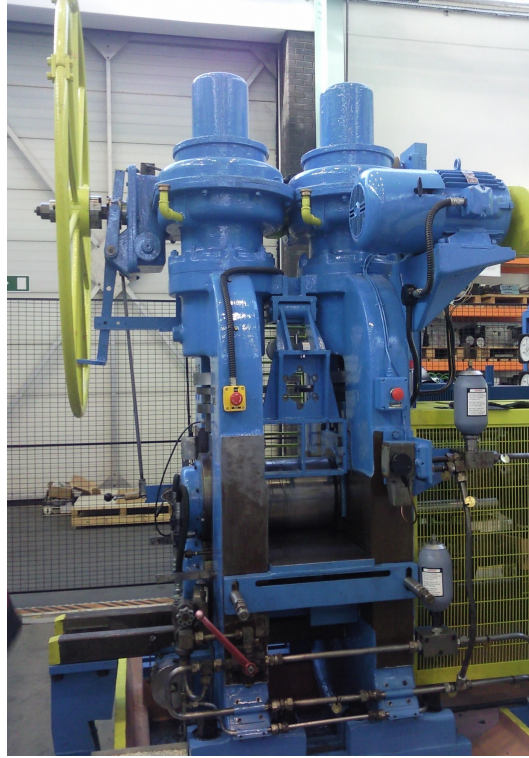


Figure 3.13: Farmer Norton rolling mill at University of Warwick.

roll diameter was 254mm. Each sample was heated to $\sim 370^{\circ}\text{C}$ for 20mins prior to rolling and at intermediate stages of rolling when cracks at the strip edges started to appear. A lubricant was used to guide the sample through the mill and every so often the rollers were cleaned to remove oxides on the surface. Rolling was carried out at the slow speed of $\sim 1\text{m/min}$ and at gradual reductions in thickness of $\sim 1\text{mm}$ per pass to prevent edge cracking. For ARB the stacked sheets were put directly into the rolling mill without any fastening at the ends as this is the normal procedure in industry. After surface preparation, the sheets were heated in the oven at 300°C for ten minutes that facilitated bond formation. Rolling was carried out at 50% reduction per pass at a speed of 1m/min . There was no lubrication.

3.5 Ti fibre extraction

After severe deformation processing under some conditions, the Ti powder was deformed into thin, elongated fibres and ribbons. In order to study the fibres, the

Al-rich matrix was dissolved, the fibres recovered and then studied by microscopy. The extraction experiments were performed by Dr. Lui at the Department of Materials, Oxford University. Thin slices of pure aluminium were added to absolute butanol and was refluxed for three hours to ensure the solvent was anhydrous. Further details can be found in [95]. The Ti and Si phases remained intact on the filter paper and were dried and studied in the SEM.

3.6 Microstructural characterisation

3.6.1 Sample preparation

Samples for optical microscopy, electron microscopy and electron back scatter diffraction examination were prepared by firstly mounting specimens in Wood's metal (50% Bi, 26.7%Pb, 13.3%Sn and 10%Cd, (wt%)) in a 12.5mm diameter holder. Samples were ground flat using 400 grit SiC paper. The polishing procedure was as follows: MD-Plan cloths with 9 μ m diamond suspension; MD-Dur cloths using colloidal silica with 10% hydrogen peroxide; followed by the same suspension on MD-Chem cloths. Finally the sample was cleaned with deionised water only on MD-Chem cloths.

3.6.2 Optical microscopy

Digital micrographs were obtained using a Polyvar optical microscope. Objective lenses of x5, x10, x20, x50 and x100 and an eyepiece magnification of x10 were used to image the macrostructure and microstructure of the specimen. No etching reagents were necessary for any microscopy analysis in this work. Optical microscopy was used only for quantitative image analysis (see below).

3.6.3 ImageJ analysis

Image analysis was used to measure the fraction of porosity in the as spray formed material and the fraction of co-injected phase in both the as-sprayed material and the deformed composites. A series of 10 images was taken with the Polyvar optical microscope under the same conditions of magnification and light settings. ImageJ, a free Java application for image analysis and processing, was used. Firstly the pixel size was converted to microns using the scale-bar provided on the image. Porosity measurements were calculated by converting the image to 8-bit grey scale resolution, then setting a grey level threshold and converting the image to binary so that the Al matrix and secondary phase was removed leaving only pores evident. Porosity was expressed as an area percentage of the analysis area. Ten images were analysed and a average of the porosity fraction was recorded. The procedure was repeated for measuring the Ti area fraction only.

3.6.4 Secondary electron microscopy (SEM)

Secondary and back-scattered electron imaging was carried out in a JEOL 6500F, and occasionally in a JSM 840A, with a field emission gun operating at 10-20kV with a beam current of 70mA.

3.6.5 Electron backscatter diffraction (EBSD)

EBSD was also carried out in the JEOL 6500F, with the sample tilted at 70° to the incident electron beam, at an accelerating voltage of 20kV corresponding to a beam current of 70mA. EBSD scans were performed in a hexagonal scan pattern with a scan step size ranging from 0.1 to 0.5 μ m. A camera binning of 8 x 8 pixels was used, with high gain and short exposure times of ~160ms and the working distance was usually ~17mm. An EDAX TSL OIM acquisition system and analysis software was used for grain size and texture measurement. Energy dispersive spectroscopy (EDS)

data was collected simultaneously while the scan was running to allow partitioning of the EBSD data on the basis of local composition. Data clean-up was modest involving increasing the dilation to 5 points per grain. A grain was defined as having at least three data points in order to remove inaccuracies associated with the measurement of grains with very few data points. When assessing the grain size and misorientation angle distribution a condition was imposed to include only defined grains in the analysis so as to avoid ill defined boundaries within a grain. EBSD data was also used to investigate texture in α -Al phase using pole figures to show how the specified crystallographic direction of grains are distributed in the sample reference frame and inverse pole figures (IPF) where the orientation distribution of a sample axis is shown on a stereogram plotted with respect to crystallographic orientation.

3.6.6 X-ray diffraction (XRD)

X-ray diffraction (XRD) analysis was carried out using a fully automated Siemens D5000 powder diffractometer employing Cu K_α radiation ($\lambda = 1.5046 \text{ \AA}$) and a secondary monochromator. The samples were continuously spun during data collection and were scanned using a step size of $0.05^\circ 2\theta$ between the range of 10° - $90^\circ 2\theta$ and a count time of 12 seconds per step. XRD scans were performed by Mr. Cullen, Dept. of Materials.

3.6.7 Focused ion beam microscopy (FIB)

The FEI FIB 200 was used for two purposes: (1) to prepare specimens for transmission electron microscopy (TEM); and (2) for a more detailed assessment of the microstructure of heavily deformed samples. FIB was operated by Dr. Gareth Hughes with the author in attendance. For both cases, the initial bulk sample, contained in a 12.5mm diameter holder, was polished as outlined in Section 3.6.1. A cross-sectional TEM specimen was prepared by firstly depositing a protective strip

of platinum with dimensions $15 \times 2 \times 1 \mu\text{m}$ onto the surface using the ion beam. Rough milling using a gallium ion beam current of 5 nA was carried out on either side of the Pt strip to remove the bulk of material prior to fine polishing. Once rough milling was completed, the specimen was $\sim 2 \mu\text{m}$ thick. The cross-section specimen was then thinned on both sides using progressively lower beam currents from 1000 pA to 300 pA resulting in a sample thickness of $\sim 1 \mu\text{m}$. The specimen was then tilted to 45° and three pre-release cuts were made to partially free the specimen - leaving it connected in three places. The specimen was then returned to 0° tilt and during the final stages of specimen polishing at 50 pA , the sample was tilted by 1.5° to produce a parallel sided specimen with a final thickness of $\sim 110 \text{ nm}$. Electrostatic forces attached the specimen to a glass rod. The sample was carefully placed on a copper TEM grid.

For imaging, the surface layer was removed by slow scanning of the ion beam at a current of 300 pA over a field of view $50 \mu\text{m}$ wide. This slow scanning removed surface oxides and revealed sub-surface structure after a minute or so of scanning. Subsequent ion induced secondary electron imaging was carried out using a beam current of 100 pA .

3.6.8 Transmission electron microscopy (TEM)

TEM was used to examine the interface of the matrix and the Ti to see whether a reaction had occurred. Sample foils were prepared by FIB as outlined in Section 3.6.7. TEM was performed in a JEOL 2010 operating at 200 kV and high resolution (HR-TEM) was performed in a JEOL 3000F with field emission gun operating at 300 kV by Dr. Kerstin Jurkschat, with the author in attendance.

A JEOL 2010 TEM equipped with an Oxford Instruments INCA X-ray analysis system was used for energy dispersive X-ray analysis (EDX). EDX analyses the characteristic X-rays produced by the interaction between the primary electron beam and the sample. The technique identified all elements present with atomic numbers

of 5 and greater with a detection limit of approximately 0.3 weight %.

3.7 Mechanical testing

3.7.1 Hardness testing

Nanoindentation was tried to obtain hardness values of the minority fibre phase after extrusion. However the fibres were too thin to achieve reliable nanoindentation readings. Vicker's hardness measurements were taken using a Wilson Instron micro-hardness tester on Al-12Si+Ti and Al-4Cu+Ti prior to deformation to compare the hardness of the Ti powder processed by different routes. A minimum load of 0.1 N was held for 15 second and hardness values were averaged from at least 15 indents.

3.7.2 Tensile testing

Tensile testing was performed on various MMC strips and bars to the ASTM E8 standard. All tests were carried out by Westmoreland Mechanical Testing and Research Ltd, Banbury, UK.

Chapter 4

Co-spray forming of Al-12Si+Ti

4.1 Introduction and objectives

This chapter describes the experiments to study co-spray forming as a new route to manufacturing Al based metal-metal composite (MMC) feedstock ingots at a scale ($\sim 300\text{kg}$ per billet in the case of PEAK material) significantly beyond previous powder metallurgy and immiscible alloy system approaches. MMCs are generally pure metal mixtures in which the minority element can recover at a rate similar to that of work hardening, thus enabling its deformation to high strains without fracture. However, in spray forming a “pure” metal is rarely processed due to its generally higher affinity for oxygen than an alloy, and narrow or invariant freezing range that makes it more awkward to spray form without excessive liquid fraction. Despite difficulties with narrow freezing range alloys, Al-12wt%Si was chosen as the “matrix” alloy initially because it has a very low melting point for an Al alloy, and solidifies as essentially pure Si and relatively dilute α -Al - so that the α -Al can withstand subsequent severe deformation used to elongate the minority element or phase.

Due to PEAK’s substantial experience in spray forming Al-Si alloys, and whilst modifications were been made to the spray forming unit at Oxford to facilitate

co-injection capability, PEAK spray formed a large Al-12Si+Ti powder composite billet, with a target of 12wt%Ti powder to be co-injected. The precise details and conditions are proprietary to PEAK.

In previous studies of these type of materials, downstream processing only sought to severely deform the composites to provide the characteristic filamentary morphology, at the expense of restricted dimensions, and generally concerned the production of drawn wire only. In this work, with large-scale feedstock material, an extended range of downstream processes were available to test the feasibility for scale-up of the final composites. Thus accumulative roll-bonding and accumulative extrusion bonding were also investigated.

4.2 Co-spray forming

The first composite billet was processed without the author's attendance so the data pertaining to metal flow rates and powder flow rates was not recorded and remain proprietary to PEAK as they form the basis for their commercial products. Commercially pure Ti powder was injected into the atomised Al-Si droplet spray through a separate set of gas jets close to the point of atomisation. The Ti powder mixed with Al-Si alloy droplets primarily during atomisation of the Al-Si melt stream, due to the very high gas velocities in this region that forces the Ti into the molten Al-Si [71]. It was assumed that a particle-droplet co-spray was formed that then started to cool and co-deposited into a billet preform with Ti particles distributed in the Al-Si matrix, as shown in Figure 4.1. The Ti particles had an irregular shape typical of manufacture by the hydride-dehydride (HDH) process and there was no obvious clustering or banding as reported for co-spray formed Al alloy-SiCp composites [96].

The spray formed alloy chemical composition was analysed using induction coupled plasma-optical emission spectrometry (ICP-OES) at London and Scandinavian Metallurgical Co. Ltd. UK, and is shown in Table 4.1. The Si concentration was

	Al	Si	Fe	Cu	Mn	Zn	Mg	Li	V
Composition	86.86	12.87	0.15	0.06	0.01	0.02	0.02	<0.0005	0.01

Table 4.1: The chemical composition of spray formed Al-12Si (wt%).

Image	Ti count	Ti area fraction (%)	Pore count	Pore area fraction (%)
1	591	10	54	0.1
2	686	8.7	109	0.1
3	651	11.2	218	0.1
4	778	13	54	0.1
5	661	11.6	197	0.4
6	661	11.5	361	0.1
7	684	12.6	80	0.1
8	712	9.9	41	0.1
9	654	13.6	114	0.1
10	658	10.2	89	0.1
Average Ti area fraction		11.2 $\pm$ 1.5	Average porosity	0.13 $\pm$ 0.9

Table 4.2: The area fraction of co-injected Ti from ImageJ analysis over 10 different SEM images in Al-12Si+Ti.

close to target at 12.87wt%, compared with the eutectic composition of 12.6wt%Si, with impurity elements at reasonably low concentrations. The injected Ti fraction according to the same chemical analysis was 11.82wt%. The billet showed no large-scale macroscopic defects.

The area fraction of co-injected Ti powder was analysed using ImageJ software. Only a small portion of the spray formed billet was kept for analysis and the majority was extruded by PEAK. Ten backscattered electron images were taken at a magnification of x100 under the same conditions of brightness and contrast and the image analysis results are shown in Table 4.2. The average area fraction of co-injected Ti was (11.2 $\pm$ 1.5)%. Similarly a measurement of the porosity area fraction was taken from each image with the grey-scale threshold set to highlight only the pores. The microstructure contained just (0.13 $\pm$ 0.09)% area microporosity, with pore diameter varying from sub-micron up to a few-microns, caused by minor residual gas entrapment, and was typical of a good quality spray formed Al-based billet.

At higher magnifications shown in the secondary electron image in Figure 4.1

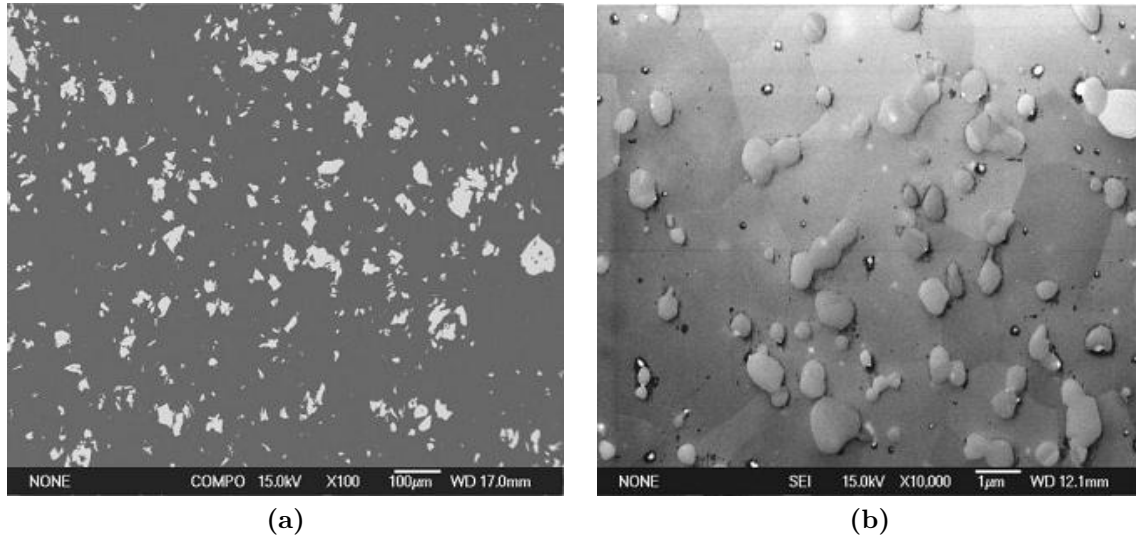
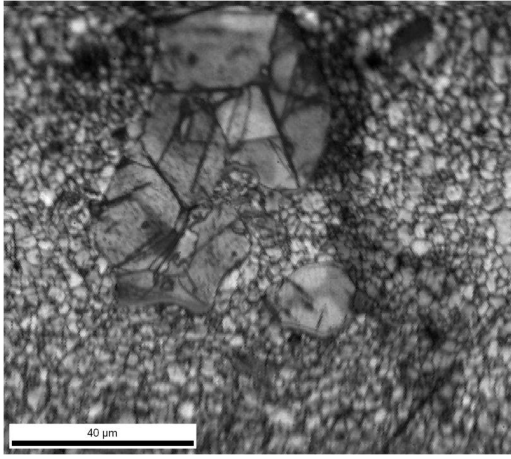
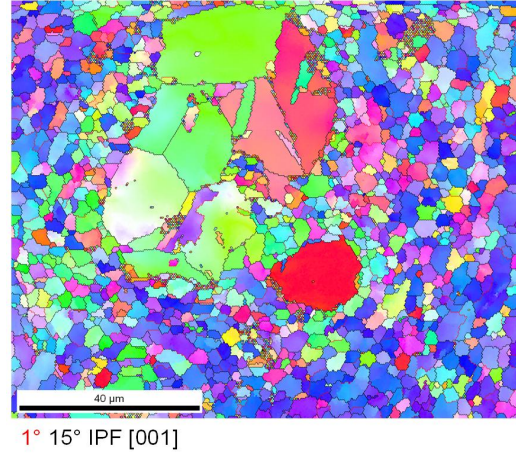


Figure 4.1: (a) Backscattered electron image of as-spray formed Al-12Si+Ti showing the morphology of Ti particles and their distribution in the α -Al and (b) Secondary electron image at higher magnifications of α -Al grains and divorced eutectic Si particles, primarily at α -Al grain boundaries.

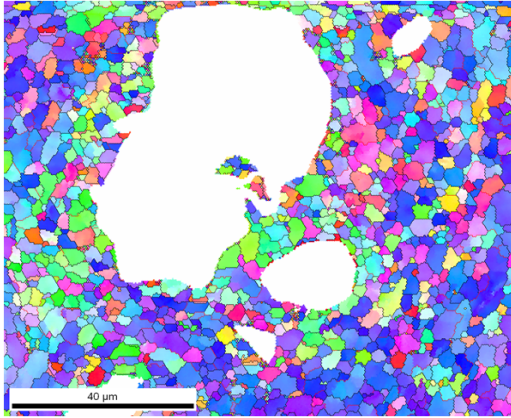
(b), the matrix consisted of $<1\mu\text{m}$ spherical Si particles that were formed from a fully divorced eutectic reaction at 577°C , as shown in the phase diagram in Figure 3.1 and as has been previously reported in sprayed eutectic [96] and hyper-eutectic Al-Si binary alloys [97]. The microstructure was fundamentally different from that of conventional cast Al-12Si regular/irregular eutectic lamellar structure [98]. The removal of over 50% latent heat in the spray phase prior to deposition [99] created a huge number of droplets containing solid α -Al dendrites that subsequently underwent copious fragmentation and remelting [5] at deposition. These fragmented Al dendrites provided an intrinsic α -Al grain refining effect, and a high number density of α -Al grains. At the eutectic temperature, thermal and growth conditions and the faceted/non faceted nature of the Si/ α -Al eutectic precluded coupled growth and the resulting eutectic structure was fully divorced, with fine-scale Si particles formed.



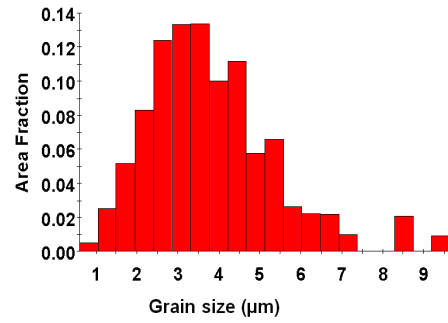
(a) EBSD image quality map of as-spray formed Al-12Si+Ti



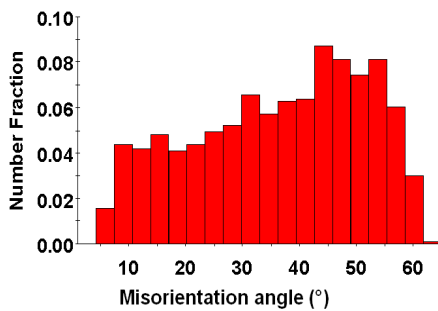
(b) A corresponding EBSD orientation map showing polycrystalline Ti particles and α -Al grains.



(c) EBSD orientation map of non Ti-rich grains only in Al-12Si+Ti, partitioned by EDS.

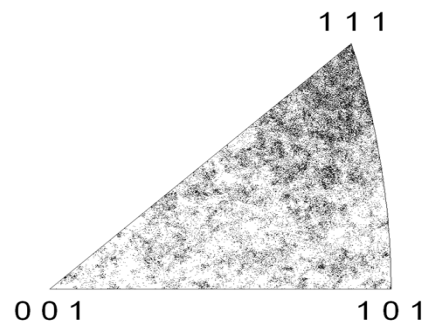


(d) Grain size distribution of the α -Al and Si grains in the as-spray formed Al-12Si+Ti.



(e) Misorientation distribution of the α -Al and Si grains in the as-spray formed Al-12Si+Ti.

[001]



(f) Inverse pole figure showing weak texture around $\langle 111 \rangle$ pole axis in the α -Al matrix grains, probably due to directional heat flow during cooling of the billet in as spray formed Al-12Si+Ti.

Figure 4.2: EBSD analysis of spray formed Al-12Si+Ti.

4.2.1 EBSD studies

The EBSD image quality map in Figure 4.2 (a) is an α -Al+Si region also containing two injected Ti particles. The corresponding EBSD orientation map in (b) shows that the α -Al grains and Si particles in the “matrix” were fine and equiaxed, and the Ti particles were polycrystalline. Low angle grain boundaries were defined as those between 1° and 15° (coloured red) and high angle grain boundaries were those above 15° (coloured black) [100]. Energy dispersive spectroscopy (EDS) data of the elemental concentration at each step was collected simultaneously in order to partition the data as shown in (c) to exclude the Ti-rich grains. The grain size area distribution for “matrix” grains is shown in (d) with an average matrix grain size of $3.4\mu\text{m}$. The α -Al grains ranged from $2\text{--}5\mu\text{m}$, and the Si particles ranged from $0.5\text{--}2\mu\text{m}$, therefore a distinct peak at $1\mu\text{m}$ representing Si particles separate from the α -Al was not evident. EDS was not used to partition the α -Al from the Si because it was difficult to accurately resolve the small Si particles at low magnifications. To maintain consistency, the Si was included for all following analysis on extruded Al-12Si matrix. An example of Si partitioned from the α -Al matrix at higher magnifications is shown in Figure 4.3.

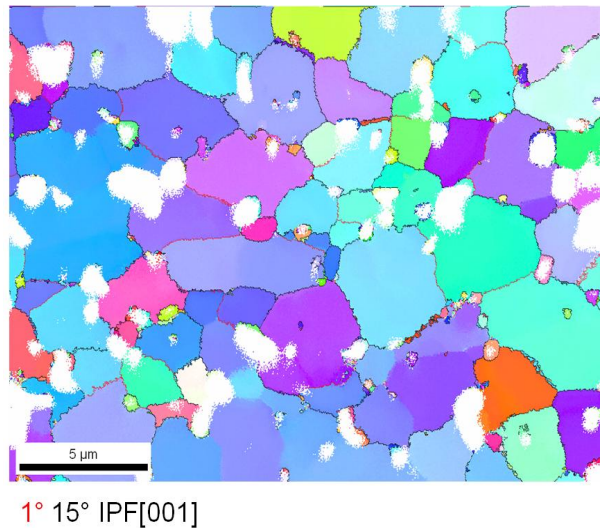


Figure 4.3: EBSD orientation map of Al-12Si matrix in spray formed Al-12Si+Ti in which EDS was used to partition the α -Al and the Si particles, showing $\sim 1\mu\text{m}$ Si particles (in white) and $\sim 4\mu\text{m}$ α -Al grains.

The majority of the matrix grains in Figure 4.2 had high angle grain boundaries as shown by the misorientation angle number distribution in (e). The inverse pole figure in (f) showed there was a preferred grain orientation in the α -Al toward $\langle 111 \rangle$ that may be due to the directional cooling of the billet during final solidification [97], with heat flow predominantly downwards into the cool collector. An XRD trace taken from the as-sprayed composite is shown in Figure 4.4. The ratio of peak intensities for the α -Al (111) and (200) reflections according to $I_{(111)}/I_{(200)}$ in Figure 4.4 were compared with that of non-textured Al from the database [101], and indicated a $\langle 111 \rangle$ texture in the α -Al, ~ 10 times stronger than random. There was no significant texture in the Ti. The precise direction in which the $\langle 111 \rangle$ texture is pointing cannot be defined because the sample position in the billet was not recorded. This is the same α -Al texture that A. Lambourne found in spray formed Al-70Si [102].

Overall, the as spray formed microstructure comprised an unusual hierarchy of length scales with Si particles of $\sim 1\mu\text{m}$ diameter as shown in Figure 4.3, a dilute α -Al matrix of grain size of $2\text{-}5\mu\text{m}$, and Ti particles with $D_{50} \sim 80\mu\text{m}$.

4.3 Downstream processing

Extrusion experiments were carried out initially at PEAK, Germany, where the spray formed billet was extruded through an eight-fold die into 30mm diameter bars at an extrusion ratio of 12:1 for each bar. The bars were extruded a second time at Oxford.

4.3.1 First extrusion

Figure 4.5 shows the microstructure of the $\Phi 30\text{mm}$ bar where only a small fraction of the Ti particles underwent significant deformation as highlighted by the yellow arrow. There was no discernible residual porosity.

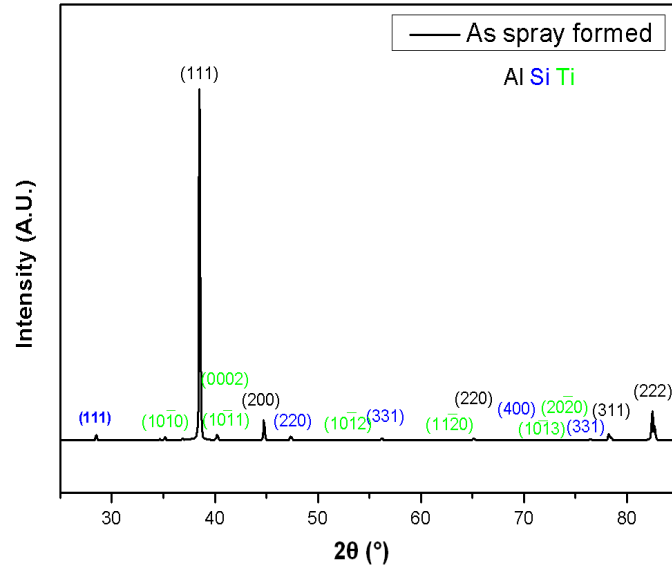


Figure 4.4: XRD trace of as-sprayed Al-12Si+12Ti showing $\langle 111 \rangle$ α -Al texture. The intensities of the Ti and Si peaks suggest that there are no preferred orientations in the Ti and Si phases.

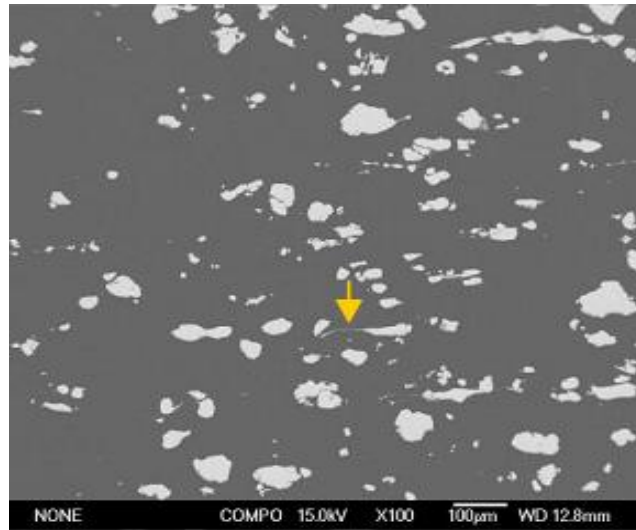
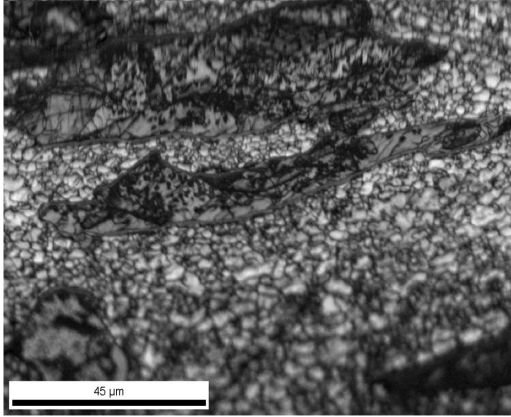
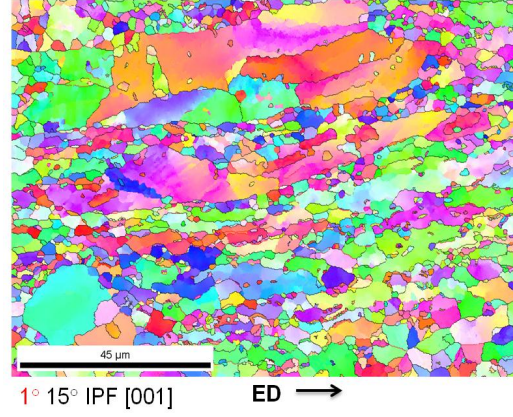


Figure 4.5: Backscattered electron image of extruded $\Phi 30$ mm bar showing slightly elongated Ti particles along the extrusion direction.

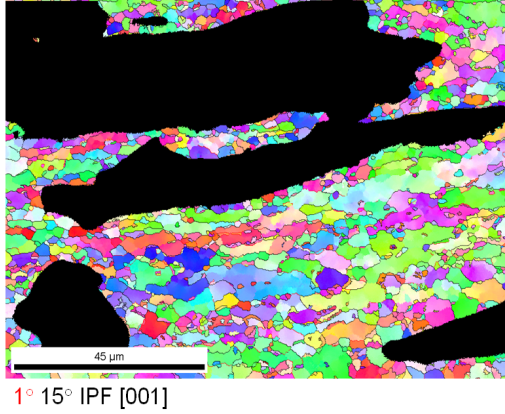
EBSD was carried out on a representative region of the 30mm bar that contained two elongated Ti particles and one undeformed Ti particle. It was difficult to produce a good quality scan of both the matrix and the Ti together, but this could be achieved on occasion by fine-tuning the exposure time and brightness conditions. In some cases there was a shadowing effect at the interface of the matrix and particles



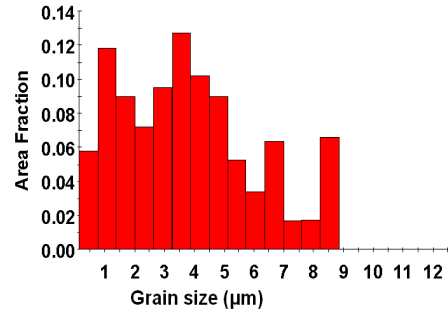
(a) EBSD image quality map of the longitudinal section of Al-12Si+Ti extruded $\Phi 30\text{mm}$ bar.



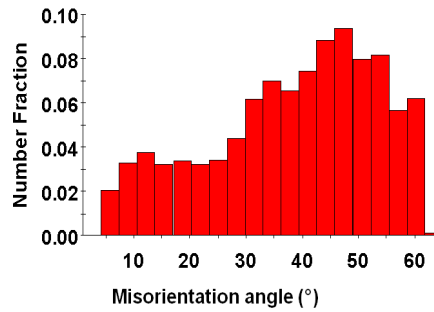
(b) A corresponding EBSD orientation map showing elongated Ti particles and $\alpha\text{-Al}$ and Si grains (ED= Extrusion direction).



(c) EBSD orientation map of non Ti-rich grains only, partitioned by EDS in extruded Al-12Si+Ti.



(d) Grain size distribution of $\alpha\text{-Al}$ and Si grains in Al-12Si+Ti $\Phi 30\text{mm}$ bar.



(e) The distribution of boundary misorientations in the Al-12Si matrix of extruded 30mm bar.

Figure 4.6: EBSD analysis of extruded Al-12Si+Ti $\Phi 30\text{mm}$ bar.

since the harder Ti did not polish as easily as the α -Al matrix. Figure 4.6 (a) is an EBSD image quality map of a typical region, showing the definition of each grain and indicating a reasonable quality scan. Again, black grain boundaries had a misorientation angle $\geq 15^\circ$ and red grain boundaries had a misorientation of $1-15^\circ$. The orientation map in (b) again shows predominantly equiaxed α -Al grains and spherical $\sim 1\mu\text{m}$ diameter Si particles were also resolved. EDS was used to partition the data to focus on the α -Al/Si matrix grains only as shown in (c). The average grain size, as shown in Figure 4.6 (d), was unchanged at $3.8\mu\text{m}$ relative to the as-sprayed grain size of $3.4\mu\text{m}$. The majority of the grain boundaries in the matrix were of high angle misorientation as indicated by the misorientation distribution in Figure 4.6 (e), although many of the large α -Al grains showed accumulated misorientation in their interior due to the work imparted by the extrusion. There was a small number of small equiaxed grains at grain boundaries and triple points that may be due to recrystallization. The elongated Ti particles usually showed strong internal contrast due to misorientation accumulation (plastic deformation and work-hardening) with some sub-grain structures developing indicative of recovery.



Figure 4.7: Al-12Si+Ti $\Phi 30\text{mm}$ bar that was further extruded to: $\Phi 7.5\text{mm}$ and $\Phi 2.5\text{mm}$ cylindrical bars and 6mm; 2.5mm; and 1mm thick rectangular strips at different deformation ratios.

Sample	Extrusion ratio	True strain	Temp (°C)	Speed (mm/min)	Force (kN)
Φ30mm bar	12	2.5	350	600	unknown
Φ7.5mm bar	200	5.3	420	102	400
Φ2.5mm bar	1808	7.5	465	600	450
6mm x 20mm strip	74	4.3	350	60	540
2.5mm x 20mm strip	162	5.1	350	44	680
1mm x 20mm strip	408	6.1	420	1.27	720

Table 4.3: Parameters used for the extrusion of Al-12Si+Ti metal-metal composites. Extrusion ratio relative to the undeformed billet, calculated as A_{in}/A_{out} .

4.3.2 Second extrusion

The level of deformation imposed in the 30mm bar, as shown by Figure 4.5, was insufficient to achieve the filamentary morphology characteristic of metal-metal composites, so larger mechanical deformations were investigated. The bars were sectioned into 50mm lengths and further extruded at Oxford University to cylindrical bars Φ7.5mm and Φ2.5mm diameter, and long rectangular strips 20mm wide of different thicknesses: 6mm; 2.5mm; and 1mm as shown in Figure 4.7 and providing a varying degree of deformation. The extrusion ratio was calculated relative to the undeformed extrusion billet at PEAK as A_{in}/A_{out} . All the extruded bars had reasonably good surface finish as shown in Figure 4.7. Table 4.3 lists the parameters used for each of the extrusions and the associated true strain.

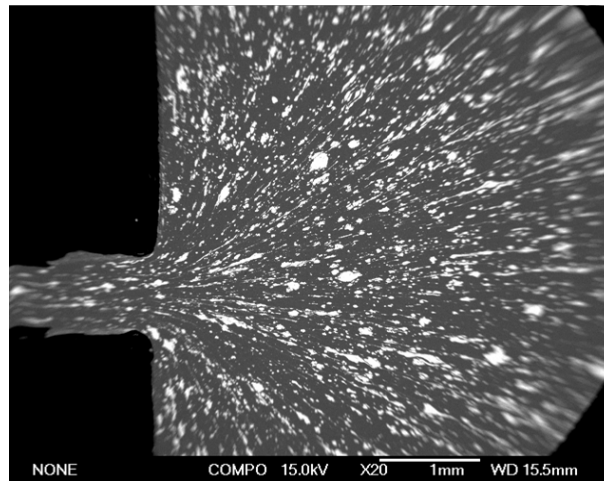


Figure 4.8: Backscattered electron image showing the extrusion of Φ30mm bar through a rectangular 1mm thick die.

SEM examination confirmed that there was a trend that with increased deforma-

tion, Ti elongation increased and finer fibres/ribbons were produced. Only detailed results from the 1mm strip are presented here.

4.4 Extruded Al-12Si+Ti 1mm strip

Metal-metal composites are sometimes referred to as *in-situ* composites due to the filamentary morphology developing within the specimen as its being deformed. Evidence of this *in-situ* deformation is shown in Figure 4.8 that shows the deformation imposed on the Ti during extrusion through a 1mm rectangular slot die.

The majority of Ti particles were deformed into fibres/ribbons of thickness 0.5-2 μ m in the longitudinal direction as shown in Figure 4.9 (a). The fibres/ribbons were of length up to 400 μ m and there was little fibre breakage. Figure 4.9 (b) shows Ti elongation and fibre formation transverse (out of the page) to the extrusion direction. Extrusion to thin strips rather than bar facilitated Ti elongation in the transverse direction also, and a rolling type deformation was induced. The convoluted morphology that is usually reported in the transverse direction of cylindrical extruded bars was not evidenced in rectangular strips since they were not axisymmetrically deformed [26]. The extended α -Al/Ti interfacial area suggests that possible strengthening could also be obtained in the transverse direction, although the fibres/ribbons are shorter at 10-50 μ m than in the longitudinal direction. The tensile strength in the transverse direction could not be tested due to the restricted width of samples (1mm x 20mm). Larger Ti particles that appeared less deformed could be very flat and thin in the transverse direction as is the case for the fibre/ribbon shown in Figure 4.9 (c) which has inadvertently been polished through.

4.4.1 Ti phase extraction

The Ti fibres/ribbons were investigated after dissolution of the α -Al matrix as outlined in Chapter 3. The Ti and Si particles remained intact on the filter paper and

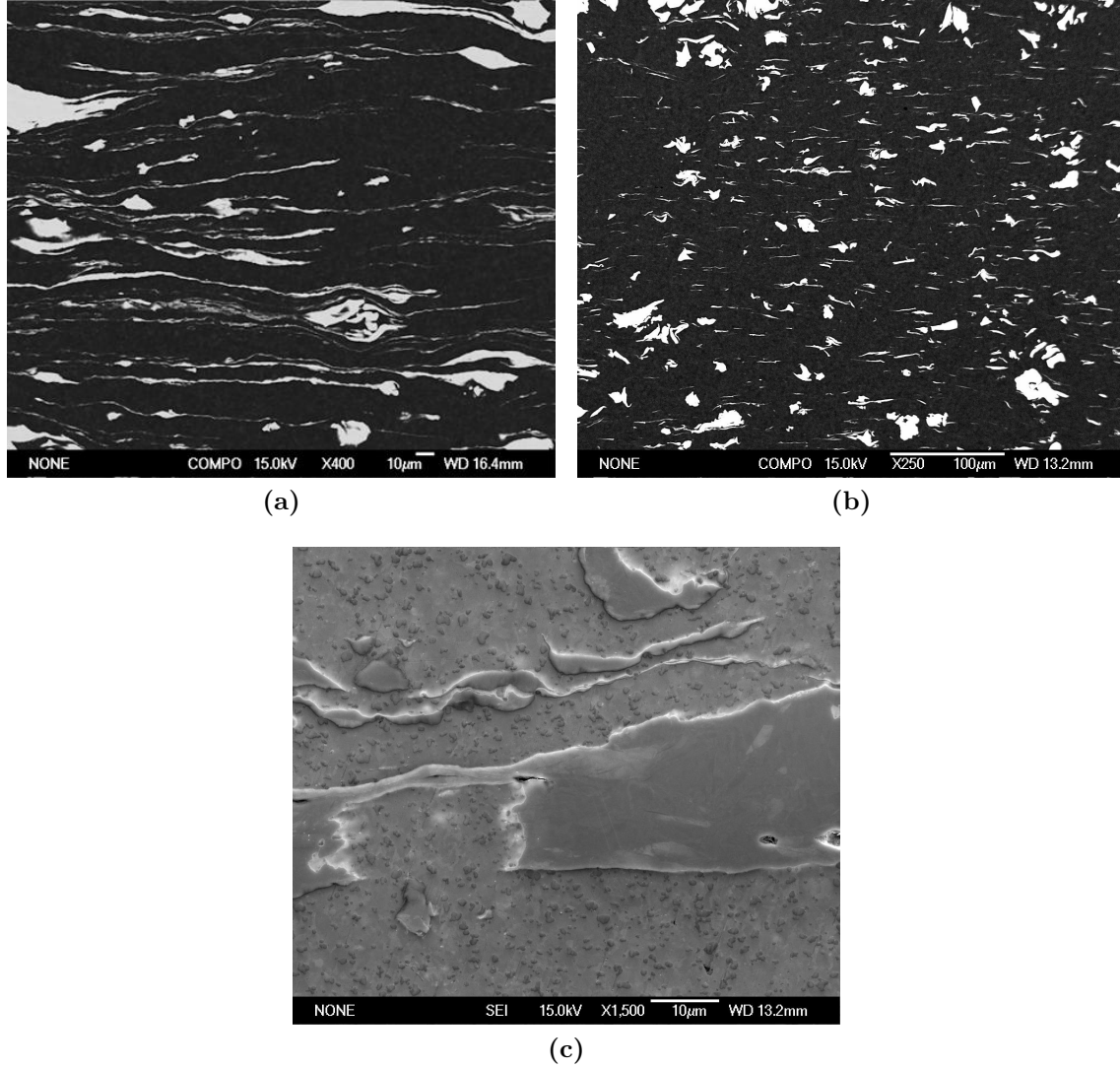


Figure 4.9: (a) Backscattered electron image of the longitudinal direction in Al-12Si+Ti showing the elongated Ti phase after extrusion through a 1mm thick die at a strain of 6.1; and (b) relatively elongated Ti in the transverse direction of Al-12Si+Ti extruded 1mm strip; and (c) secondary electron image of extruded 1mm Al-12Si+Ti showing an example of a larger Ti particle deformed into a thin ribbon lying close to the sample surface.

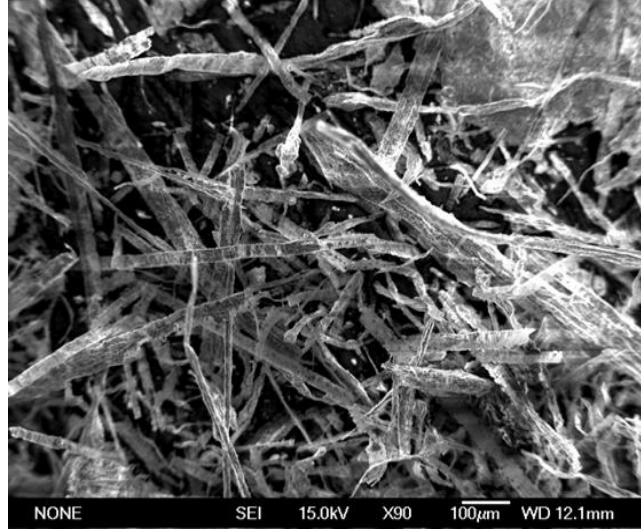
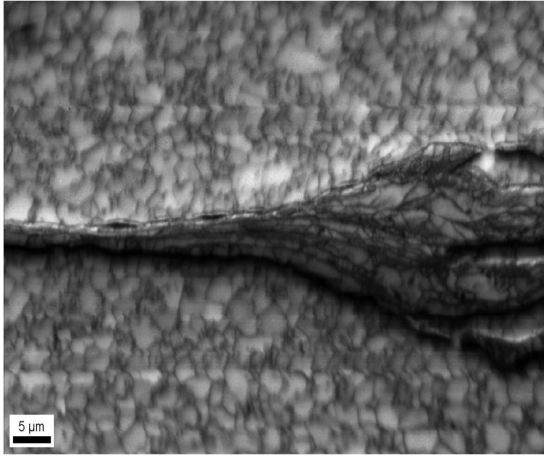


Figure 4.10: SEM image of extraction of the Ti ribbons/fibres by dissolution of the α -Al.

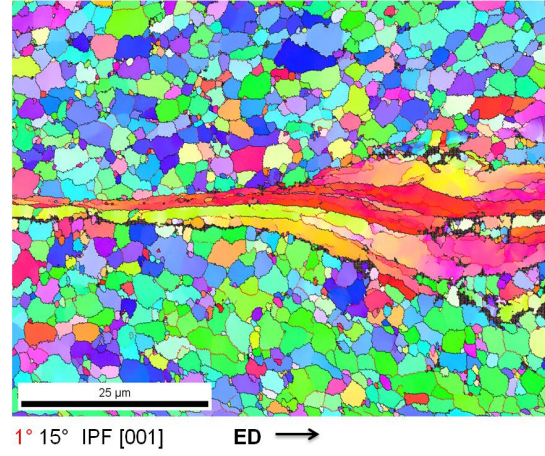
were studied in the SEM, as shown in Figure 4.10. The fibres were 100's of microns in length, supporting the impression that fibre breaking was not widespread, and showing a more ribbon-like rather than fibre-like morphology.

4.4.2 EBSD studies

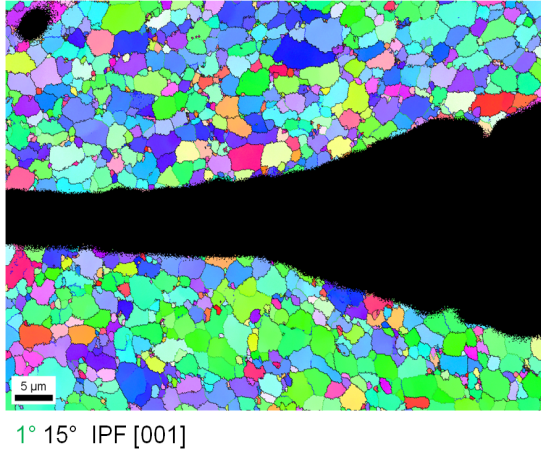
EBSD was performed in the longitudinal direction of the 1mm strip over a region containing a single elongated Ti particle as shown in the image quality map of Figure 4.11 (a). Equiaxed and recrystallised α -Al matrix grains and a single elongated polycrystalline Ti particle with accumulated misorientation are shown in the orientation map in (b). Low angle grain boundaries were again defined as those between 1° and 15° (coloured red) and high angle grain boundaries were those above 15° (coloured black). Smaller, low dislocation density recrystallised grains were not observed within the Ti filaments suggesting that dynamic recrystallisation in Ti did not take place, although recovery may be operating in the most severely deformed fibres/ribbons. Spitzig *et al.* [24] reported similar qualitative observations for the less deformable Nb in Cu-20vol%Nb composites. EDS was used to partition the data to identify the Al-Si matrix grains only as shown in Figure 4.11 (c), and the corresponding grain size distribution is shown in (d). Despite the large deformation and due



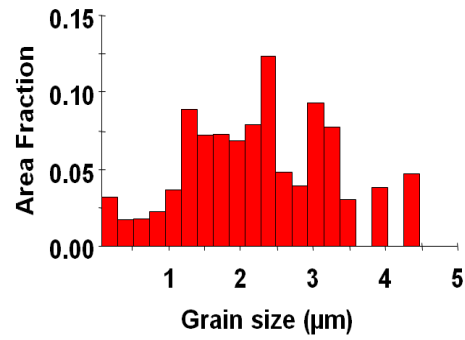
(a) EBSD image quality map of the longitudinal cross-section of Al-12Si+Ti extruded 1mm strip.



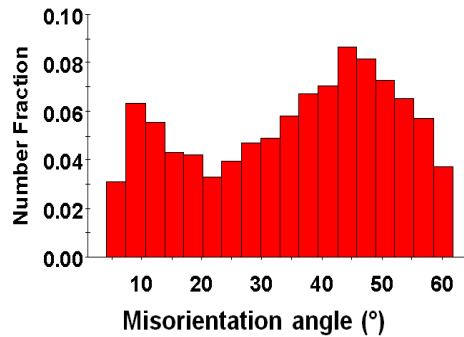
(b) Corresponding orientation map suggesting recrystallised α -Al grains and work-hardened, elongated polycrystalline Ti.



(c) EBSD orientation map where EDS was employed to partition the EBSD data so that α -Al-Si-rich regions only are displayed.



(d) The distribution of α -Al and Si grains in extruded Al-12Si+Ti 1mm strip.



(e) Misorientation distribution of α -Al and Si grains in the extruded Al-12Si+Ti 1mm strip.

Figure 4.11: EBSD analysis of extruded Al-12Si+Ti 1mm strip.

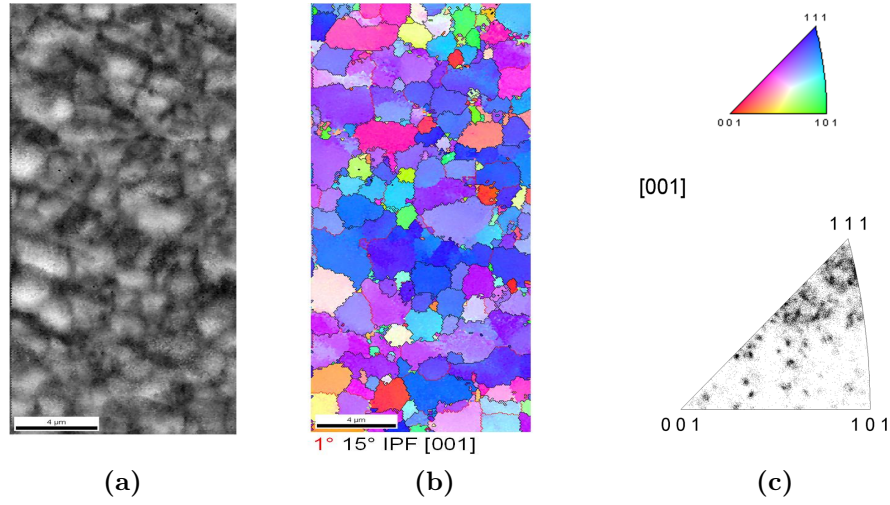
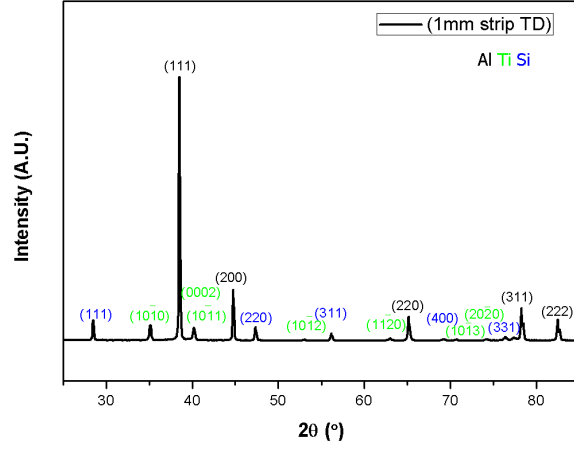


Figure 4.12: Image quality map (a) and orientation map (b) of the Al-12Si matrix in the transverse direction (extrusion out of the page) of the Al-12Si+Ti 1mm strip. The inverse pole figure in (c) shows some preferred orientation in the $\langle 111 \rangle$ direction. The orientation key is shown above.

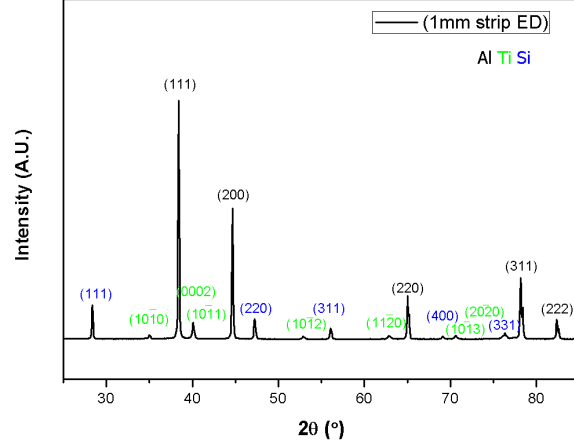
to recovery and recrystallisation processes, the average grain size of the α -Al and Si grains in the 1mm strip matrix was again largely unchanged at $2.4 \pm 0.7 \mu\text{m}$ relative to the as-sprayed average grain size of $3.4 \pm 0.9 \mu\text{m}$. EBSD was also carried out in the transverse direction of the Al-12Si matrix in the 1mm strip. Figure 4.12 shows (a) the image quality map and (b) the orientation map of a Al-12Si+Ti extruded 1mm strip ($\eta=6$) showing some preferred orientation in the $\langle 111 \rangle$ direction as shown by the majority of grains coloured blue that represented $\langle 111 \rangle$ orientation as shown by the orientation key in (c). Further evidence of $\langle 111 \rangle$ texture was shown by the inverse pole figure in (c). Extruded pure Al develops $\langle 111 \rangle$ and $\langle 100 \rangle$ double fibre texture which is typical for FCC metals [103], although according to Bevk, for Al the only preferred orientation is $\langle 111 \rangle$ [3].

4.4.3 XRD studies

Figure 4.13 shows evidence of $\langle 111 \rangle$ texture in α -Al in the XRD trace (a) taken from the transverse section (TD) (face perpendicular to the extrusion direction) of the 1mm strip. The ratio of intensities of (111) and (200) reflections were again compared with a non-textured Al sample from the database [101], and indicated



(a)



(b)

Figure 4.13: XRD trace in (a) the transverse direction (TD) of extruded Al-12Si+12Ti 1mm strip (face perpendicular to the extrusion direction) showing $\langle 111 \rangle$ texture in α -Al and (b) the extrusion direction (ED) of the same sample showing Al peaks that match those of a random orientation found in the database.

a $\langle 111 \rangle$ texture in the α -Al, ~ 5 times random. In the longitudinal direction as shown in Figure 4.13 (b), the peaks were shown to match those of a non-textured Al sample. Therefore a degree of $\langle 111 \rangle$ texture exists in the α -Al as shown in the transverse direction of the extruded strip. The XRD trace also shows evidence of Ti fibre texture with relatively strong $\langle 10\bar{1}0 \rangle$ fibre texture as previously reported for Ti in a wire drawn Al-Ti composite [30].

4.5 Microstructural insensitivity to strain

The EBSD orientation maps of extruded 1mm strip in Figure 4.11 (c) shows equiaxed grains with only weak texture. The grains showed little internal sub-structure identified by colour changes within a grain related to local misorientation. Three phenomena might explain the insensitivity of the microstructure to strain and all are related to the presence of the Si particles: particle stimulated nucleation; Zener pinning; or geometric dynamic recrystallisation. The approximately spherical $1\mu\text{m}$ spherical Si particles may act as nucleation sites for the recrystallisation of the α -Al in a phenomenon termed particle stimulated nucleation (PSN). PSN has been reported for Al-0.8wt%Si containing $3\mu\text{m}$ Si particles [104], in spray formed and extruded SiC reinforced 8090 composites [105], and in spray formed and extruded Al-Si-Li alloys [51]. Non deformable particles within the softer matrix subject to deformation give rise to local strain incompatibility that is accommodated by the generation of dislocations at the matrix-particle interface. These have been termed geometrically necessary dislocations. These particle induced high dislocation densities provide sufficient driving force for the nucleation of new grains that then grow and consume extended regions of worked material. Because the α -Al is dilute and free from elements associated with solute drag e.g. Mg, the deformed grains readily recrystallize so that the retention of elongated textured and heavily worked grains is very restricted.

Alternatively, grain boundary pinning by closely spaced small ($<1\mu\text{m}$) non-deformable Si particles may account for the apparent insensitivity of the microstructure since this Zener pinning effect can have a strong influence on recrystallisation kinetics and grain size is maintained during recrystallisation. Santos *et al.* [106] suggested that fine Si particles in spray formed and extruded hypereutectic Al-Si prevented crystal lattice rotation and blocked grain boundary movement during deformation [106]. The tendency for either PSN or Zener pinning depends upon the particle volume fraction and size. According to [12], the Si particle size of $\sim 1\mu\text{m}$ and volume fraction of 10-20% lies at the borderline of these conditions.

The tendency for Zener pinning or PSN can be summarised schematically in Figure 4.14 [12], where the solid lines indicate PSN behaviour and the dashed lines mark the conditions for Zener pinning, according to the size and volume fraction of particles. The tendency for PSN or Zener pinning has been assessed using the graph in Figure 4.14 by previous researchers such as [51]. Al-12wt%Si corresponded to a volume fraction of $\sim 10\%$ Si estimated by the lever rule and for $1\mu\text{m}$ particles, a grain size of $\sim 2.5\mu\text{m}$ is suggested by Figure 4.14 - typical of those measured here. The red line on the graph representing these values suggests PSN is operating.

The effect of the size of the particles on the efficiency of PSN during dynamic recrystallisation has been suggested to follow the form:

$$D \approx dF_v^{-1/3} \quad (4.1)$$

where D is the resultant grain size (from PSN), d is the diameter of the particles and F_v is the volume fraction of the particle. When the efficiency of PSN equals unity, each particle nucleates one grain [12].

A predicted grain size of $\sim 2.5\mu\text{m}$ is indicated in Figure 4.14, although an actual Al grain size of $\sim 4\mu\text{m}$ was obtained by EBSD, suggesting that the efficiency for PSN is less than 1 at ~ 0.6 in this case. However an efficiency of 0.6 is still relatively high considering the conditions for PSN were close to the minimum and therefore

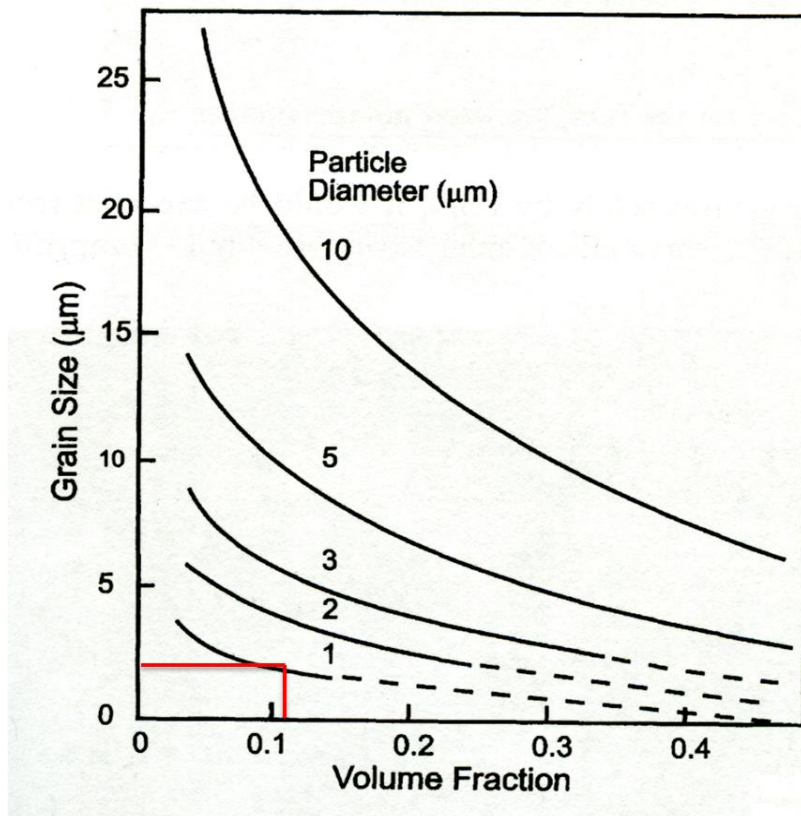


Figure 4.14: The resulting grain size due to PSN is predicted according to the size of the particles (Si) and their volume fraction (assuming a PSN efficiency of 1). The dashed lines show conditions favouring Zener pinning over PSN (indicated by a solid line) [12].

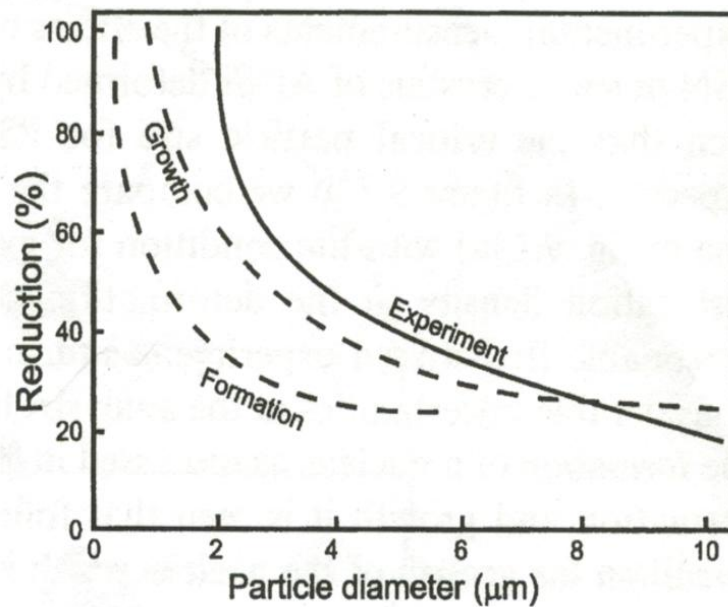


Figure 4.15: The effect of particle size and strain (reduction) on the tendency for PSN [12].

the nucleation efficiency may be low.

For a recrystallized nucleus to form, the maximum misorientation within the deformation zone must be sufficient to form a high angle boundary (10° - 15°) with the matrix [12]. The growth of the nucleus/sub-grain is subjected to a retarding pressure due to its radius of curvature and a driving pressure from the dislocation density (stored energy). The nucleus will grow if the driving pressure is greater than the retarding pressure. The conditions for PSN to occur can be defined by a critical particle diameter which is a function of dislocation density (strain). The critical particle diameter defines whether the nucleus will grow beyond the deformation zone. Figure 4.15 shows the conditions for nucleation that depend on both the particle size and strain (reduction). As the strain increased, the critical particle diameter for PSN to occur is reduced. The theoretical conditions for the formation and growth of the nuclei stimulated by particles is shown in the dashed line. For growth to occur larger particle sizes and higher strains are required, and the conditions for growth of nucleus is the determining factor for PSN. The solid line in Figure 4.15 shows the conditions for the occurrence of PSN in single crystals of Al-Si deformed by cold rolling [107]. Formation of new grains at particles only occurs above the solid line. The work in this thesis suggests some evidence for PSN at smaller particles sizes of $\sim 1\mu\text{m}$ than found by experiment in Figure 4.15, but are consistent with theoretical predictions.

Whilst the evidence for PSN has been strong thus far, the persistence of texture in the α -Al was somewhat unexpected. For deformed polycrystals there is a large range of orientations present in the deformation zones and therefore the range of orientations for potential recrystallization nuclei is greater. This should result in an almost random distribution of recrystallisation orientations. Therefore a third alternative explanation for the microstructure was investigated.

The two criteria for PSN are affected by the deformation temperature: the formation of nuclei within deformation zones is affected because at high temperatures

the dislocations may be able to bypass particles without forming deformation zones; and the growth of nuclei beyond the particle is affected because the stored energy is reduced at elevated temperatures. Thus the likelihood for PSN occurrence after hot deformation may be reduced.

During hot deformation, dynamic recovery and dynamic recrystallisation occurs as distinct from static annealing processes during post-deformation. Thermally activated deformation and recovery processes result in microstructural change that is dependent on the deformation temperature and strain rate, and is often described by the Zener-Holloman parameter (Z):

$$Z = \dot{\epsilon}_m \exp\left(\frac{Q}{RT}\right) \quad (4.2)$$

where Q is the activation energy for deformation and is taken to be the activation energy for self diffusion, which for Al is 142kJmol^{-1} ; R is the gas constant, T is the absolute temperature, and

$$\dot{\epsilon}_m = \left(\frac{6VD_{in}^2 \ln R_e}{D_{in}^3 - D_{out}^3}\right) \quad (4.3)$$

where V is the ram velocity, D_{in} is the billet diameter, D_{out} is the extruded diameter and R_e is the extrusion ratio.

Figure 4.16 shows the variation of the critical particle diameters for the formation and growth of particle deformation zones as a function of the Zener-Holloman parameter (Z). “Nucleus formation-limited” implies that the controlling factor for PSN is the formation of a nucleus within in the deformation zone. “Nucleus growth-limited” means that the controlling factor for PSN is growth of the recrystallised nucleus beyond the deformation zone. At low values of Z (10^{12}s^{-1}), the conditions for PSN are governed by those for the deformation zone formation, but at higher Z values the conditions for PSN are determined by the conditions for growth of the recrystallised nucleus. Experimental investigations have confirmed this model [108, 109]. Follow-

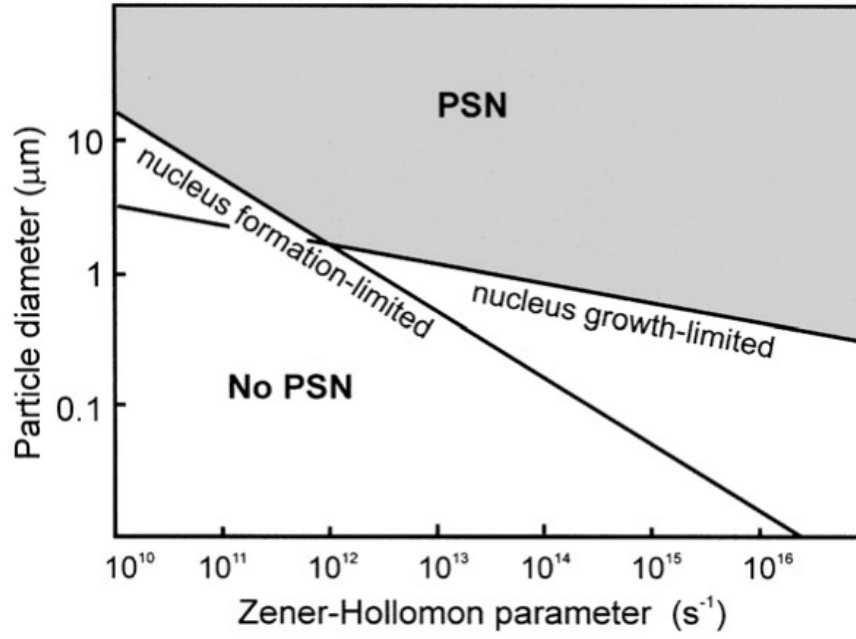


Figure 4.16: The deformation conditions for particle stimulated nucleation [12]

ing Figure 4.16, the Zener-Holloman parameter was estimated to assess whether PSN could be operating, and values for the extruded Al-12Si+Ti bars are shown in Table 4.4.

D_{in} (mm)	Size out (mm)	D_{out} equivalent (mm)	R_e	V (mm s ⁻¹)	$\dot{\epsilon}_m$ (s ⁻¹)	Temp (K)	Z (s ⁻¹)
103.9	30	30	12	10	1.47	623	1.18×10^{12}
30	7.5	7.5	16	1.7	0.96	693	4.84×10^{10}
30	2.5	2.5	144	10	9.95	738	1.12×10^{11}
30	6x20	12.4	5.9	1	0.38	623	3.07×10^{11}
30	2.5x20	8.0	14.1	0.73	0.40	623	3.19×10^{11}
30	1x20	5.0	35.3	0.02	0.02	693	7.66×10^8

Table 4.4: The Zener-Holloman parameter for each of the extruded Al-12Si+Ti bars.

Taking the Si particle diameter at $\sim 1\mu\text{m}$ and the Zener-Holloman parameter as $7.66 \times 10^8 \text{ s}^{-1}$ for the 1mm strip, according to Figure 4.16, the experimental conditions lie just outside the region of PSN.

Thus, an alternative mechanism that may be occurring during deformation is geometric dynamic recrystallization (GDR). During dynamic recovery grain boundaries develop serrations, and the wavelength of these serrations is equivalent to the

subgrain size. Upon rolling or extrusion the original grains become flattened as shown schematically in Figure 4.17. During high temperature deformation the subgrain size is generally found to be independent of strain [12]. Consequently, the fraction of high angle boundaries increases with strain and eventually the size of the serrated grain boundaries became comparable to the grain thickness as shown in Figure 4.17 (b). Interpenetration of the scalloped boundaries will occur, resulting in a microstructure of small equiaxed grains with a grain size comparable to the subgrain size (Figure 4.17 (b)). Without the operation of any new microscopic recrystallisation mechanism, an equiaxed microstructure evolves with a high fraction of high angle grain boundaries. This microstructure is commonly formed in Al and its alloys deformed to large strains [110].

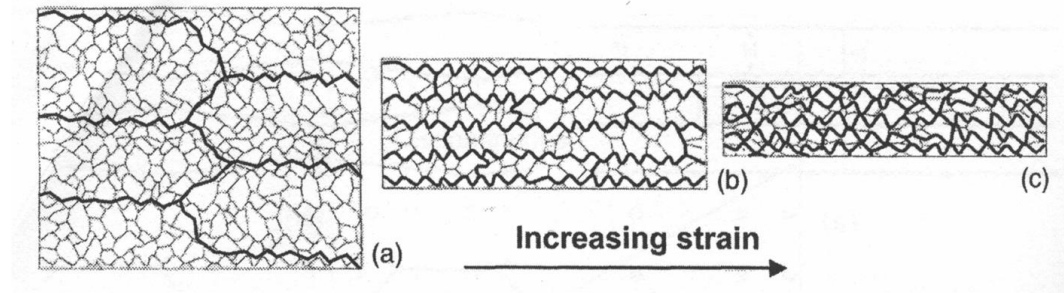


Figure 4.17: An illustration of geometric dynamic recrystallisation. As the strain increases the serrated high angle grain boundaries (thick lines) become closer, although the sub-grain size remains approximately constant. Eventually the high angle grain boundaries impinge resulting in a microstructure of mainly high angle grain boundaries [12].

A feature of geometric dynamic recrystallisation is that the subgrain size is generally found to be independent of strain and that there is little high angle grain boundary migration, and therefore the texture remains largely unchanged [111]. Evidence for microstructural insensitivity to strain and retained texture are present in this work suggesting that GDR may be operating instead of PSN. Further studies on powder processed composites are carried out in section 4.7.1 by comparing the α -Al matrix microstructure in the presence and absence of Si particles, to provide stronger support for either PSN or GDR.

4.6 Mechanical properties

The yield stress (defined as 0.2% proof stress), ultimate tensile strength and elongation to failure of extruded 30mm bar, 6mm strip and 2.5mm strip are shown in Figure 4.18. Although the most deformed specimen was the 1mm strip, it was extruded at a higher temperature of 420 °C compared with 350 °C for the others and therefore was excluded from the analysis. As the extrusion ratio increased from 12:1 to 74:1 to 162:1, the yield stress and ultimate tensile strength increased. The yield stress of the 2.5mm strip increased by 35% relative to the 30mm bar and the tensile strength was increased by 9%. Elongation to failure remained comparatively high at $\sim 17\%$, even after a true strain of 5 (extrusion ratio of 400:1). The total strain and fraction of Ti in this study were both lower than attained in the small batches of powder processed Al-20vol%Ti with strains >10 and which showed more dramatic strengthening [30]. Nonetheless, these mechanical results, and particularly the microstructural studies, (discussed more later) provided encouragement for a spray forming based approach to scale-up of metal-metal composite manufacture.

Figure 4.19 is a typical stress-strain curve from Al-12Si+Ti extruded 2.5mm strip, showing smooth continuous curves with no indication of “fibre pull-out” or toughening, or any discontinuous processes. The stress-stress curves from the other extruded strips showed similar continuous shapes.

To assess the effect of the minority Ti phase on the mechanical properties shown above, a Al-10wt%Si billet with co-injected spherical alloyed Ti powder was spray formed at Oxford, in which there was an initial volume of sprayed billet free of any Ti to retrieve sufficient unreinforced monolithic Al-10Si for extrusion. Al-10Si was extruded at 350 °C at an extrusion ratio of $\sim 15:1$ to a 7.5mm diameter bar to obtain as close a comparison with the Al-12Si+Ti 30mm bar as possible. As shown in Figure 4.18, the resulting yield strengths were quite similar, with the UTS of the Al-12Si+Ti only $\sim 10\text{MPa}$ higher than that of Al-10Si.

At low levels of deformation strain the composites strength can be approximated

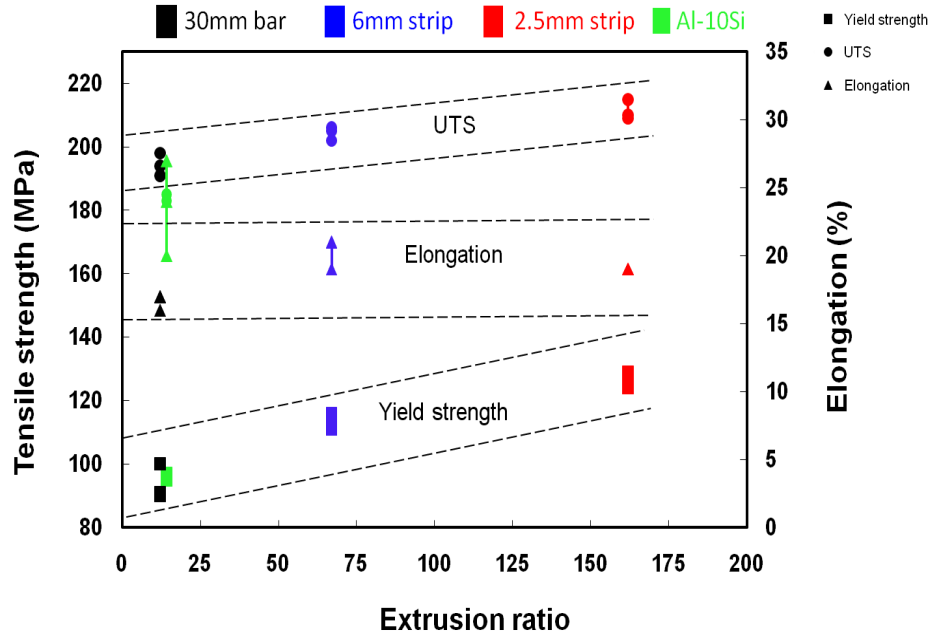


Figure 4.18: Mechanical properties of extruded 30mm bar, 6mm strip and 2.5mm strip. The 30mm diameter bar was compared to spray formed Al-10Si at similar extrusion ratio (shown in green).

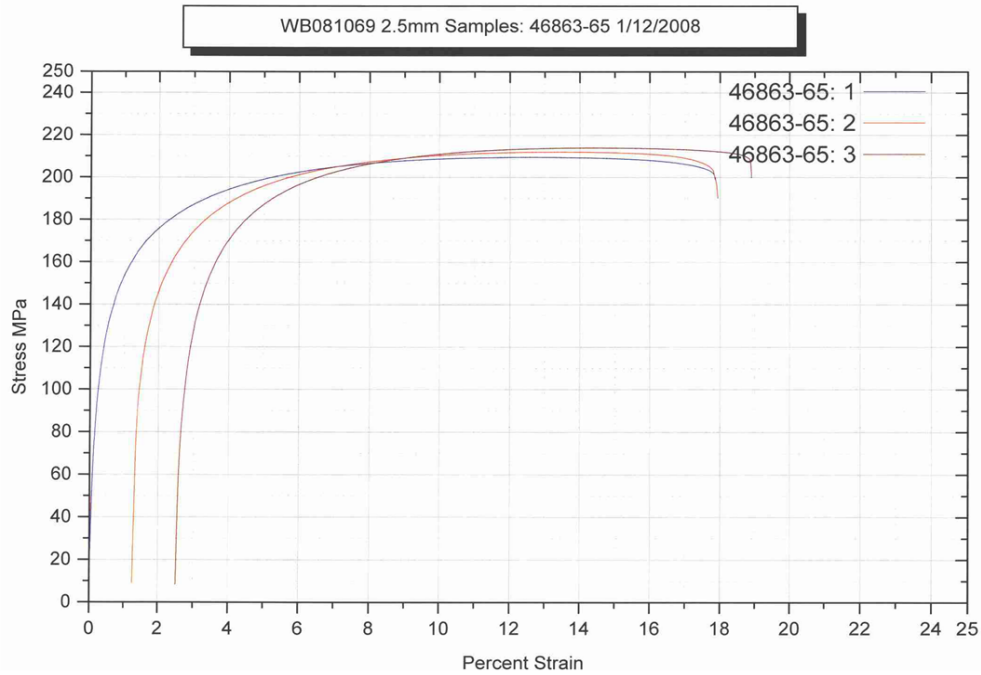


Figure 4.19: An example of the raw stress-strain curves from Al-12Si+Ti extruded 2.5mm strip.

by a rule of mixtures [3] as shown in equation (2.1). In order to apply Equation (2.1), it is necessary to know each constitute mechanical properties, ideally as a function of total strain (work hardening). Hyun *et al.* [112] studied the mechanical behaviour

of commercially pure Ti at intermittent stages during deformation processing by ECAP. The UTS of Ti after a strain of 2.25 (equivalent to 3 ECAP passes and similar to that of the extruded 30mm bar) was 558MPa. Using $\sigma_f = 558\text{MPa}$, $\sigma_m = 184\text{MPa}$ for monolithic Al-10Si, and $V_f = 7.4\%$ gives $\sigma_c = 200\text{MPa}$ which is in reasonable agreement with experiment at 194MPa. Therefore at this comparatively low deformation strain, overall strength was based on rule of mixtures behaviour and other strengthening processes associated with interfacial strengthening have not yet come into play. For example, for Al-20vol%Nb, the UTS started to deviate from rule of mixtures only above a strain of 8 [37]. Therefore, the increase in yield strength as deformation strain increases is due to work hardening, mostly in the Ti.

The elongation to failure of unreinforced Al-10Si was higher than Al-12Si+Ti at $\sim 23\%$, and suggested composite ductility was reduced by adding the Ti, and might indicate (1) brittle behaviour is being induced by reactions between α -Al and Ti. In addition, the increase in ductility of Al-10Si may be to some extent due to the slight reduction in the volume fraction of Si particles.

4.6.1 TEM studies

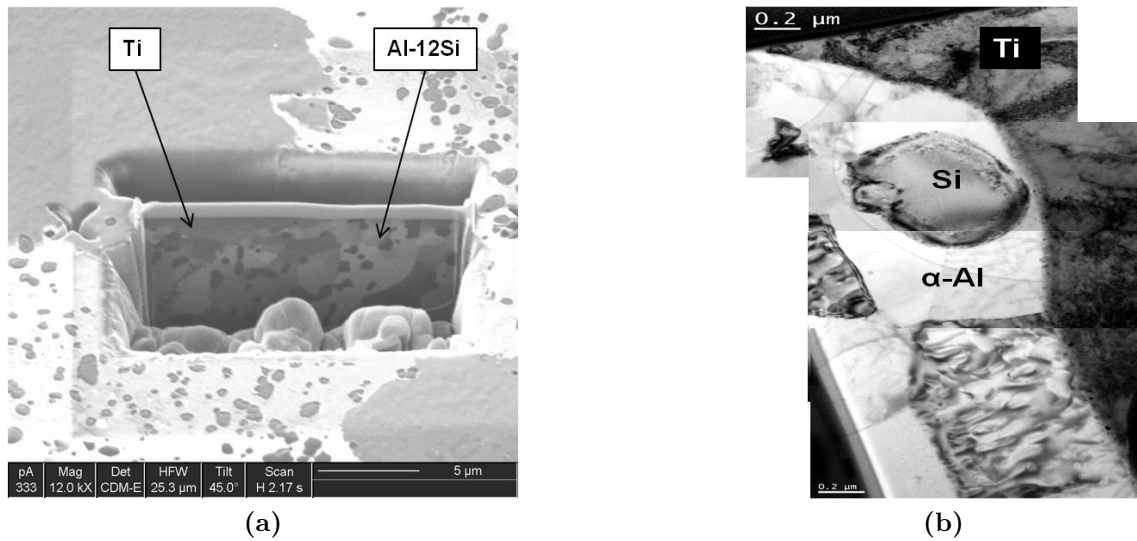


Figure 4.20: (a) Focused ion beam micrograph showing the area selected for TEM investigations that included the interfacial region between the α -Al and Ti minority phase in as-spray formed Al-12Si+Ti and (b) TEM image of the as-sprayed α -Al/Ti interface and Si particle in Al-12Si+Ti.

To investigate whether a reaction had occurred at the interface between Ti and α -Al, and to study the microstructure of both phases in more detail, TEM was employed. Specimens from the as-sprayed material and the 1mm strip were produced using focused ion beam microscopy (FIB). The as-sprayed FIB specimen, shown in Figure 4.20, encompassed an interface of the Ti and the Al-12Si matrix. A TEM micrograph is shown in Figure 4.20 (b) with energy dispersive X-ray analysis (EDX) used to identify the phases marked. There was no discernible Ti reaction at the interface and the Ti fibre showed high dislocation density and entanglement. Some of the α -Al grains were relatively free of dislocations. A similar approach for the 1mm strip FIB specimen is shown in Figures 4.21 (a) and (b), again showing a relatively low dislocation density in the α -Al, even after an extrusion ratio of $\sim 400:1$; and the Ti fibres/ribbons again accumulated a comparatively high dislocation density. Similar findings were outlined by Spitzig *et al.* [24,36] who studied Cu-X immiscible alloys (X=Nb, Ta, Cr) and reported a relatively modest dislocation density in the fcc matrix, and suggested that the Cu underwent dynamic recovery and recrystallization during deformation resulting in large equiaxed Cu grains for the highest strain studied ($\eta=13$).

Significant interfacial reaction is prevented by the comparatively quick solidification times during spray forming of 10^2 - 10^3 Ks $^{-1}$ [52]. The cooling rate increases with co-injection of cold particles which will decrease the average spray enthalpy as the initially cold particles are brought into equilibrium with the hot metallic alloy matrix [113]. The low melting point of the near eutectic Al-12Si compared with Ti also contributes to no discernible Al-Ti interfacial reaction. There was also no discernible interfacial oxide at any of the magnifications used in the TEM. The insert in Figure 4.21 (b) also shows a $\sim 0.5\mu\text{m}$ Si particle impinging on a Ti fibre after extrusion to a 1mm strip. This close interaction between Si and Ti was not seen in TEM investigations of as-spray formed Al-12Si+Ti.

Figure 4.22 (a) shows Si particles a few microns apart producing indentations

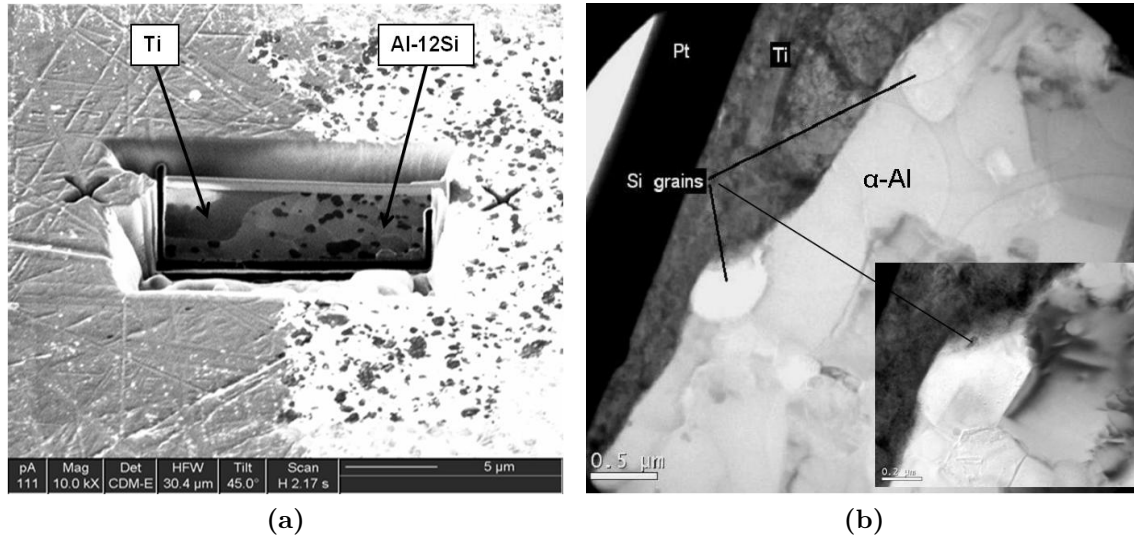


Figure 4.21: (a) Focused ion beam micrograph of Al-12Si+Ti extruded 1mm strip showing the boundary region between the Al-12Si matrix and Ti minority phase that was milled to produce a TEM specimen. TEM image of the selected region is shown in (b) and reveals the α -Al/Ti interface with embedded Si particles.

and kinks along a deforming Ti fibre in Al-12Si+Ti. Figure 4.22 (b) shows a Ti fibre, obtained by extraction, decorated with Si particles. During the filtering and drying of the extracted Ti and Si, it was possible that Si particles adhered preferentially to the Ti fibre but the close interaction of some Si particles with heavily deformed fibres/ribbons in cross-section and on this extracted fibre tended to suggest that hard Si particles interacted with the Ti, and may have even assisted in deforming the Ti phase by rotating during deformation, and acting as “micro-rollers” helping to impart the applied stress to the Ti.

4.7 Powder processed metal-metal composites

Following on from the idea that the Si may play some positive role in the deformation, it would be logical to produce a similar co-sprayed billet without Si particles to assess their role in deformation processing, for instance using unalloyed Al as the matrix. However it was judged too risky to spray form unalloyed Al due to its higher explosivity/reactivity and higher melting point. Therefore powder processed

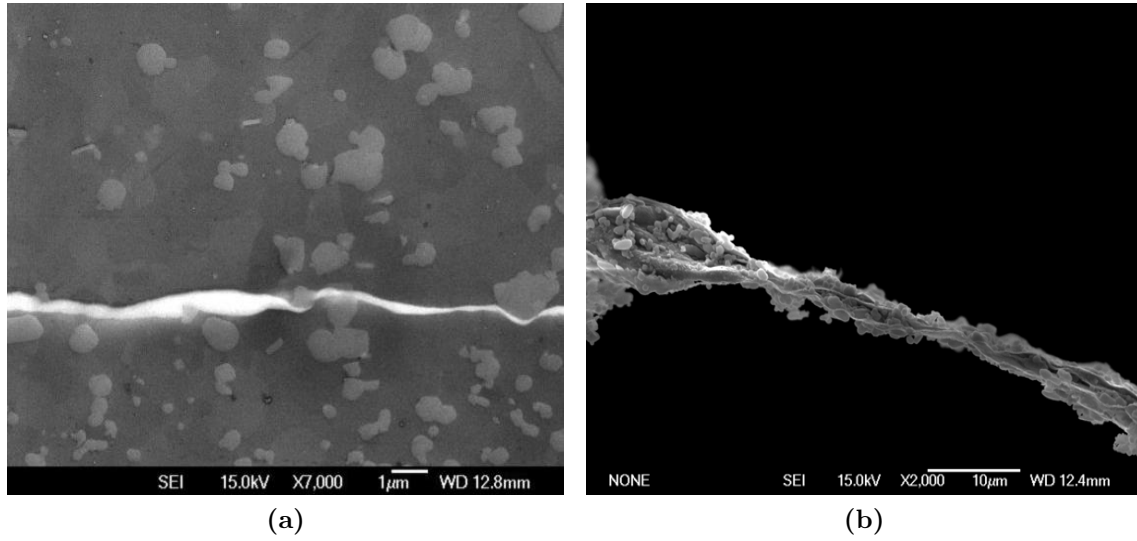


Figure 4.22: (a) Secondary electron image showing the interaction between Si particles and the elongated sub-micron Ti fibre/ribbon of the Al-12Si+Ti extruded 1mm strip and (b) secondary electron image of Ti and Si obtained by extraction showing Si particles decorating the Ti fibre/ribbon.

Al-12Si+12Ti and Al+12Ti composites were prepared instead by powder mixing, hot compacting and extruding at a ratio of 144:1 ($\eta \sim 5$) and a temperature of 420°C, to 2.5mm diameter wires. The specific role of Si on Ti deformation is discussed later. Information on the powders was provided in section 3.2.

4.7.1 EBSD studies

EBSD was carried out on the matrix region of both composites away from the Ti particles, to assess whether the microstructure and grain morphology differed. Figure 4.23 (a) is an EBSD image quality map of the Al-12Si matrix of powder processed Al-12Si+12Ti and (b) shows the corresponding orientation map. The α -Al grains were equiaxed with an average grain size of $\sim 1\mu\text{m}$. The α -Al microstructure was similar to the matrix of spray formed Al-12Si+12Ti orientation map in Figure 4.2 (c), but slightly finer. The average Si particle size measured by EBSD was $\sim 0.2\mu\text{m}$ and the α -Al average grain size was $\sim 1\mu\text{m}$. The inverse pole figure in (c) shows a near-random orientation of the α -Al-Si grains. For the powder processed Al+12Ti composite EBSD was carried out over a same sized region of the α -Al matrix. Figure

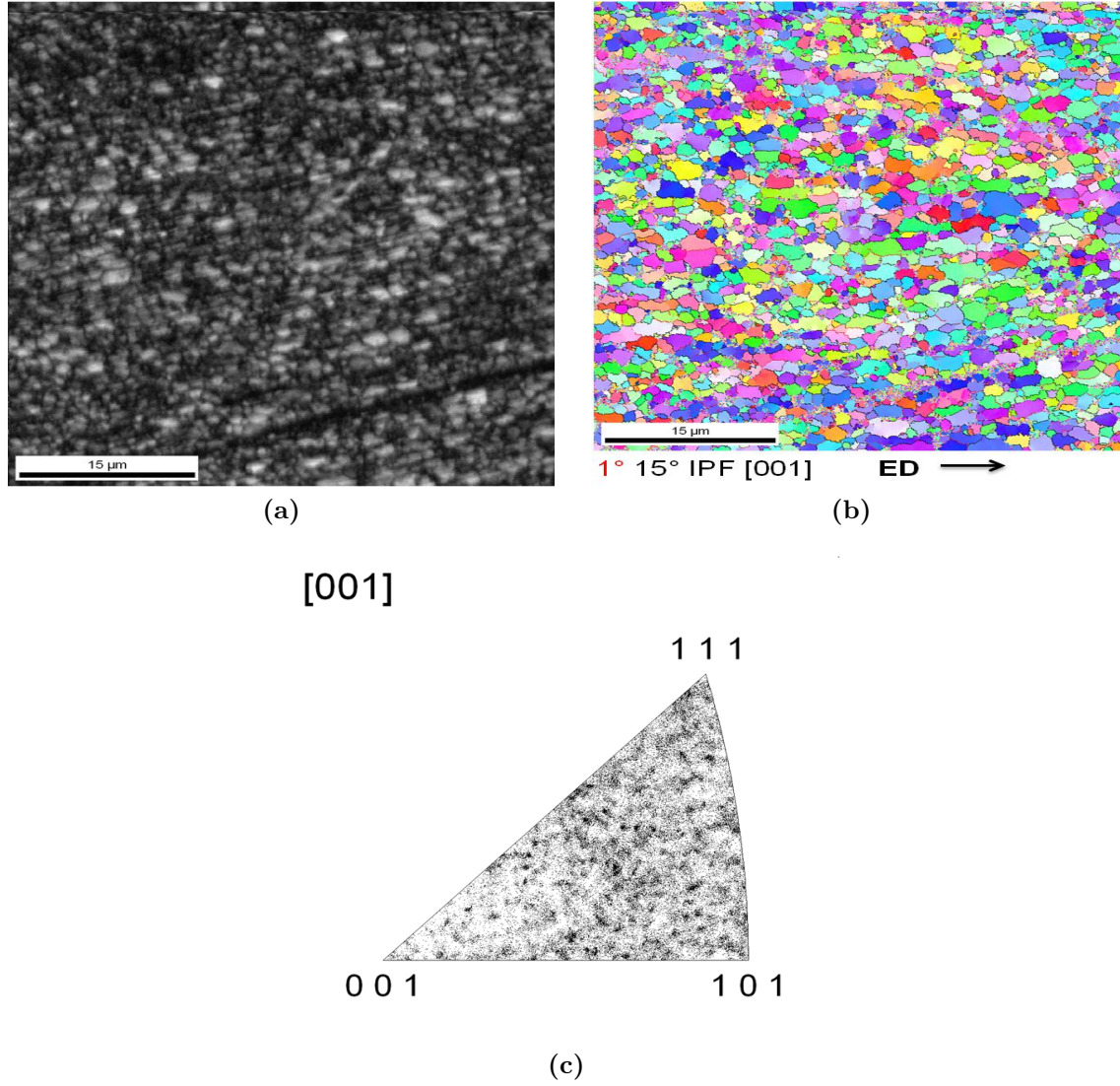


Figure 4.23: (a) EBSD image quality map showing data collection in the Al-12Si matrix region of powder processed Al-12Si+12Ti; (b) corresponding EBSD orientation map showing grain boundaries $>15^\circ$ in black and those between 1° and 15° in red; and (c) inverse pole figure showing a near-random orientation of the α -Al-Si grains.

4.24 (a) is an image quality map of the matrix region in the Al+12Ti composite and (b) is the corresponding orientation map of α -Al without the inclusion of Si particles, with now a more elongated grain morphology and a larger average grain size of $2.7\mu\text{m}$. The inverse pole figure in Figure 4.24 (c) shows preferential orientation of the Al grains along the $\langle 110 \rangle$ planes. Should geometric dynamic recrystallisation be operating as potentially was the case for spray formed Al-12Si+Ti, the α -Al grains would not have elongated in the absence of Si. These results support the idea that particle stimulated nucleation was most likely occurring in the Al-12Si matrix due to the Si particles, in both spray formed and powder processed invariants.

4.7.2 Mechanical properties

The mechanical properties of powder processed Al-12Si+12Ti and Al+12Ti extruded wires were investigated and the yield stress (defined as 0.2% proof stress) and ultimate tensile strength are shown in Figure 4.25. The elongation properties were not included in the plots because for Al-12Si+12Ti the specimen broke in the grips during testing after 9% elongation; the Al+12Ti wire did not break in the grips and had an elongation at failure of 17%. The average yield stress and UTS of Al-12Si+12Ti was 139MPa and 239MPa respectively, with the composite showing an increase of $\sim 26\%$ in yield stress and $\sim 64\%$ in ultimate tensile strength relative to Al+12Ti. Figure 4.26 is a stress-strain curve from Al-12Si+Ti extruded 2.5mm wire showing smooth continuous curves. The stress-strain curves from Al+12Ti composite also showed similar continuous curves. Even accounting for the small number of tests, the significant improvement in tensile properties with the inclusion of Si suggests that Ti deformation and therefore Ti work hardening may be enhanced by the presence of the small Si particles. To assess this theory further powder processed Al-12Si alloy was extruded to a 2.5mm diameter bar under the exact same conditions as powder processed Al-12Si+12Ti and the Al+12Ti composites to examine whether the strength of the powder processed Al-12Si+12Ti composite obeyed a

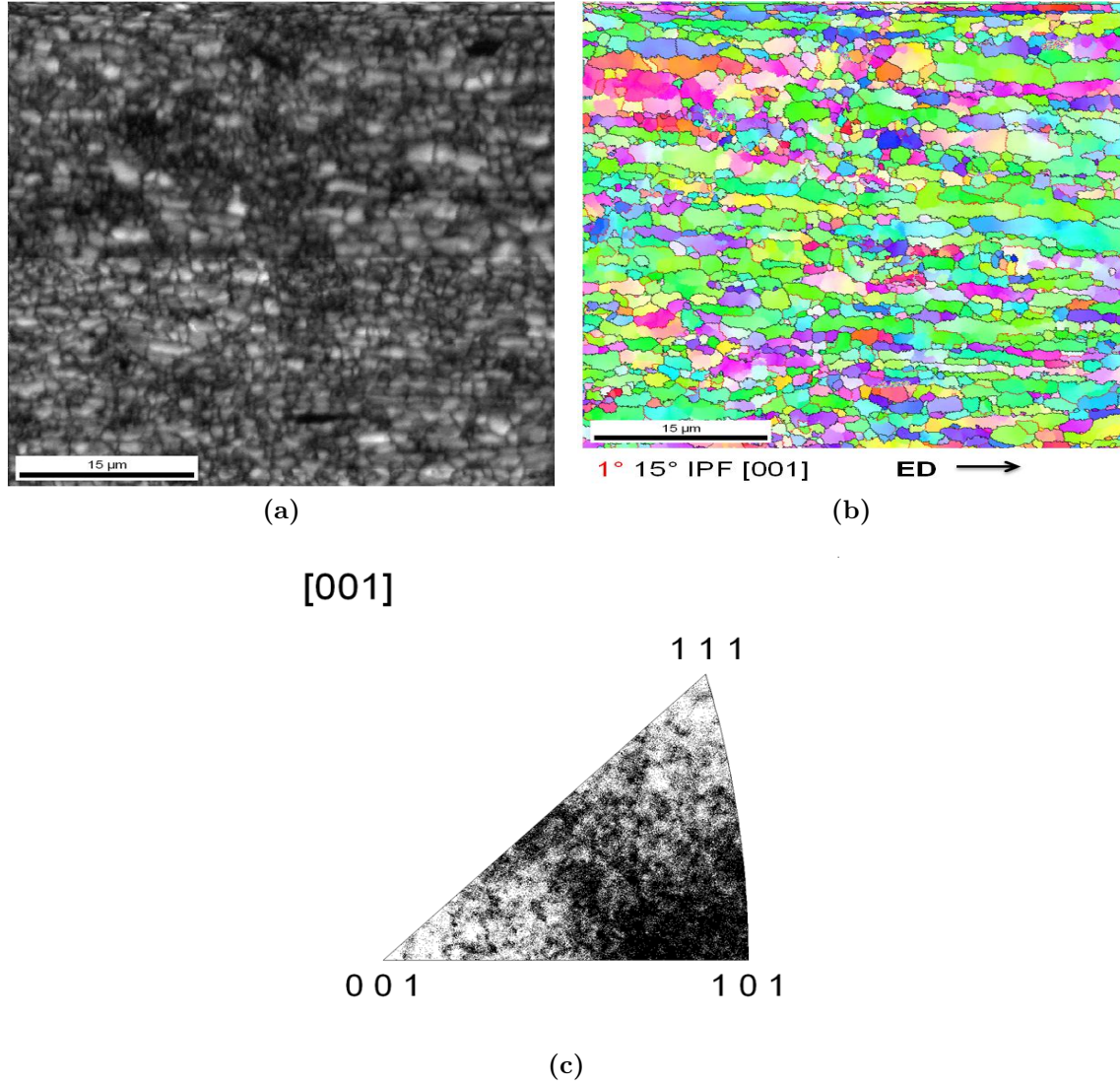


Figure 4.24: EBSD image quality map showing data collection in the Al+12Ti matrix region of powder processed Al+12Ti; (b) corresponding EBSD orientation map showing grain boundaries $>15^\circ$ in black and those between 3° and 15° in red; and (c) inverse pole figure showing preferred orientation of the Al matrix grains.

“rule of mixtures”. The resulting ultimate tensile strength was $\sim 195\text{MPa}$ which is within close agreement to literature where the ultimate tensile strength of as-cast and ECAPed Al-12Si (with a comparable strain of ~ 5), was 190MPa [114]. Hyun *et al.* [112] studied the mechanical behaviour of commercially pure Ti at intermittent stages during deformation processing by ECAP at 410°C . After 6 ECAP passes the UTS was 669MPa . The level of deformation was equivalent to a strain of 4.6 which was reasonably close to a strain of 5 induced in Al-12Si+12Ti composites in this work. Assuming the volume fraction of Ti in Al-12Si+12Ti was 7.4%, the estimated strength of the powder processed Al-12Si+12Ti is 230MPa , and is in reasonable agreement with experiment at 239MPa for the extruded Al-12Si+12Ti composite. Therefore, the difference between the mechanical properties in Al+12Ti and Al-12Si+Ti is largely due to the higher strength of the Al-12Si matrix. Pure Al processed by casting and ECAP at a strain of ~ 5 had a UTS of $\sim 130\text{MPa}$ [115].

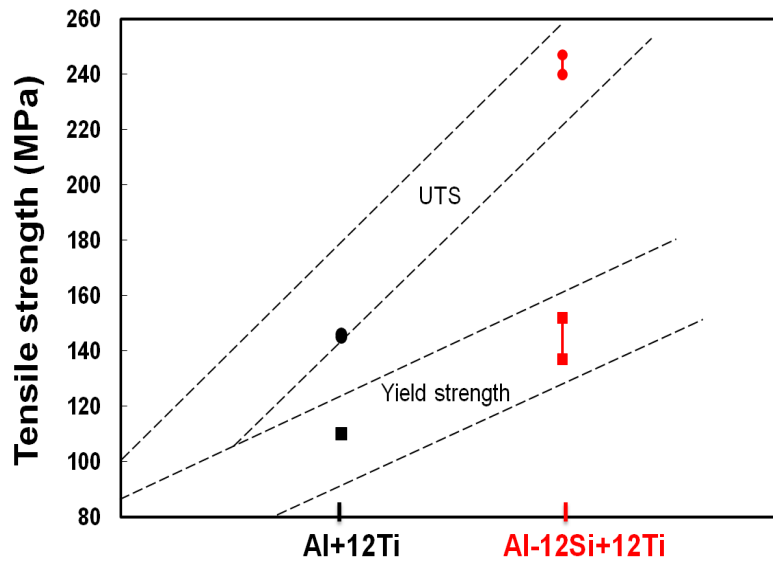


Figure 4.25: Mechanical properties of extruded 2.5mm diameter wire powder processed composites Al-12Si+12Ti and Al-12Ti.

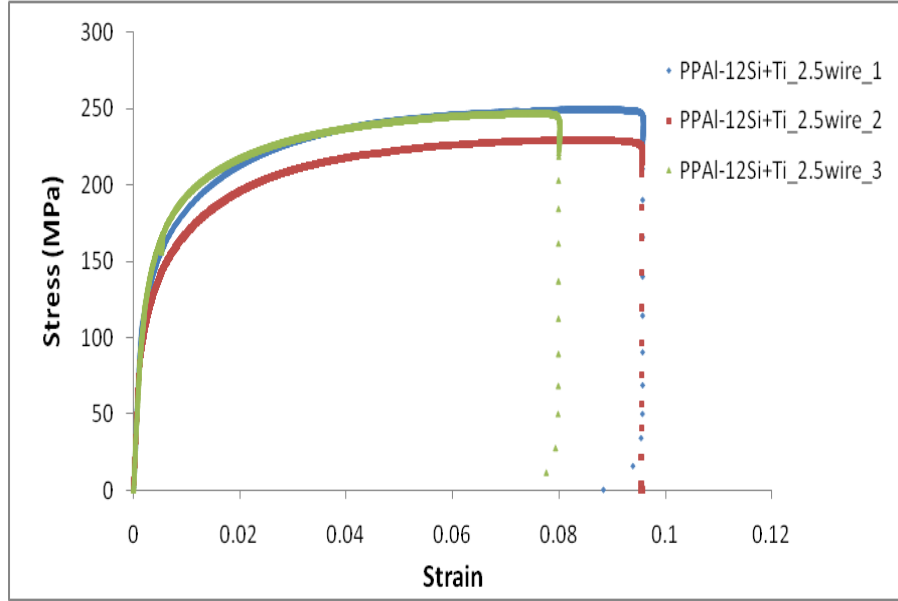


Figure 4.26: An example of the raw stress-strain curves from powder processed Al-12Si+12Ti extruded 2.5mm wire.

4.7.3 The effect of Si on Ti deformation

To assess further whether Si enhanced the deformation of Ti, SEM studies of the powder processed Al-12Si+12Ti and Al+12Ti composites were compared. In these composites the Ti powder used was processed by mechanical milling and not the hydride-dehydride process as was the case for the spray formed composites, and therefore tended not to elongate so readily. Powder morphology, processing conditions and oxygen content are major factors that determine deformation capability and are discussed further in the following chapter. However, for comparison purposes, mechanically alloyed Ti powder was used and it was hoped this was acceptable in this case since the primary interest was whether Ti deformation/elongation was enhanced by Si particles or not. Figures 4.27 (a) and (b) are SEM images taken from a longitudinal section of the extruded $\Phi 2.5\text{mm}$ bars of powder processed Al-12Si+12Ti and Al+12Ti respectively. Only a slightly greater proportion of Ti particles were elongated in the presence of Si, despite the difference in properties.

At higher magnifications in the powder processed Al-12Si+12Ti and Al+12Ti extruded composites as shown in Figure 4.28 (a) and (b), Ti elongation again ap-

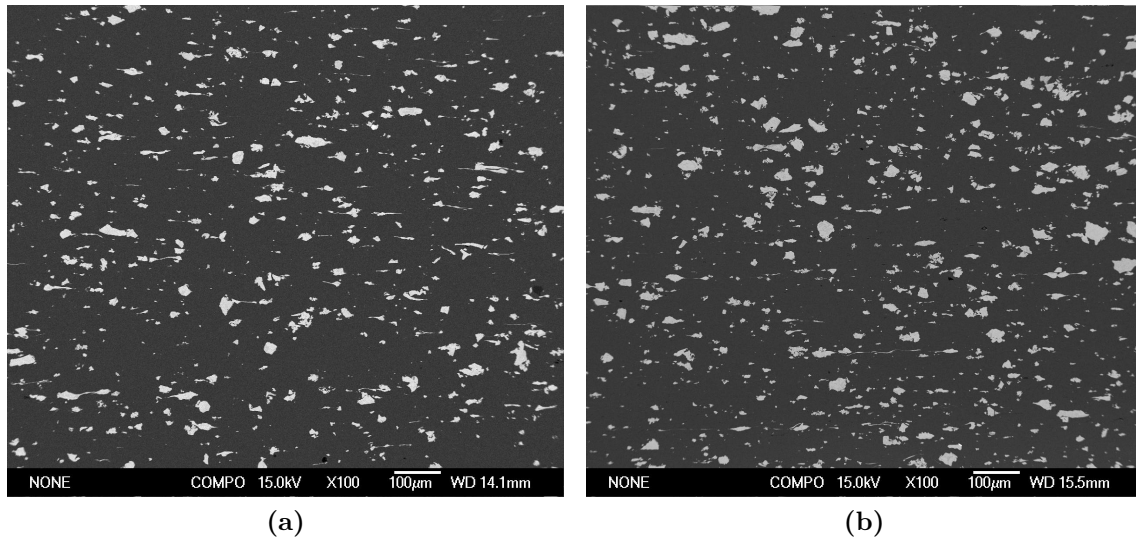


Figure 4.27: Backscattered electron images of the longitudinal section of extruded powder processed Al-12Si+12Ti (a) and Al+12Ti (b), comparing the extent of Ti deformation.

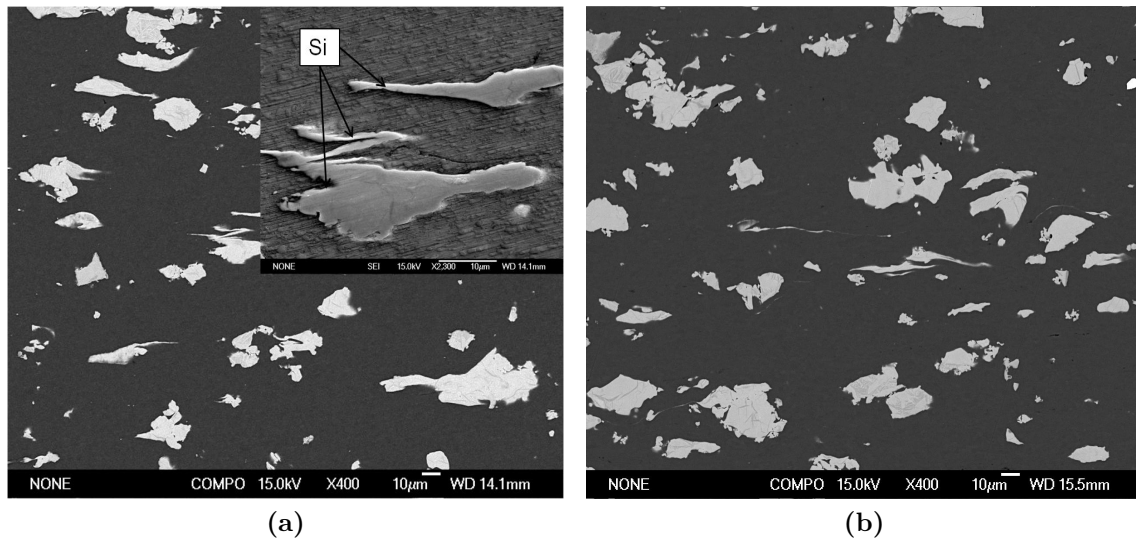


Figure 4.28: Backscattered electron images of the longitudinal section of (a) extruded powder processed Al-12Si+12Ti, with insert showing Si/Ti particle interaction during deformation and (b) Al+12Ti, comparing the extent of Ti deformation at higher magnifications.

peared only slightly enhanced by the presence of Si particles. However from the higher magnification insert in Figure 4.28 (a), Si appears to have played a role in Ti deformation by impinging at the Ti edges and “micro-rolling” or “extruding” some of the Ti into a fibrillar morphology. All of the “zig-zagged” Ti shaped particles were along the extrusion direction with a Si particle generally found at the corner. However the extent of Ti deformation was modest. Perhaps the Ti powder in this study was simply too work-hardened to be sensitive to the Si or the oxygen concentration was too high for sufficient ductility to conclusively reveal whether Si enhanced the deformation of Ti or not (later it was discovered that Ti was only 96% pure and as shown in the following chapter, this most likely affected the extent of deformation). Although annealing the Ti was considered, this was not pursued to avoid the chance for further oxygen contamination at high temperature. Alternatively, to enforce further deformation on the Ti, a higher flow stress matrix could be used, or by extruding at a lower temperature, and consequently a higher extrusion force. However, the extrusion press capability limit of $\sim 720\text{kN}$ was reached during both extrusions, and there was insufficient time for further matrix-powder combinations.

In summary, the microstructural evidence presented here does not conclusively support the idea that Si was aiding deformation although it is intensively interacting with the Ti fibres/ribbons during extrusion. It might be useful to use TEM to assess dislocation structures around the Si particle in order to confirm whether Si rotates or not. Ti elongation can by no means be attributed to the increase in tensile properties of Al-12Si+12Ti relative to Al+12Ti as shown in Figure 4.25, because firstly the increase in interface is not pronounced and secondly, as previously discussed, a significant deviation from the rule of mixtures due to interfacial strengthening is not expected to come into play until higher strains of ~ 8 [37].

As described in the literature review, various mechanisms have been proposed for the enhanced tensile properties of heavily deformed MMCs, and it is generally accepted that the larger the interfacial area arising from progressively more

deformed and elongated minority phase, then the more barriers there are to dislocation (slip) propagation per unit volume [24]. The following experiment was devised to contribute some understanding of the extent to which minority phase morphology dominates strengthening. Powder processed Al-12Si+12Ti were extruded at a strain of ~ 5 to 2.5mm diameter wire. However, in this case the Ti powder was manufactured by gas atomisation and was near-spherical in morphology ($d_{50}=89\mu\text{m}$, 99.6% purity, $\text{O}_2=0.15\%$).

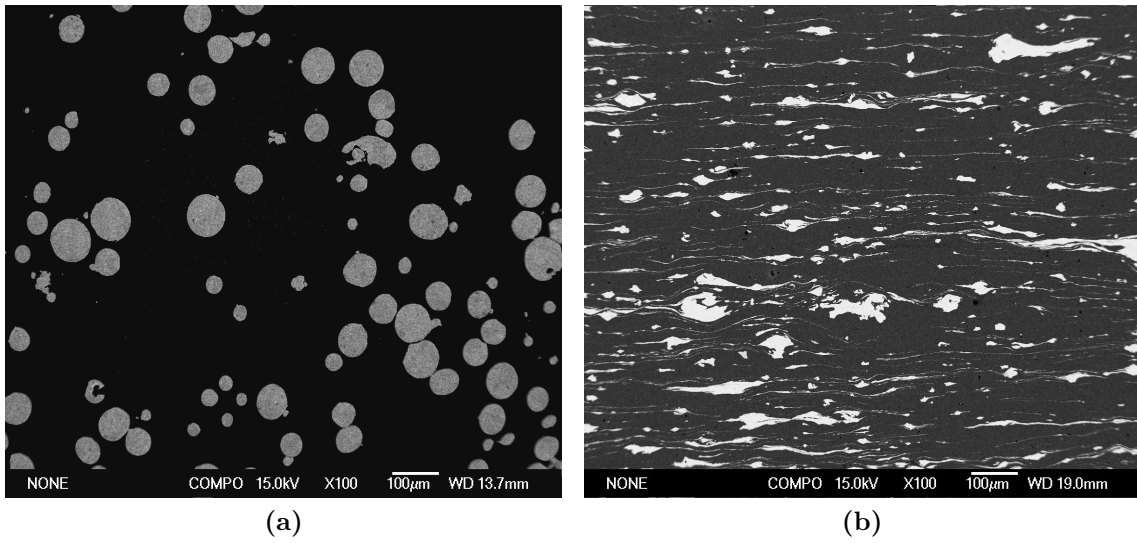


Figure 4.29: Secondary electron images of (a) powder processed Al-12Si+12Ti consisting of undeformed spherical Ti and (b) spray formed Al-12Si+12Ti showing elongated Ti minority phase after extrusion to a strain of ~ 5 .

Spherical powders were shown to resist deformation (discussed more in the following chapter) and is confirmed by the SEM image of the extruded Al-12Si+12Ti_{sph} composite in Figure 4.29 (a). This material was compared with spray formed Al-12Si+Ti that contained angular Ti powder processed by a hydride-dehydride route and most of which underwent extensive elongation to fibres/ribbons, as shown in Figure 4.29 (b). Both composites experienced a deformation strain of ~ 5 and the most significant difference between them was the morphology of the Ti powder. The resultant mechanical properties in Figure 4.30 show the two materials have practically the same yield stress and ultimate tensile strength, confirming that at low deformation strains (<8), elongation of minority phase and increased interface does

not enhance the strength; rather strengthening is derived from work-hardening of both phases but still complying with the “rule of mixtures”. In hindsight, this experiment was not as well controlled as hoped to isolate the effect of one variable because the initial hardness of the spherical Ti was 255MPa compared with 159MPa for the angular Ti. Therefore, with no interface effects, or effect of morphology, the composite with spherical Ti might be expected to be stronger than the composite with elongated angular Ti, whereas strengths are similar. Therefore, either the Ti plays no role in composite properties and strength is dominated by the matrix, or else the change in Ti morphology to fibres does contribute to strength via work-hardening and/or interfacial strengthening effects.

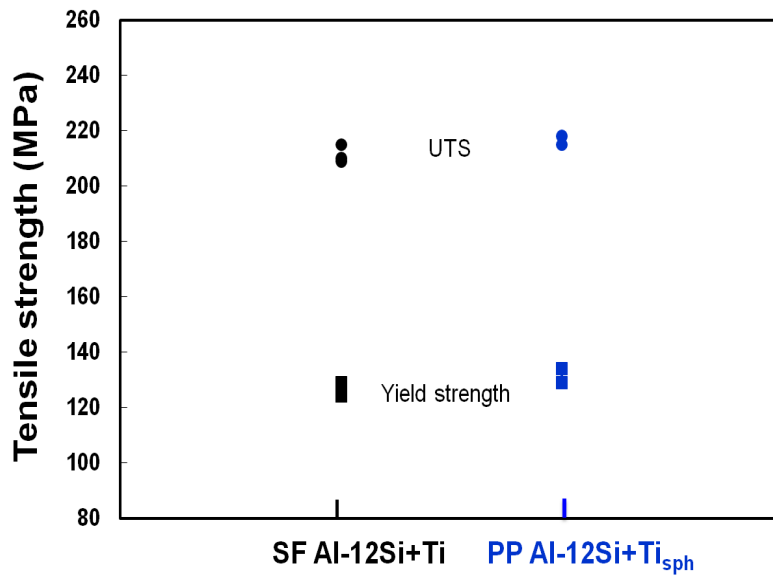


Figure 4.30: Comparison of mechanical properties of spray formed Al-12Si+Ti (shown in black) and powder processed Al-12Si+Ti (shown in blue). Both materials were extruded to a strain of ~ 5 .

4.8 Accumulative roll bonding (ARB) of spray formed Al-12Si+Ti composites

The strains induced in the composites by extrusion were relatively low when compared to Al-Ti powder processed to a strain of 13.9 by Russell [30]. In order to assess the response of the material to higher strains, spray formed Al-12Si+Ti strips of 1mm thickness were subjected to 3 ARB cycles resulting in a total true strain of 8.4.

The majority of Ti particles were reduced to sub-micron thickness as shown in Figure 4.31 (a). Whilst it may appear that the fibres/ribbons were breaking, when viewed at higher magnifications using secondary electron imaging as shown in Figure 4.31 (b), fibre breakage was less commonly observed, supporting previous ideas that the filamentary phase should continue to elongate if capable of a high recovery rate [26]. Figure 4.31 (c) shows deformation of the Ti fibres in the transverse direction (rolled out of the page) where over 50% of the fibres are $<5\mu\text{m}$ thickness. Evidence of elongation in the transverse direction was suggested by SEM studies in the extruded 1mm strip and was now more fully developed after rolling. Trybus *et al.* [76] observed equivalent strengths in both the longitudinal and transverse direction of rolled Cu-Nb composites.

FIB was also used to investigate the microstructure of the ARB material and FIB micrographs along a longitudinal section are shown in Figure 4.32 (a) and (b), revealing Ti fibres/ribbons $\sim 2\mu\text{m}$ in thickness, Al grains of $\sim 1\mu\text{m}$ and similar sized Si particles. The α -Al grains were only modestly refined at $\sim 1\mu\text{m}$, compared to ~ 2.4 in the extruded condition due to the increase in strain from ~ 6 to ~ 8.4 after ARB. Grain refinement here did not occur in the extruded materials and could be due to an additional component of shear deformation, due to the friction between the roll and sheet during dry rolling, that is reported to significantly increase the strain and promote grain refinement in rolled materials [10].

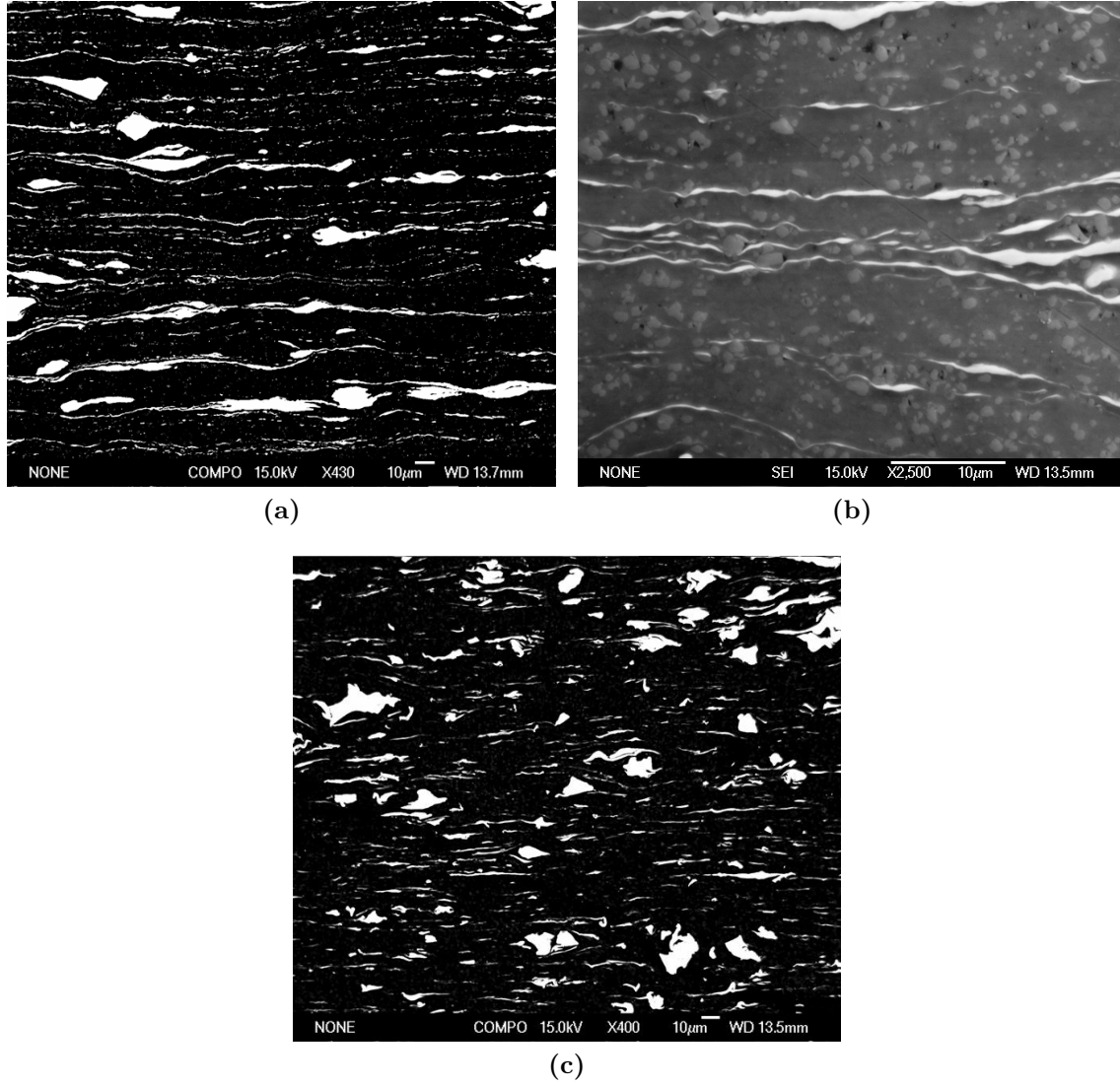


Figure 4.31: (a) Backscattered electron image showing sub-micron Ti fibres/ribbons after 3 cycles of ARB was carried out; (b) secondary electron image of (a) at higher magnifications showing elongated sub-micron Ti fibres/ribbons that were not in fact breaking; (c) backscattered electron image of the transverse section showing slightly elongated Ti fibres/ribbons.

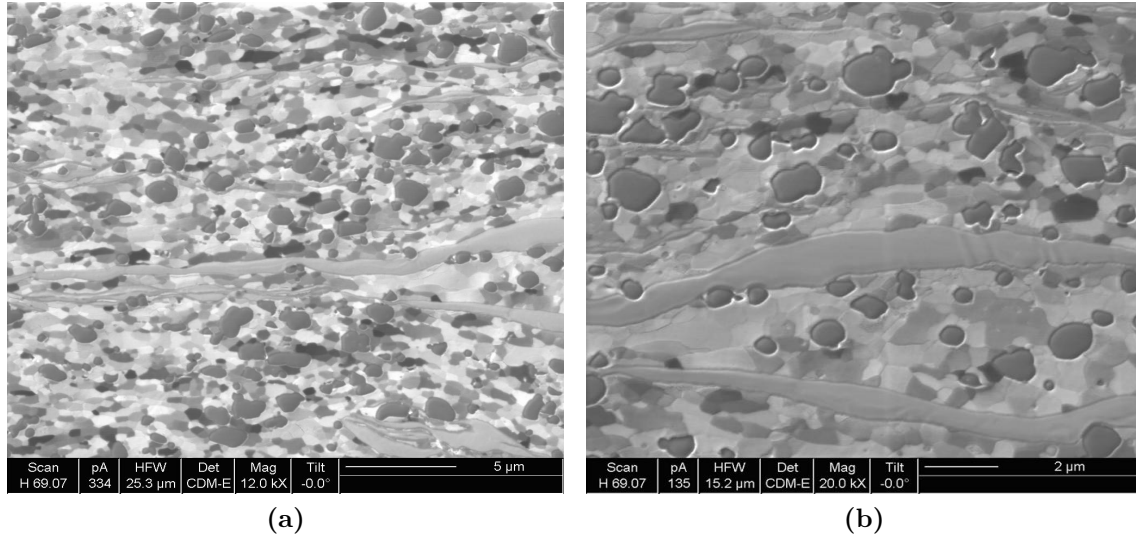


Figure 4.32: (a) Focused ion beam micrograph showing Ti fibres/ribbons, Al grain structure and Si particles in Al-12Si+Ti after 3 cycles of ARB and (b) shows the microstructure at higher magnifications.

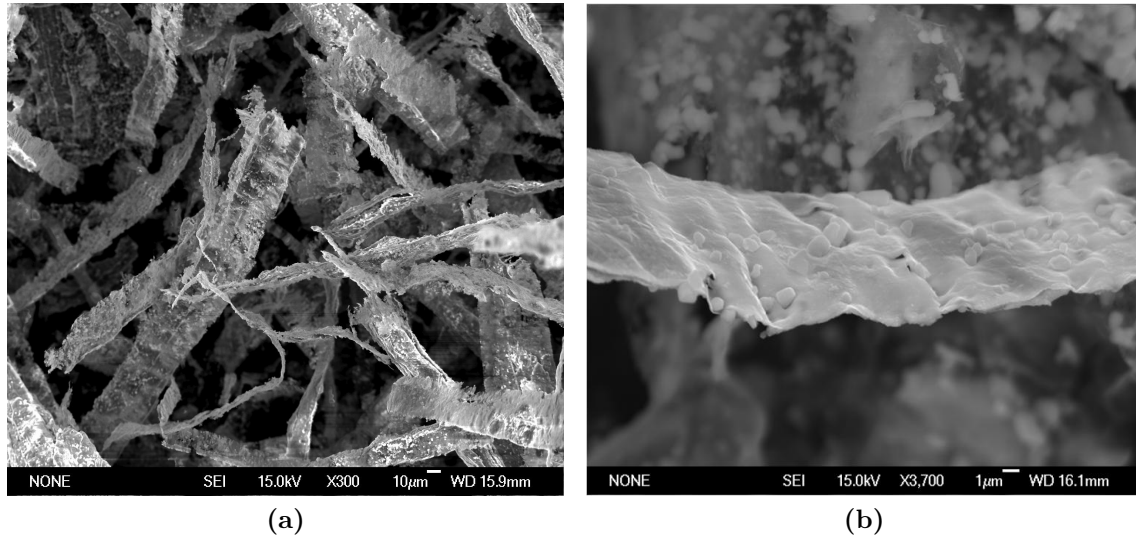


Figure 4.33: (a) Secondary electron image showing Ti ribbons extracted from ARB Al-12Si+Ti and (b) at higher magnifications shows a Ti ribbon a few nanometres in thickness with Si particles embedded on the surface suggestive of participation in Ti deformation.

Figure 4.33 (a) shows the Ti fibres/ribbons after dissolution of the α -Al matrix. After 3 ARB cycles the fibres/ribbons are deformed into flat ribbons with a very thin cross-section. Most of the Ti ribbons were over $500\mu\text{m}$ long with thickness as small as tens of nanometres.

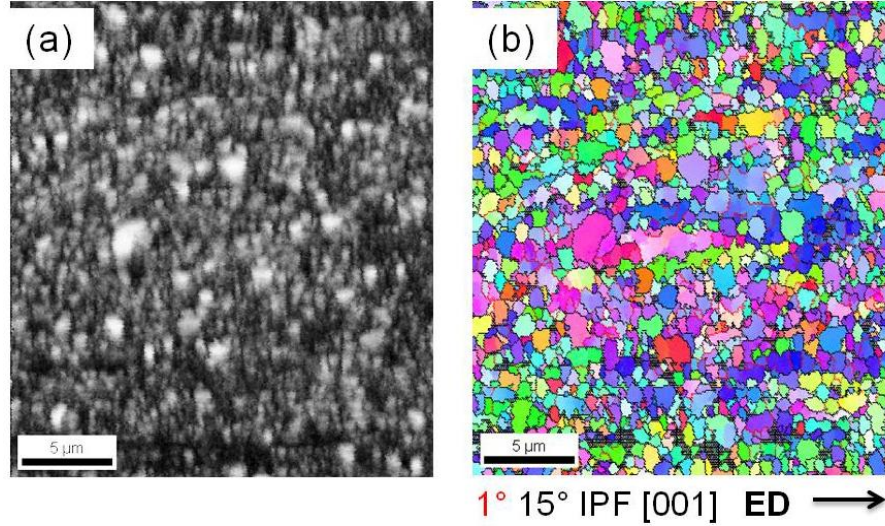


Figure 4.34: EBSD image quality map (a) and orientation map (b) revealing refined equiaxed Al and Si grains after a deformation true strain of ~ 8.4 .

Figure 4.34 (a) is an image quality map of the matrix region of Al-12Si+Ti after ARB to 3 cycles and shows the definition of most grains, indicating a relatively good quality scan. The corresponding orientation map in Figure 4.34 (b) shows equiaxed α -Al grains and spherical Si particles. Again low angle grain boundaries were defined as those between 1° and 15° (coloured red) and high angle grain boundaries were those above 15° (coloured black). There was some grain refinement in α -Al as the average grain size of the Al-12Si matrix was now $\sim 900\text{nm}$ as shown in Figure 4.35 (a), indicating PSN efficiency increased after more severe deformation processing ($\eta=8.4$), and is consistent with trends previously shown in Figure 4.15. The majority of the grain boundaries were of high angle character as shown in the misorientation distribution in Figure 4.35 (b), supporting PSN that encouraged refined and equiaxed α -Al grains.

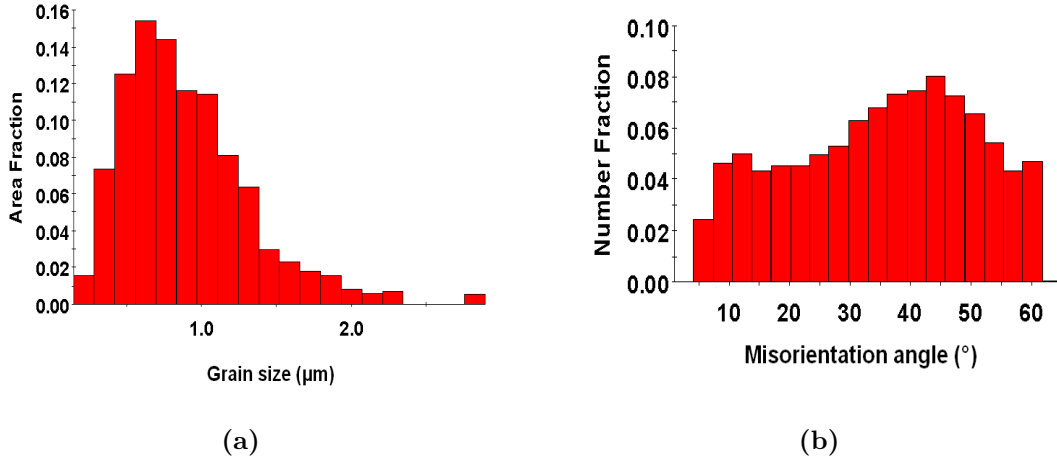


Figure 4.35: (a) The distribution of α -Al and Si grain sizes in accumulative roll bonded Al-12Si+Ti material and (b) shows the misorientation distribution.

4.9 Conclusions

Spray forming with co-injection has been established as a feasible route to the manufacture of metal-metal composites at large scale. The Al-12Si+12Ti industrial scale billet comprised refined equiaxed α -Al grains ($\sim 5\mu\text{m}$), spherical Si particles ($\sim 1\mu\text{m}$) and uniformly distributed Ti particles ($D_{50}=80\mu\text{m}$), and was free from measurable interfacial reactions or oxides. Deformation processing was carried out to a true strain of ~ 8.4 , providing elongated Ti fibres/ribbons of sub-micron thickness. Microstructural insensitivity of the α -Al grains to maintain a fine, near-constant grain size irrespective of total strain was attributed to either geometric dynamic recrystallization or particle stimulated recrystallization, but stronger evidence for the latter was supported by powder processed composites. It was suggested that during deformation, the Si particles played a role in imparting stress to the Ti particles to produce fibres/ribbons of sub-micron thickness, but powder processed composites could not reproduce this behaviour because the Ti powder used in this case was already heavily work hardened. The morphology of the minority phase was also shown to be important in controlling the extent of its deformation. Accumulative roll bonding showed encouragement as a deformation processing route to scale-up.

Chapter 5

Co-spray forming of Al-4Cu+Ti

5.1 Introduction and objectives

The previous chapter described investigations of Al-12Si+Ti as a system to assess the feasibility of metal-metal composite production by co-spray forming, followed by downstream processing. Although this system provided strong encouragement - homogeneity, lack of interfacial reaction, no oxide, scale - metallurgically and property-wise it was rather unsuitable with a high fraction of brittle Si, low Ti fibre fraction, and some difficulties in providing sufficient deformation to deviate from rule of mixtures tensile mechanical performance. In this chapter, an Al-Cu alloy as the matrix is investigated.

For reasons already outlined in Chapter 2, Ti remains a sensible choice for minority reinforcing phase in an Al matrix. Given the compromises provided by Al-Si detailed in the previous chapter, a shift to Al-4Cu was investigated for the following reasons: (1) the flow stress of Al-4Cu [92] and pure Ti [93] at a temperature of 675K and a strain rate of 0.01/s are 80MPa and 125MPa respectively; and (2) Al-4Cu is an age-hardenable alloy that potentially allows the matrix flow stress to be manipulated and its effect on Ti deformation to be studied. Disadvantages may include a melting point raised from $\sim 577^{\circ}\text{C}$ to 645°C (when compared with Al-12Si) and

extended metastable freezing range of $\sim 100^{\circ}\text{C}$ (rather than invariant freezing) both of which may increase the tendency for Al-Ti reactions. All billets were made at Oxford.

5.2 Powder co-injection

A critical aspect of the co-injection system was ascertaining if the system could provide the Ti flow rates reproducibly for sufficiently long times so that a useful fraction of the final billet contained the target amount of Ti. A very large amount of time was spent on understanding the injection system and its control.

It should be recognised that the DACS powder pump is a radical design, replacing the fluidised bed or Archimedian screw feed otherwise used for powder feeding in previous Al-SiC_p composites by spray forming and in the powder industry more widely. The particular advantages of the DACS approach were suggested to be: (1) ability to flow irregular powders across a wide range of sizes; (2) high flow rate, suitable for co-spray forming and up to kg/min; (3) powder flow rate entirely independent of injection pressure and carrier gas flow rate; and (4) robustness. While all these attributes were eventually realised, it was a prototype system and there was little knowledge-base to draw on, either in Oxford, PEAK, or indeed at DACS.

During experiments, it was discovered that the filters in the powder chambers were too coarse and a proportion of powder was passing through them, collecting in the vacuum filters, rather than exiting through the delivery pipe to the atomiser and that a good vacuum could not be maintained throughout an experiment. Subsequently, fine mesh filters ($2\mu\text{m}$) were used as shown in Figure 5.1 (a). These filters were double sided with a 1mm steel mesh at the back for stabilisation purposes and prevention of tearing. After each run the filters were cleaned in deionised water using an ultrasonic bath. Figure 5.1 (b) shows the container that holds the filters in place in the powder chamber.

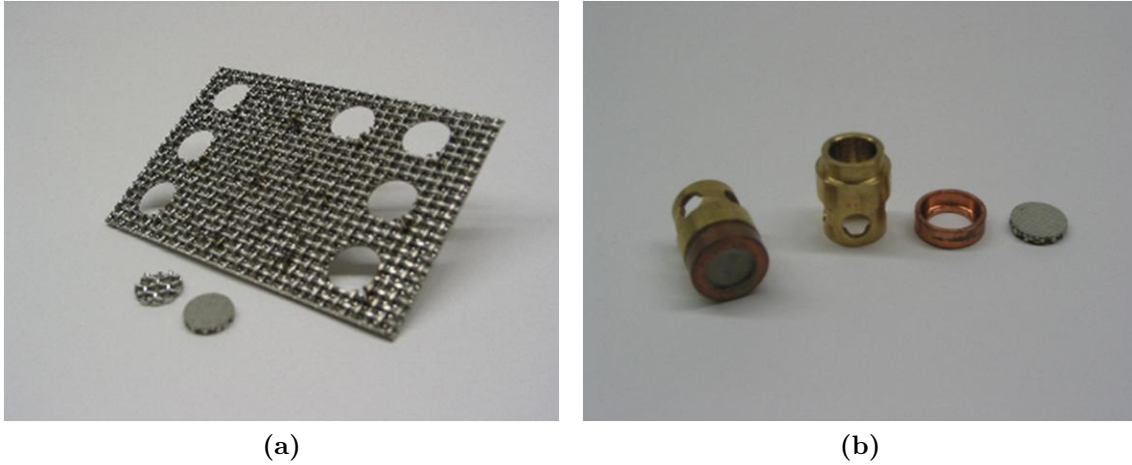


Figure 5.1: (a) Powder chamber filters of double sided mesh that are held by a brass container in (b) that is placed to the rear of the powder chamber.

Various pump parameters were studied to obtain the required powder flow rate consistently. The mass flow rates were recorded from both the amount leaving the hopper, and the amount delivered to the collection hopper in separate experiments. The flow rates exiting the hopper were more regular than flow rates recorded at arrival, due to occasional obstruction of powders in the lengthy delivery pipe. For experiments shown below, the flow rates were recorded at the collector, thus replicating a spray forming co-injection experiment. Figures 5.2 (a)-(f) shows a set of typical experiments to measure the spherical stainless steel powder flow rate as a function of time and as a function of pump frequency in the range 3-11Hz ((a) to (e)) and with a reduced vacuum chamber volume in (f). At lower frequencies, in particular at 5Hz, faster flow rates of powder were obtained, however there was not a significant difference between the different frequencies. In this case, Figure 5.2 (c) shows that at 7Hz the best consistency of flow at $\sim 0.05\text{kg/s}$ was achieved. Restricted chamber size made little difference to the flow rate when compared to the standard flow rate at 7Hz in Figure 5.2 (c). In addition, the use of vibration and the powder feed pressure were studied but were not major factors in affecting flow rate. The fluidisation pressure was kept constant at 0.2bar.

Figure 5.3 (a) shows the powder flow rate of spherical stainless steel powder.

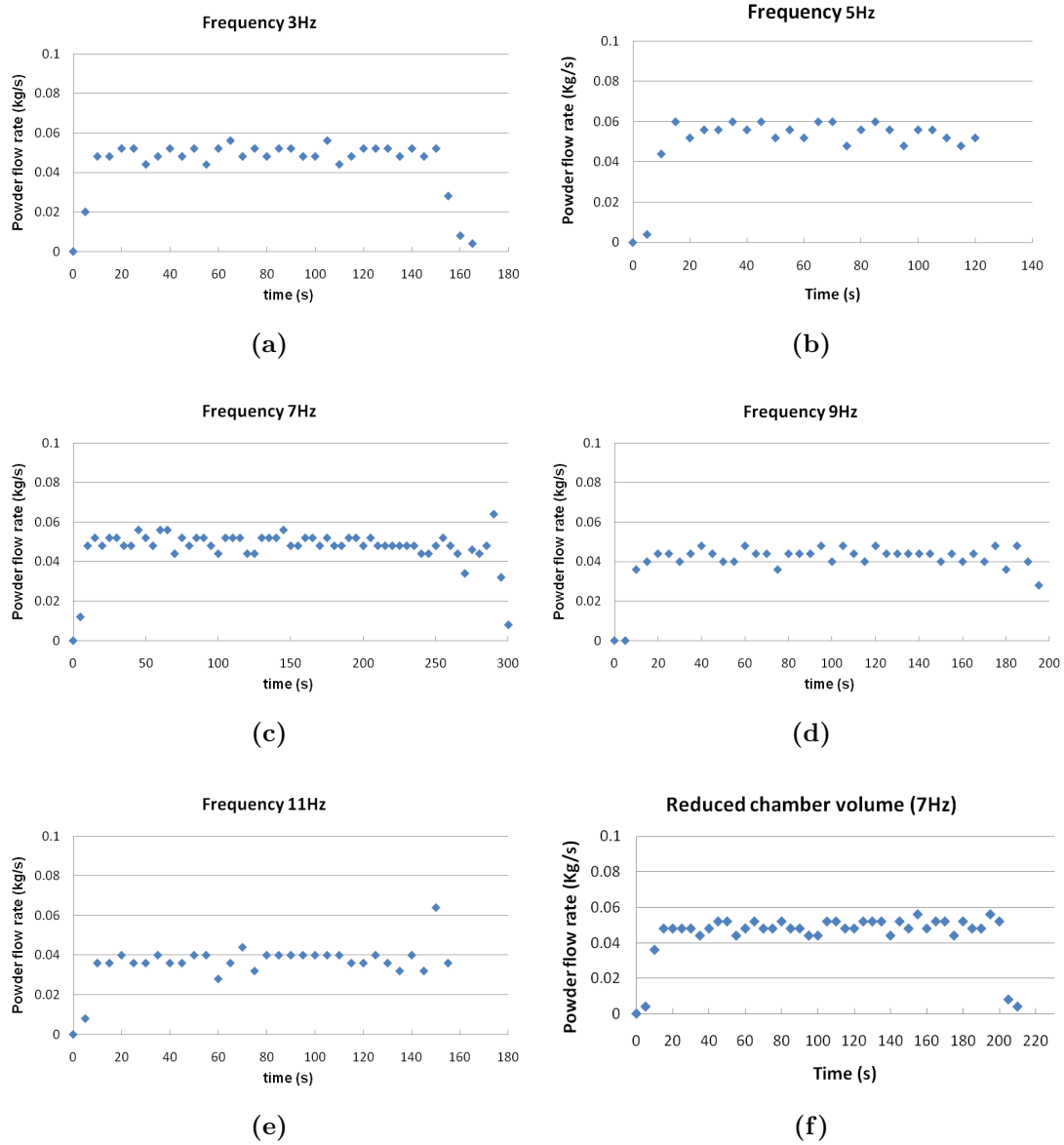


Figure 5.2: Calibrating powder pump at different frequencies (a) - (e) and reduction in powder chamber size (f) using gas atomised stainless steel powder.

The exit flow rate was slightly higher than the rate of powder delivered to the collection hopper. The first co-spray formed composite billet processed at Oxford was Al-10Si with injected Ti-6Al-4V. For testing the capabilities of the unit, alloyed powder was injected due to its lower reactivity than pure Ti. Figures 5.3 (b) and (c) show the powder flow rate of Ti-6Al-4V that was recorded during a dry run of powder through the system, with extraction turned on. Figure 5.3 (b) shows a wider distribution of powder flow rates than in (c) although both were tested at the same conditions. There were a variety of conditions that may play a role: cleanliness of delivery pipe; temperature of the powders; human error since the mass flow rate was manually recorded every 5 seconds; and cleanliness of the powder chamber and filter membranes. Figure 5.3 (d) shows the flow rate of “pure” spherical Ti powder. Powder flow rates were recorded during these dry runs with powder passing in to the spray forming chamber, as in a spray forming experiment.

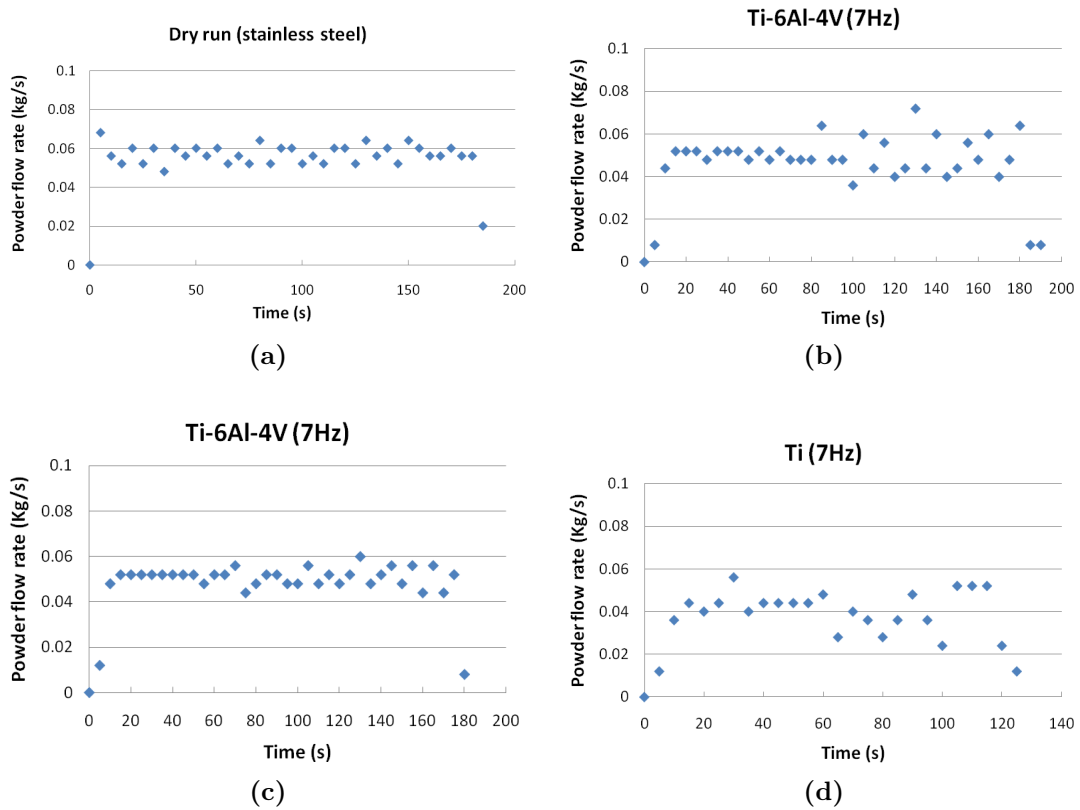


Figure 5.3: Powder flow rates of (a) stainless steel, (b) and (c) Ti-6Al-4V, and (d) pure Ti powder during dry runs at a pump frequency of 7Hz under the same conditions.

During calibration using Ti powder, it was discovered that the filter below the hopper lid posed a safety risk, through the accumulation of fines on the filter surface. When fine powder was mixed with sufficient oxygen and in the presence of static there was a risk of explosion, particularly during powder handling when vacuum cleaners were used to clean filters. Consequently the filter was removed, and insignificant amounts of powder travelled upwards through to the nitrogen release valve at the top of the hopper. A pressure gauge was installed on the hopper lid so that the gas pressure in the hopper could be monitored. Due to concerns with powder handling, no further calibrations with Ti powder were carried out, but the work had showed that a tolerable degree of reproducibility in flow rate through the pump and to the chamber could be achieved.

5.3 Co-spray forming

Three co-spray formed billets of Al-4Cu with injected commercially pure Ti powder were manufactured. The first two billets were essentially proving trials and were carried out while waiting for Ti powder processed by hydride de-hydride method to arrive because this powder had been shown to deform well in the Al-12Si+Ti material in Chapter 4. The three billets manufactured are referred to as AlCuTi1, AlCuTi2 and AlCuTi3 with further details of manufacture outlined in Chapter 3. The co-injection pump was set-up as described in section 3.3.3, and remained on standby for 20 minutes prior to pouring in order to run sufficient N_2 through the system to ensure the exclusion of oxygen during spray forming. During spraying, Ti powder was injected via the primary atomiser into the Al-4Cu melt stream close to the point of atomisation and was integrated into the melt stream due to the very high gas velocities in this region [71]. A particle-droplet co-spray was formed that then co-deposited into a billet preform. At 30s intervals the Ti powder hopper was vibrated in an effort to ensure powder was not sticking to the hopper walls or

obstructing the flow through the exit by compacting and clogging at the base.

5.3.1 AlCuTi1

The experimental parameters for billet AlCuTi1 are shown in Table 3.3. Spray forming was carried out at a Al-4Cu pouring temperature of 750°C [116]. After approximately 3mins of spraying and after a relatively good shape billet formed, Ti co-injection was started for a few seconds to assess any effect on the molten alloy stream. Once it was clear that no vigorous reaction or other concerning behaviour was taking place, co-injection was turned on and the remainder of the 3.8kg of Ti powder was injected. However, it was noted that there was a change in appearance of the billet top surface after a minute or so of injection, indicating either a reaction occurred or perhaps the billet surface was too cold and powder was bouncing off the surface. The volume fraction of injected Ti was $\sim 14\%$, according to the average mass flow rate of Ti from the hopper scales, and the average mass flow rate of Al-4Cu. Since this billet was intended essentially as a proof of concept experiment, the actual volume fraction of incorporated into the billet was not quantified in detail until the final AlCuTi3 billet.

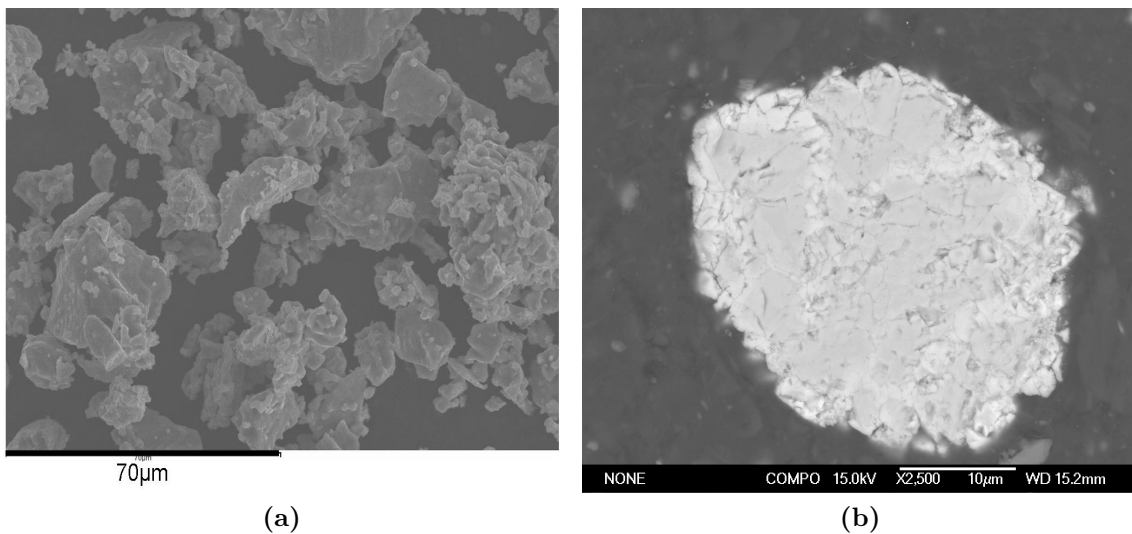


Figure 5.4: (a) Angular morphology of the mechanically milled Ti powder used in billet AlCuTi1 and (b) a cross-sectional view of the same Ti powder showing polycrystalline grains.

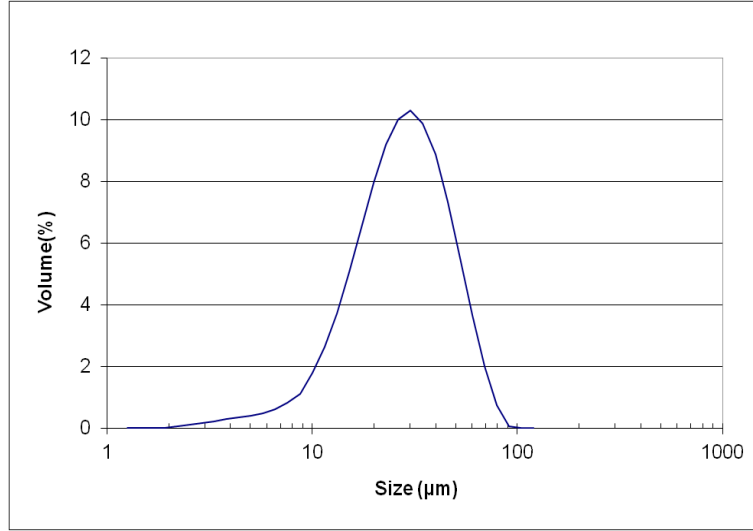


Figure 5.5: Malvern particle size distribution for Ti powder processed by mechanical milling.

The morphology of the Ti powder used in AlCuTi1 was irregular, angular and typical of mechanical milling, as shown in Figure 5.4. A cross-section of a Ti particle is shown in Figure 5.4 (b), with a fine-scale grain size ($\sim 4\mu\text{m}$) of polycrystalline Ti. The volume mean Ti particle size was $\sim 28\mu\text{m}$ as shown by the Malvern particle size distribution in Figure 5.5. Figure 5.6 (a) shows the spray formed billet that weighed 35.8kg and was 27cm in diameter and 21cm in height. The billet was considered a satisfactory first attempt at processing metal-metal composites by spray forming. However, the exterior of the billet had a rough surface, generally indicative of a “cool” billet. The region of Ti injection is shown in the billet interior in Figure 5.6 (b). The billet contained major bands of radial voids, that developed only after co-injection had started. Overall, the suggestion was that the billet temperature was too cold after the addition of a high flow rate room temperature Ti powder. The layering of the radial voids might also suggest that the delivery of the Ti powder may be pulsed. This was not recorded by the hopper weight loss since Ti exited the hopper in regular intervals, and thus is most likely due to semi-regular, sudden unclogging of Ti in the delivery pipe (5m in length) between the hopper and the atomiser. Such sudden bursts of Ti injection were occasionally remarked on the real-time video of the atomisation. Excessive cooling of the billet surface reduces the

liquid fraction so that insufficient droplet/powder re-melting and mixing occurs, and individual powder particles retain their identity, and the powdering surface fails to cohere into a continuous surface, which is then manifest as these large radial voids.

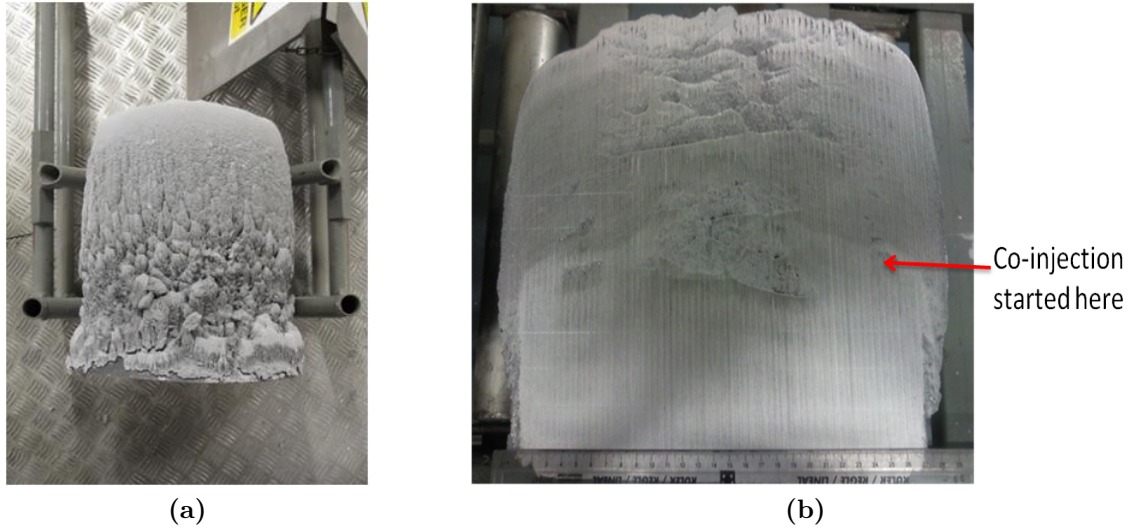


Figure 5.6: (a) Co-spray formed Al-4Cu+Ti composite billet containing mechanically milled Ti powder (AlCuTi1) and (b) a cross sectional view of the billet where the red line marks the start of coinjection.

As shown in Table 3.4, the Cu concentration at $\sim 4.5\%$ was close to the target of 4%. According to ICP-OES analysis AlCuTi1 contained 15.82wt% Ti. Figure 5.7 (a) shows the Al-4Cu matrix prior to injection with polygonal grains typical of spray forming and a residual porosity slightly higher than normally expected for a well-optimised Al alloy. Figure 5.7 (b) shows the region of Ti injection showing that most Ti particles were discrete and not agglomerated but that where Ti particles were close to one another, or comparatively large Ti particles were present, the local porosity was significantly increased - again due to the chilling effect of the cold Ti that restricted droplet flow, remelting and mixing. Al-Ti interfacial reaction was not evident at the resolution of basic optical and SEM techniques.

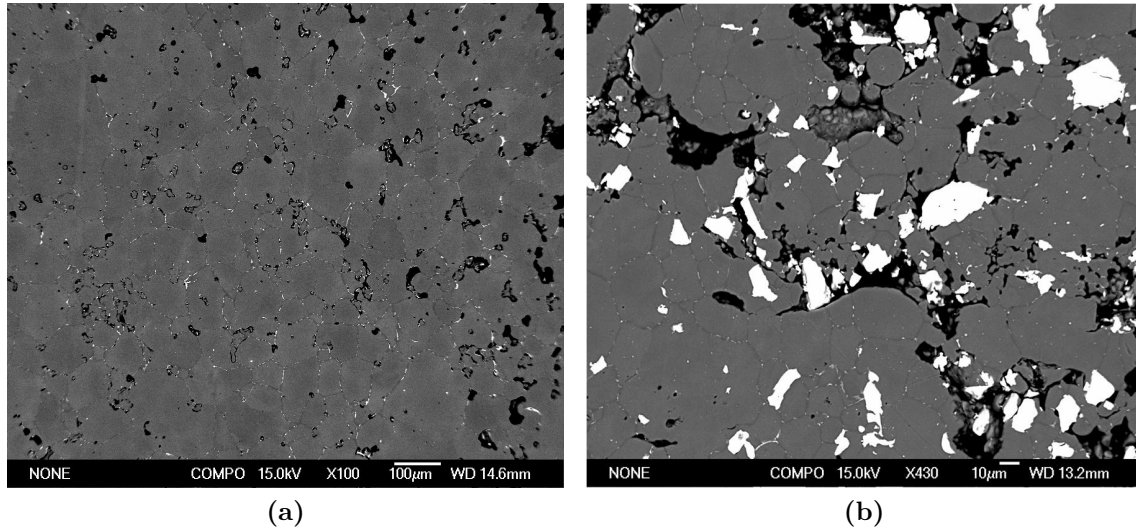


Figure 5.7: (a) Backscattered electron image of Al-Cu matrix before Ti injection in AlCuTi1, and (b) from the region of Ti co-injection in as sprayed AlCuTi1.

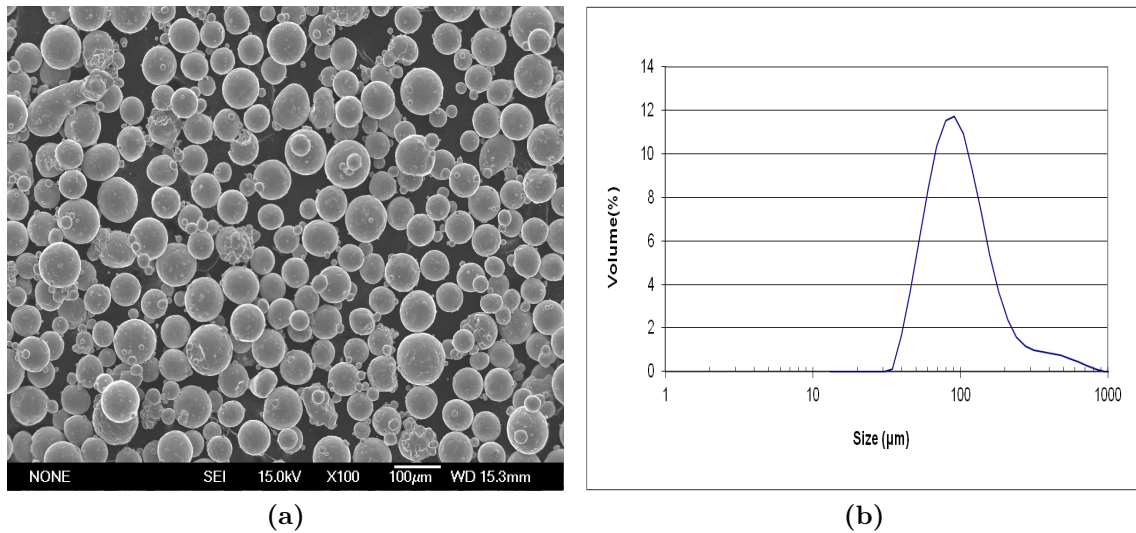


Figure 5.8: (a) Spherical morphology of gas atomised Ti powder used in billet AlCuTi2, and (b) Malvern particle size distribution for Ti powder processed by gas atomisation used in billet AlCuTi2.

5.3.2 AlCuTi2

The experimental parameters for billet AlCuTi2 are shown in Table 3.3. In an effort to improve the billet quality in the co-injection region, the gas flow rate was reduced by a reduction in the diameter of holes in the secondary atomiser in order to reduce the gas mass flow rate and therefore the overall cooling effect of the gas on the molten stream. The gas/melt flow ratio (G/M) was calculated according to Equation 5.1:

$$G/M = \left[\frac{(0.611)(F)(P_s)}{M_f} \right] \quad (5.1)$$

where $0.611\text{m}^3/\text{min}$ is the nitrogen flow rate when using a x1 atomiser, F is the scaling factor is related to the size of secondary atomiser bobbin and M_f is the metal flow rate. For AlCuTi2 the scaling factor was reduced from 4.77 in AlCuTi1 to 2.83. The secondary gas pressure P_s was $\sim 6\text{bar}$. The metal flow rate for AlCuTi2 was $7.6\text{kg}/\text{min}$ thus resulting in a gas/metal ratio of 1.83, reduced from 2.17 in AlCuTi1. Again, $\sim 4\text{kg}$ of Ti powder was coinjected, but in this case the powder morphology was spherical as shown in Figure 5.8 (a), and was produced by gas atomisation and according to the Malvern particle size distribution in Figure 5.8 (b) had a volume mean Ti particle size of $\sim 112\mu\text{m}$. The ram withdraw speed was increased from $0.4\text{mm}/\text{s}$ to $0.6\text{mm}/\text{s}$ because the first billet was too short and wide. Otherwise the experimental procedure was the same as for AlCuTi1.

Ti powder flow rate was recorded according to the mass of powder leaving the hopper per second. Spherical Ti powder flowed better than angular powders. Figure 5.9 shows a total Ti mass of 4.64kg was injected at an average rate of $2.4\text{kg}/\text{min}$. According to the mass flow rates of both the powder ($\sim 3\text{kg}/\text{min}$) and the melt ($\sim 7.6\text{kg}/\text{min}$), the volume fraction of injected Ti was $\sim 16\text{vol}\%$. However, the billet once again appeared excessively chilled as shown in Figure 5.10 (a), despite the reduced gas/melt ratio from 2.17 to 1.83.

The cross-section in Figure 5.10 (b) shows the same qualitative behaviour as AlCuTi1. Spherical powders flowed more regularly and faster than angular powders because they rotated easily over each other and did not occasionally clog in the pipes as was the case for angular powders. Perhaps a more pulsed/irregular powder injection rate in AlCuTi1 allowed the billet temperature to “recover” during low rates of injection, leading to lower levels of porosity between bands. The chemical composition of the billet is shown in Table 3.4 and the Cu concentration at $\sim 4.05\%$ was close to the target of 4%. As with AlCuTi1, $\sim 16\text{wt}\%$ Ti was injected into AlCuTi2.

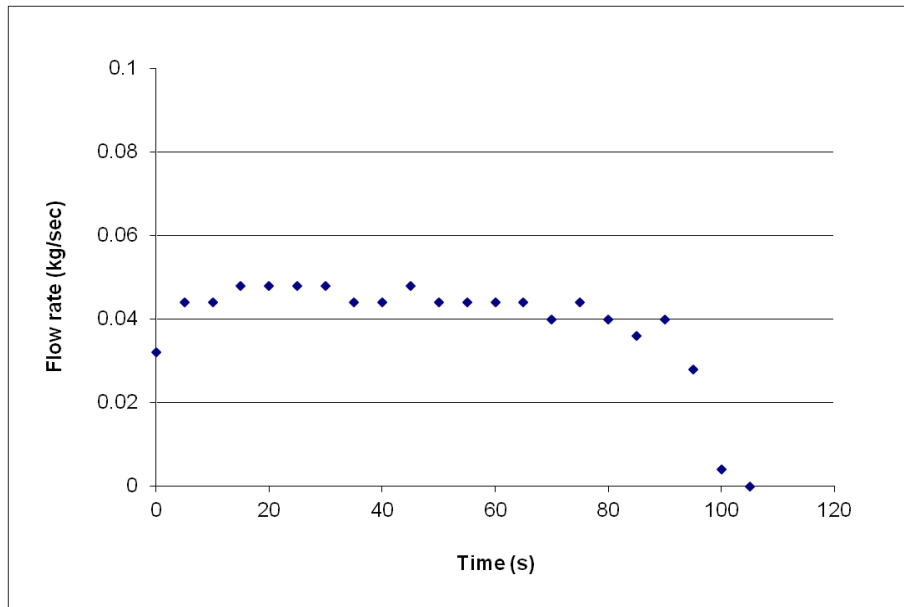


Figure 5.9: The powder flow rate of spherical Ti powder injected in billet AlCuTi2, recorded by the balance beneath the hopper.

Figure 5.11 is a backscattered electron image showing the injected spherical Ti powders in the Al-4Cu matrix with the Ti powder fairly uniformly distributed, with good bonding between the matrix and the particles. The area fraction of Ti was roughly similar to the area fraction in AlCuTi1 (Figure 5.7 (b)).

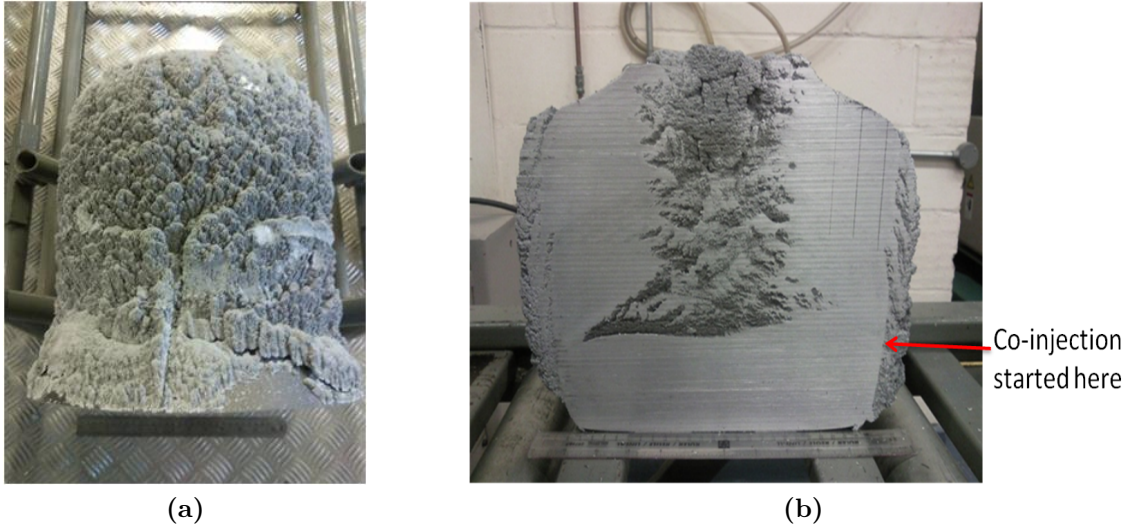


Figure 5.10: (a) Co-spray formed Al-4Cu with injected spherical Ti (AlCuTi2) and (b) a cross-section of billet AlCuTi2 where the region of co-injection is visible at the center.

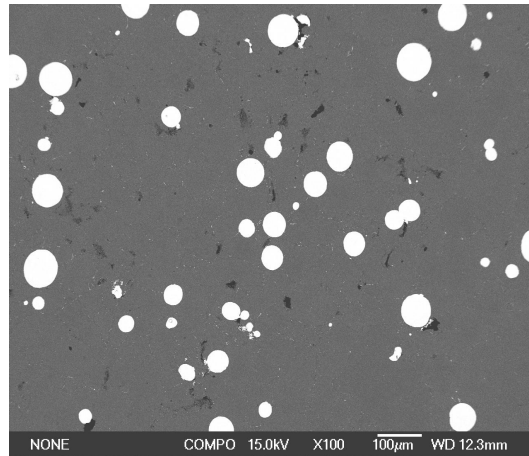


Figure 5.11: Backscattered electron image of the region of co-injection of spherical Ti into AlCuTi2.

5.4 Co-spray forming of AlCuTi3

In a final attempt to optimise the process of co-injection further, spray forming conditions were altered. Table 3.3 showed a summary of the parameters used for all the Al-4Cu+Ti billets. For AlCuTi1 and 2, insufficient Ti powder was incorporated into the billet and in order to provide the $\sim 20\text{vol}\%$, suggested to be required for anomalous strengthening [3]. The co-injection pump rate operated at a pump frequency of 7Hz and gave $\sim 2.5\text{kg}/\text{min}$, according to previous runs (although peak values at $3\text{kg}/\text{min}$ were obtained for some calibration experiments). Since the pump

performed tolerably well and concerns remained about the safety and cost of utilising very large amounts of Ti powders, it was decided instead to reduce the metal flow rate of Al-4Cu in an attempt to achieve $\sim 20\text{vol}\%$ of Ti powder.

The metal flow rate for previous experiments was $\sim 7.5\text{kg}/\text{min}$ and it was calculated that a reduction in the metal flow rate of $\sim 25\%$ to $5.7\text{kg}/\text{min}$ was required. The cross-sectional area of the zirconia melt delivery nozzle was reduced by 25% from 5.7 to 5mm. For billet AlCuTi3, the total amount of Ti powder was increased to 10kg, to provide sufficient material for downstream processing. The chemical composition of the resulting billet is shown in Table 3.4. The Cu concentration at $\sim 4.14\%$ was close to the target of 4% and the Ti powder was increased to 18.32wt% and was $\sim 50\%$ greater than the fraction of Ti injected into Al-12Si billet in Chapter 4 that contained 11.87wt% Ti.

It was unsurprising that powder injection had a substantial cooling effect on the billet surface. Cantor *et al.* co-spray formed Al with 20vol% injected SiC and found that it was necessary to increase the alloy melt superheat to restore the spray enthalpy to its optimum level. Consequently large scale porosity was eliminated and a homogeneous distribution of SiC was achieved [117]. This procedure was not adopted for AlCuTi1 and 2 because of - unlike SiC - the danger of a runaway $\text{Al} + \text{Ti} \rightarrow \text{Ti}_x\text{Al}_y$ exothermic reaction. However, given the benign nature of the first two billets, the melt temperature was now increased from 750°C to 850°C .

Ti powder produced by the hydride dehydride process (HDH) was chosen for the final composite billet as this was the powder injected by PEAK in the Al-12Si+Ti billets previously described. The powder again had an angular morphology as shown in Figure 5.12 (a). A cross-section of a Ti particle in Figure 5.12 (b) shows polycrystalline grains. The powder had a volume mean particle size of $\sim 52\mu\text{m}$ according to the Malvern particle distribution in Figure 5.13.

As with previous experiments, the billet was initially sprayed without co-injection to ensure the billet was forming well and to provide a region for analysis and down-

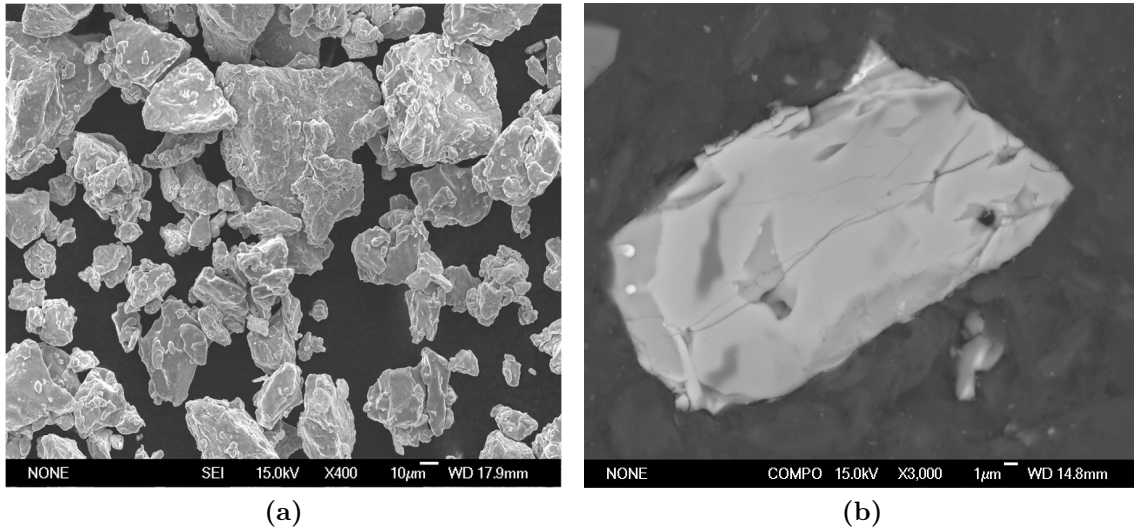


Figure 5.12: (a) Ti powder processed by the hydride-dehydride (HDH) process and (b) a cross-section of the HDH Ti powder.

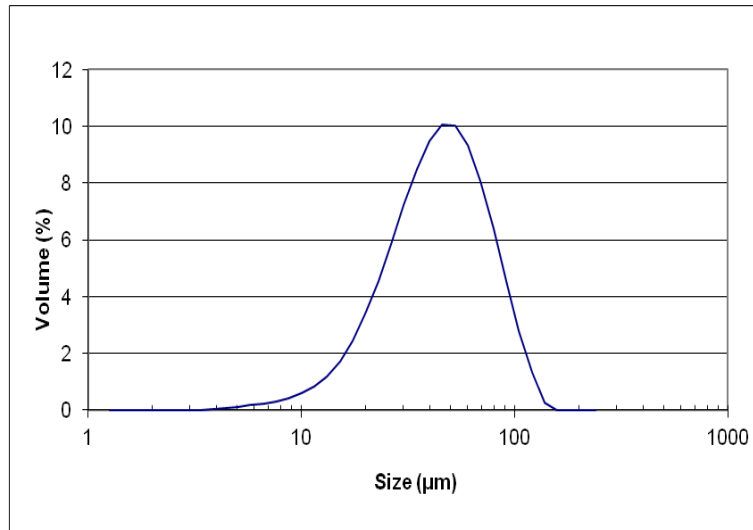


Figure 5.13: Malvern particle size distribution for Ti powder processed by hydride-dehydride (HDH) process.

stream processing without any minority phase. After 3mins of spraying and after a layer a few cms thick was formed, co-injection was turned on remotely from the control room. The Ti powder flow rate as a function of injection time is shown in Figure 5.14, indicating that the powder rate leaving the hopper (not necessarily entering the billet) was regular but slightly below the target of 0.04kg/s (corresponding to 2.5kg/min).

Figures 5.15 (a) and (b) show the billet exterior and cross-section respectively

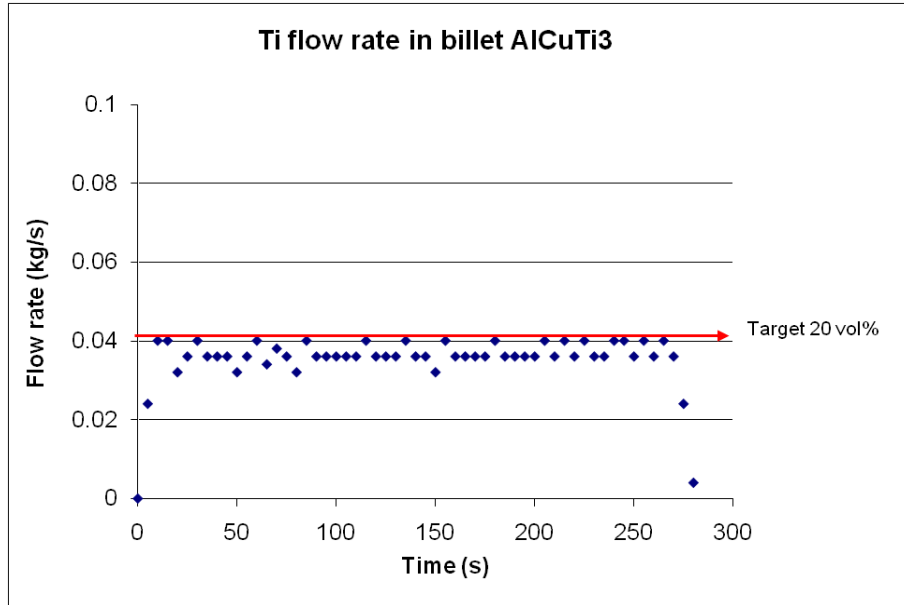


Figure 5.14: The powder flow rate of angular Ti powder injected in billet AlCuTi3, recorded by the balance beneath the hopper.

and again reveal a “cold” billet with macroscopic radial defects in the billet center. Thus, an increase in melt temperature of 100°C was insufficient compensation for the significant relative increase in powder fraction. However, at this stage, an even larger increase in superheat was not considered sensible.

Possible explanations for the porosity at the centre of the billet are: 1. The scan angle may not be wide enough so the billet centre axis is starved of hot, higher liquid fraction material (which also can happen for monolithic billets); or 2. The Al spray is scanning correctly but the cold Ti solid particles, which are comparatively large and higher density, are introduced close to the spray axis by the primary and are not deflected as readily as the molten Al by the secondary gas - therefore, the Ti tends on average to stay close to the billet axis and in this way, the centre of the growing billet is quenched by the excessive Ti. The latter interpretation is supported by the filling of the centre-line pore by large amounts of free Ti powder which simply fell out during sectioning. This localised chilling may be exacerbated in the core of the Oxford billets because of the comparatively high target volume fraction, and the need to re-optimize both the position of the spray scan mid-point relative to the

collector so that the axis centre receives more sprayed Al alloy, and possibly to the shape of the scan cycle itself.

Despite the macro-pores, there was a region of co-injection billet approximately 2cms thick below the first macroscopic defect that was free of macro-pores and could be used for downstream processing.



Figure 5.15: (a) Al-4Cu+Ti composite billet processed by spray forming (AlCuTi3) and (b) a cross-section of AlCuTi3 where the region of co-injection is visible throughout most of the billet.

ImageJ quantitative image analysis software was used to measure the Ti fraction. Eight different regions equidistant from each other through the axial direction of the billet were studied in the SEM as shown in Figure 5.16. Ten backscattered electron images were taken from within each region at the same magnification. The average Ti fraction was then plotted as a function of axial distance from the billet base, as shown in Figure 5.17. Initially in the lower part of the billet, the area fraction of injected Ti was on target at $\sim 15.2\%$ area fraction ($\sim 20\text{vol}\%$). The previously described cooling effect of the powder started to inhibit the remelting of smaller pre-solidified and mushy droplets on the billet surface, and top surface liquid fraction decreased. Although it is generally the case that incorporation occurs mainly in the atomisation zone, some solid Ti maybe incorporated directly on impact with the billet surface, and the efficiency of this process decreased as the liquid

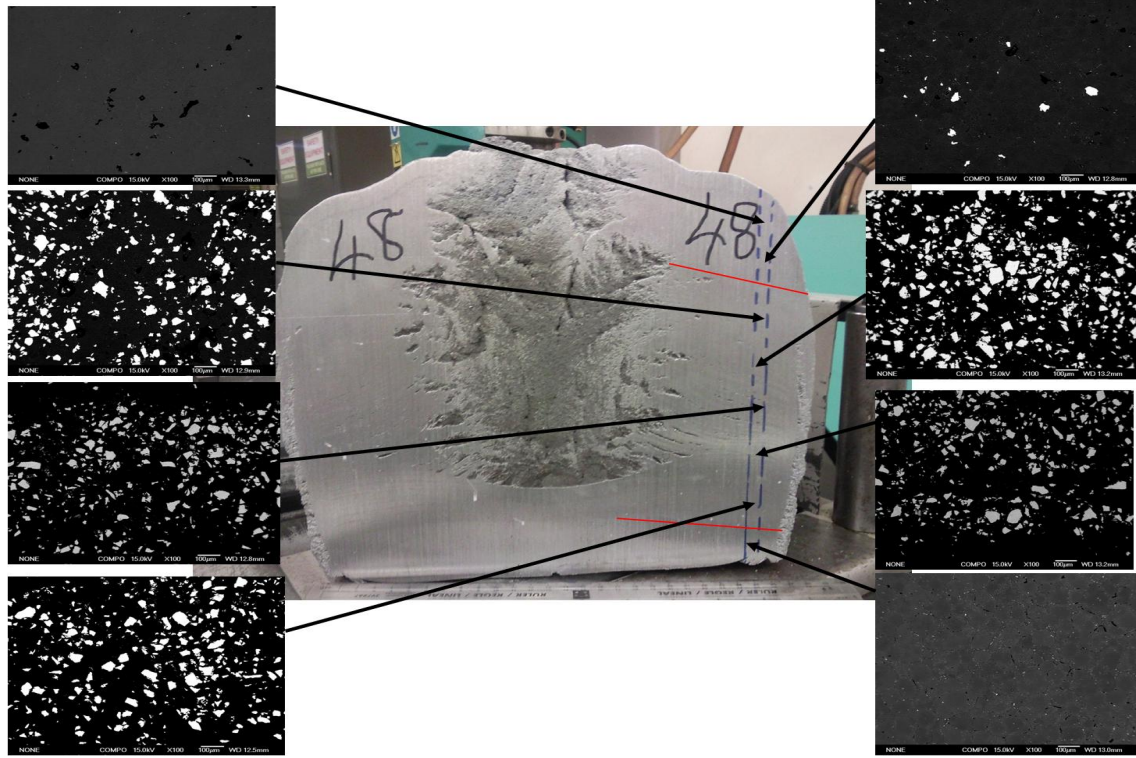


Figure 5.16: Backscattered electron images showing the amount and distribution of injected Ti powder at 8 different axial regions of the billet. The lower red line refers to the approximate region where Ti injection was started and the upper red line signifies the end of Ti injection.

fraction decreased. Therefore there was thereafter a reduction in the volume fraction to $\sim 8\text{vol}\%$. This may be exacerbated on occasion by the pulsing or “banding” previously described.

Gupta *et al.* successfully incorporated $\sim 17\text{vol}\%$ Al_2O_3 particles that were $3\mu\text{m}$ in size into an Al-Cu alloy (2519) [67] and Cantor *et al.* incorporated $20\text{vol}\%$ of SiC into aluminium alloy droplets, with particulate size ranging from $10\text{-}20\mu\text{m}$ [117]. Lavernia *et al.* co-injected $25\text{vol}\%$ SiC into aluminium alloy stream [118]. Therefore, the required volume fraction of injected powder by spray forming should be achievable. However, the injected particle diameters in this work were much larger ranging from $\sim 28\mu\text{m}$ in AlCuTi1, to $\sim 112\mu\text{m}$ in AlCuTi2. Both billets were processed under similar conditions, but the macroscopic porosity was greater in AlCuTi2.

The incorporation of a solid phase into the liquid phase can occur at three different regions: in the region of atomisation; during flight of droplets/particulate

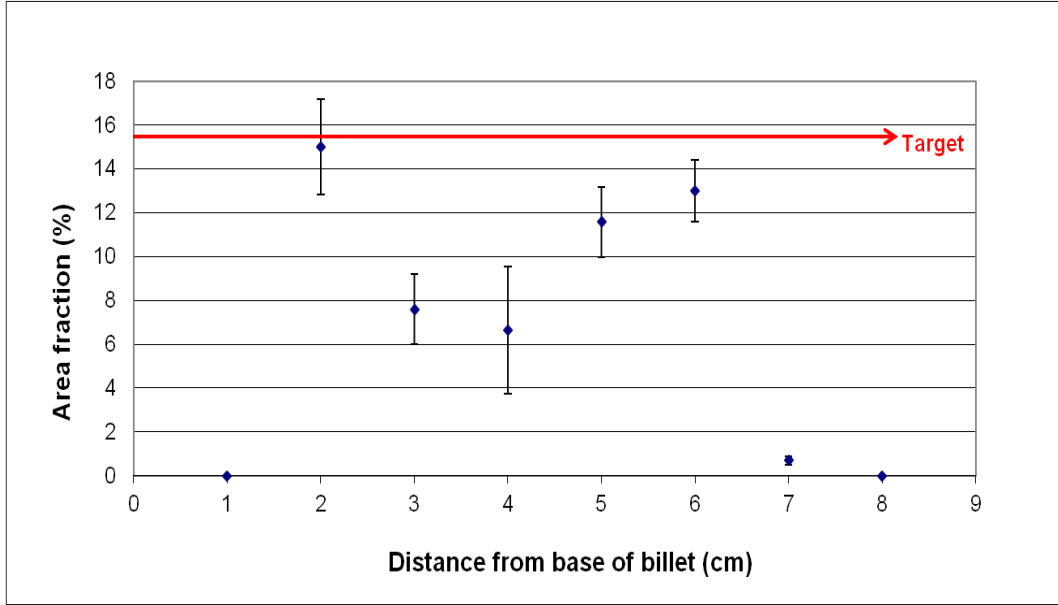


Figure 5.17: The measured area fraction of Ti powder integrated into the billet according to ImageJ analysis over 10 backscattered images taken from 8 different regions as shown in Figure 5.16.

to the billet; or at the point of deposition. Incorporation is most efficient at the region of atomisation because the gas velocity is highest and entrained particles can be accelerated into the liquid metal. One tentative explanation may be that the velocity of larger particles will be slower as they are injected around the melt stream, and overall their efficiency of incorporation is reduced because of insufficient kinetic energy to overcome the surface tension/wetting and viscous forces of the melt stream. In addition, the cooling effect of the particles increases the solid fraction of droplets impinging at the deposit surface so that there was insufficient filling of interstices between adjacent droplets leading to a porous structure. Thus, subsequent powder additions could not be incorporated into the billet and the volume fraction failed to reach levels achieved by previous researchers [12, 67, 117]. The average thermal condition on the top surface of the growing billet could be better maintained by turning off injection every ~ 30 seconds but this would lead to a strongly banded structure. Alternatively, more efficient incorporation might be promoted by sieving of powders to obtain only $10\text{-}20\mu\text{m}$ powder size range, however this would produce safety issues related to fine powder handling and excessive cost.

	Pore count	Area scanned (μm^2)	Porosity area fraction (%)
Al-4Cu base	546	29300	0.5
Al-4Cu+Ti base	18144	19700000	7.1
Al-4Cu+Ti center	32205	15800000	6.8

Table 5.1: The porosity area fraction of AlCuTi3, comparing regions of Al-4Cu with Al-4Cu+Ti.

Detailed microstructural analysis and further downstream processing was carried out using material from the region below the onset of porosity where the injected Ti volume fraction was approximately 20vol%. The porosity before and after co-injection was also analysed using Inca image analysis software in the SEM JSM6480 by Dr. Chris Salter, which could better distinguish between the three phases present: pores, matrix and Ti. Table 5.1 shows the Al-4Cu porosity was 0.5% area fraction prior to co-injection and was typical for a high quality Al-based alloy. The region of Ti injection contained $\sim 7\%$ area fraction porosity. Similarly the porosity increased as the volume fraction of ceramic particulates increased in a study carried out by Gupta *et al.* [67]. Similar levels of Al_2O_3 were injected and the fraction of porosity was slightly lower at 6.4vol% [67].

5.5 Interfacial reaction

Figure 5.18 (a) suggests that a larger fraction of Ti was incorporated into AlCuTi3 compared to the previous two experiments. The Ti particles were well-distributed in this region which was near the base of the billet. Large scale pores $30\text{-}60\mu\text{m}$ were frequently evidenced at the Ti/matrix interface. Upon closer examination, Figure 5.18 (b) reveals that a Ti/Al-4Cu interfacial reaction occurred at the increased melt temperature of 850°C . On closer inspection of AlCuTi1 and AlCuTi2, it was revealed that an interfacial reaction also occurred as shown in Figure 5.19 (a) and (b), but to a lesser degree than in AlCuTi3.

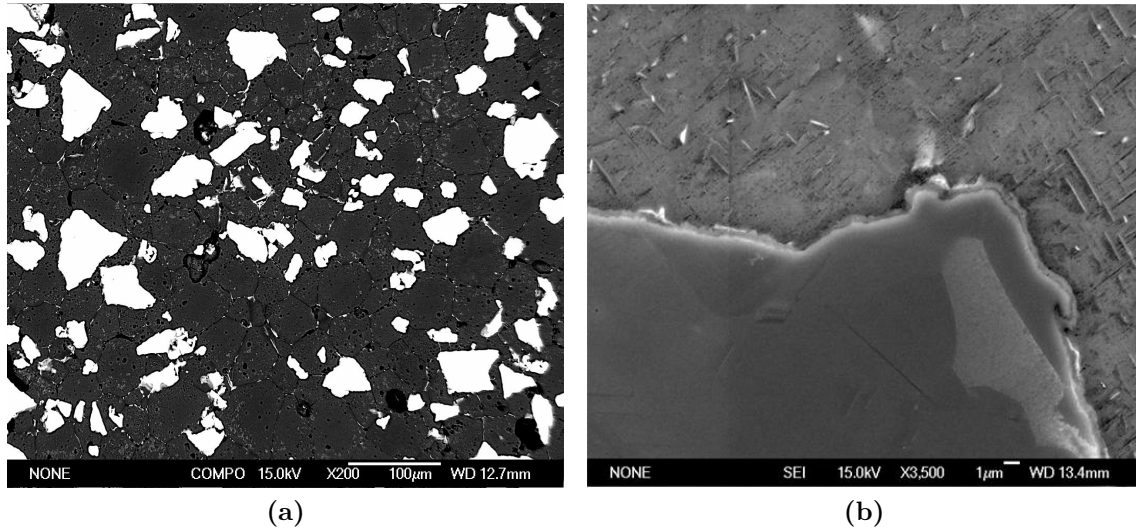


Figure 5.18: (a) Backscattered electron image of AlCuTi3 showing a large fraction of evenly distributed Ti particles and (b) at higher magnifications shows evidence of a Ti-matrix interfacial reaction.

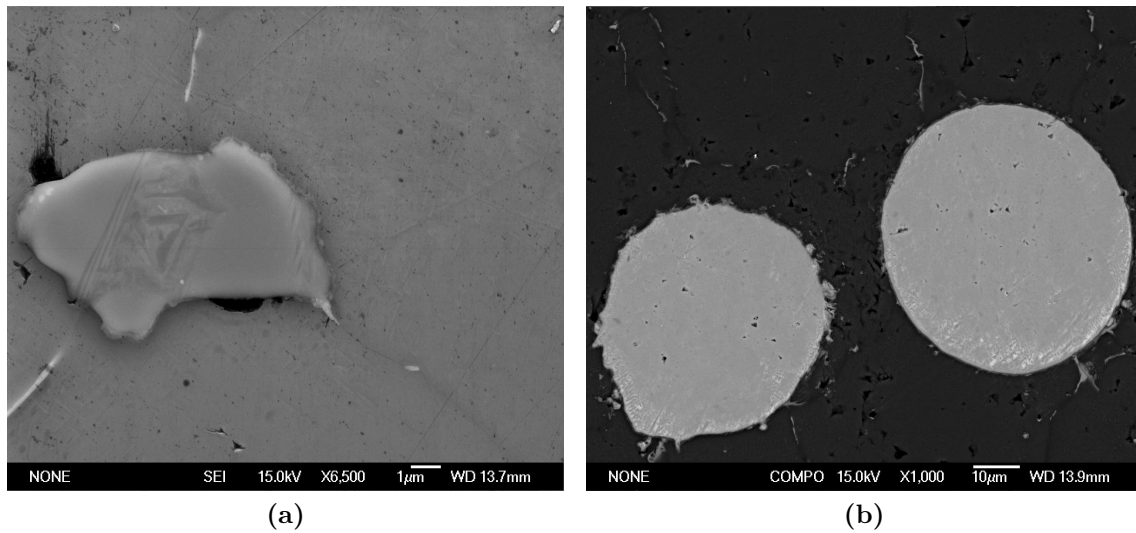


Figure 5.19: A slight Ti-matrix interfacial reaction was also evident in billet AlCuTi1 (a) and AlCuTi2 (b) both of which were spray formed at a temperature 100°C lower than in AlCuTi3.

5.6 Precipitates in spray formed Al-4Cu+Ti

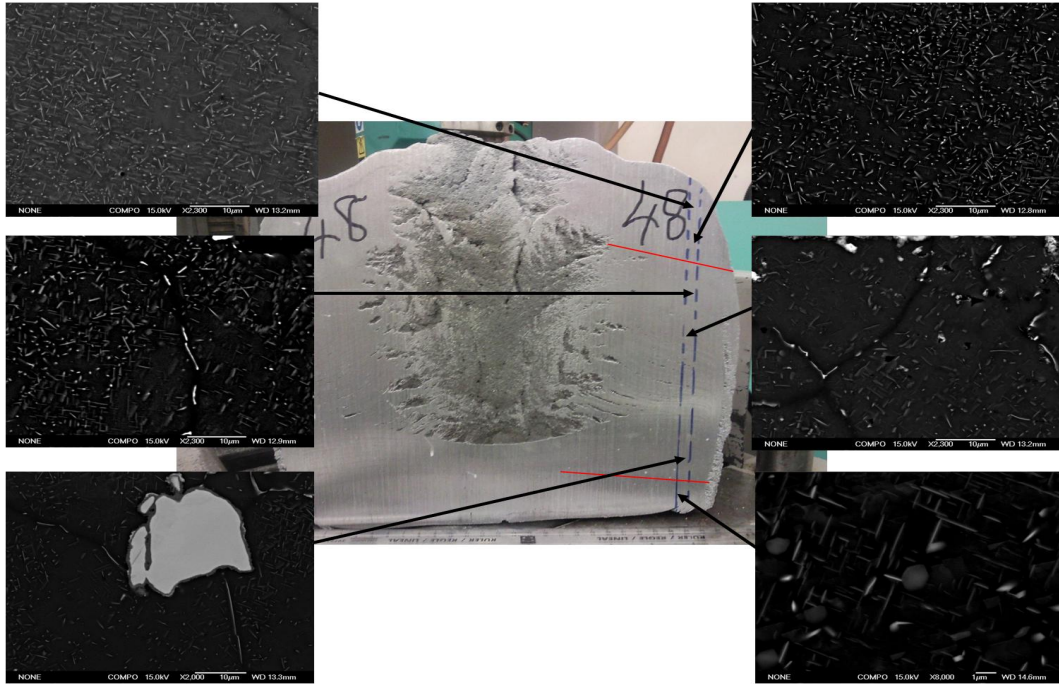


Figure 5.20: Backscattered images taken from 6 regions between the top and base of billet AlCuTi3 showing θ' precipitates in the as-sprayed microstructure.

Figure 5.20 shows evidence of θ' precipitates in the as-sprayed microstructure that extended throughout much of the billet. The bottom left figure shows θ -Al₂Cu primarily at grain boundaries and was formed directly from the liquid by the terminal eutectic reaction. Of the six backscattered images taken from different regions up through the axial direction of the billet, the precipitates appear particularly oriented in the region prior to Ti injection (bottom right).

The XRD trace in Figure 5.21 shows the (200) peak of Al-4Cu was higher compared to the Al intensity of a non-textured reference trace in the XRD database [101]. The Al-4Cu+Ti trace did not show evidence of texture, suggesting the introduction of Ti relieved the texture, as seen previously in spray formed Al-12Si+Ti. The injection of a large volume fraction of room temperature Ti powder to the molten alloy stream had a quenching effect on the Al-4Cu matrix and as the billet gradually cooled, it underwent a heat treatment similar to that of ageing. Al-4Cu at the base of the billet may also be initially quenched by the substrate, and then re-heats and

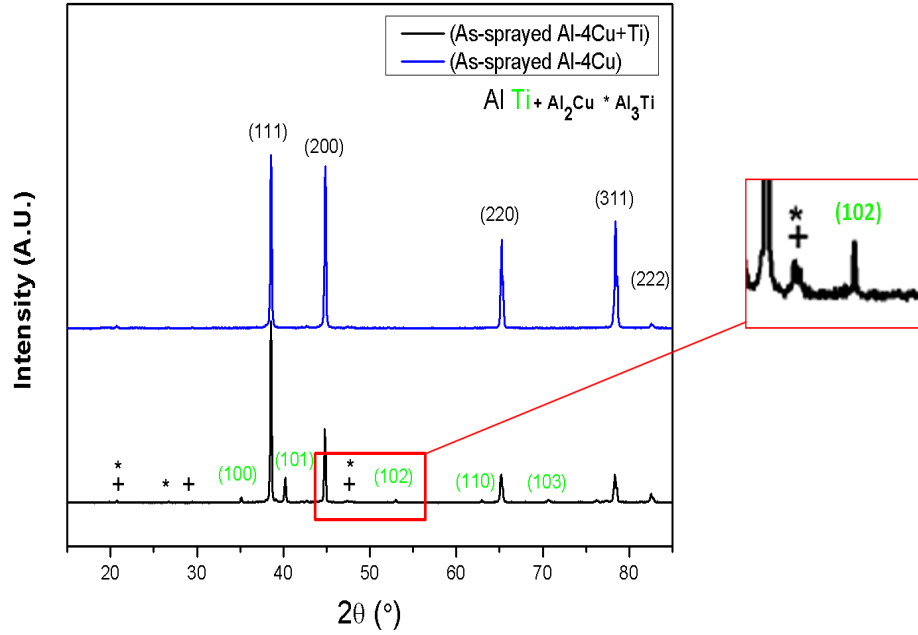


Figure 5.21: XRD traces of randomly orientated as-sprayed Al-4Cu+Ti and the base of the billet (Al-4Cu) that is less randomly orientated. The red box shows the Al_2Cu peak and Al_3Ti peak at a magnification.

“ages” as spray forming continues. The XRD trace shown in Figure 5.21 also shows Al_3Ti shown by the peaks labelled with stars.

Figures 5.22 (a) and (b) show evidence of θ' Al_2Cu precipitates also in AlCuTi1 and AlCuTi2 and again the injection of Ti had a quenching effect during billet formation, and subsequent reheating and slow cooling rates replicated that of heat treatment/ageing providing a partially aged spray formed alloy. Microhardness measurements showed an increase in hardness to $75 \pm 3\text{Hv}$ compared to unaged Al-4Cu that had a hardness of 60Hv [119]. The precipitation appeared more copious in the Al-4Cu monolithic regions at the billet base than in the Al-4Cu with Ti powder, and may simply be due to the stronger reheating effect and length of ageing experienced by the first deposited material.

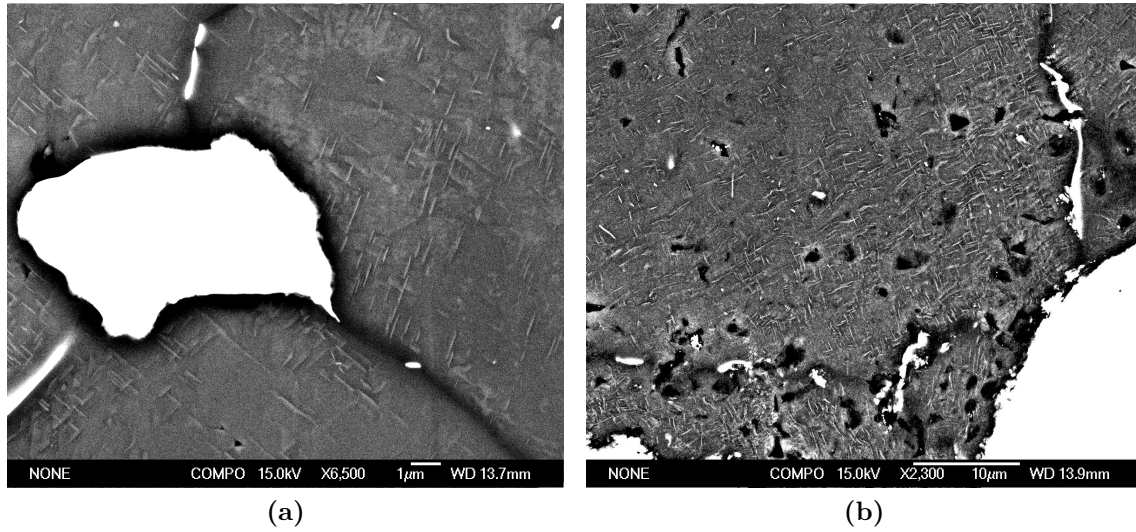


Figure 5.22: Backscattered electron images showing evidence of θ' Al₂Cu precipitates in (a) AlCuTi1 and in (b) AlCuTi2.

5.7 FIB and TEM

TEM studies were carried out to confirm the reaction phase identified by XRD. FIB was used to prepare samples for TEM analysis. A region at the interface of a Ti particle and the matrix was selected as shown in Figure 5.23 (a). Details of FIB specimen preparation were outlined in Chapter 3. The thin TEM specimen obtained from the FIB was then analysed in the TEM by Dr. Kerstin Jurkshat with the author in attendance. Figure 5.23 (b) shows a relatively low magnification TEM image of α -Al matrix and an interfacial reaction with Ti. The dark feature on the left is the Pt layer. The interfacial reaction was identified by EDX as containing Ti. Preliminary selected area diffraction (SAD) was then performed from within the Ti-rich interface zone and the resulting SAD patterns were analysed by Dr. Jurkshat and were suggested to be Al₃Ti, but further investigation on better quality samples is needed for confirmation (note: Al₃Ti was identified in the XRD patterns taken from the same sample).

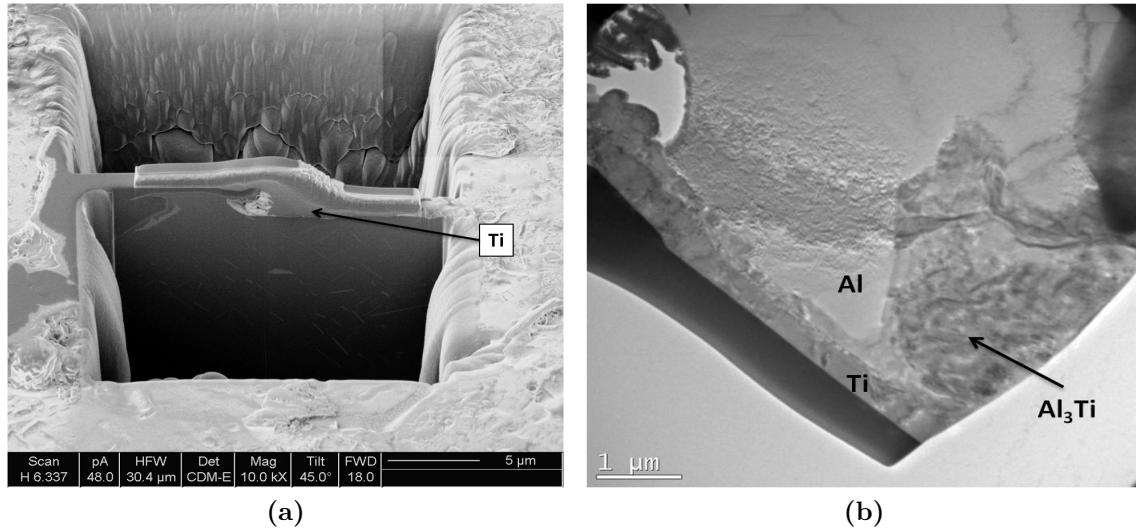


Figure 5.23: (a) A TEM specimen prepared by FIB that contained the interfacial reaction, a Ti particle, and the Al-4Cu matrix and (b) a transmission electron micrograph showing regions of relatively pure Al, relatively pure Ti and the Al₃Ti interfacial reaction layer according to EDX measurements.

5.8 EBSD

Figure 5.24 shows an EBSD image quality map and orientation map of the as-sprayed microstructure, prior to Ti injection, comprising polygonal α -Al grains with high angle grain boundaries. Although the majority of the grains were polygonal, some grains show higher energy “wavy” grain boundaries. The average grain size was 82 μm according to the EBSD data in Figure 5.25, which was similar to spray formed Al-4Cu by Grant *et al.* [120]. On Ti injection, EBSD showed a smaller matrix grain size of $\sim 51 \mu\text{m}$. Grain size reduction due to particle injection has been previously reported in spray formed metal matrix composites [121] e.g. a 67% reduction in grain size in Al-Li-SiC_p relative to the unreinforced Al-Li matrix was reported by Gupta *et al.* [73].

The injected room temperature particulate cools the atomized melt and the billet leading to shorter overall solidification times and reduced time for microstructural coarsening. The co-injected Ti particulate are not a potent nucleant for Al and are too large for this, but may indirectly act as a nucleant by enhancing dendrite fragmentation. Zhang *et al.* studied the effect of cold 3-7 μm sized particles and

found that the thermal shock effect increased for larger particles, and the critical wetting angle increased accordingly, thus increasing the nucleation density [7]. Consequently, the sudden quenching of the liquid droplets in the spray may enhance nucleation density and contribute to the reduction in grain size.

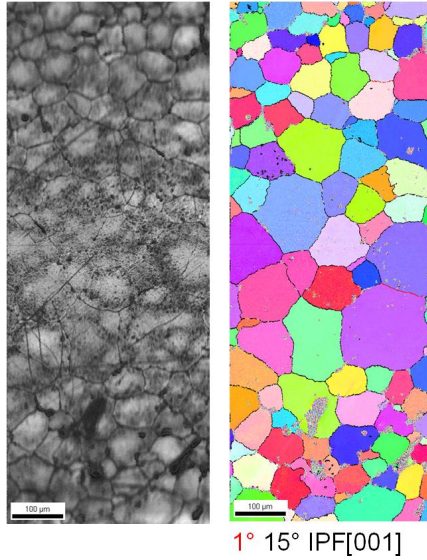


Figure 5.24: Image quality and orientation map of as sprayed matrix in AlCuTi3.

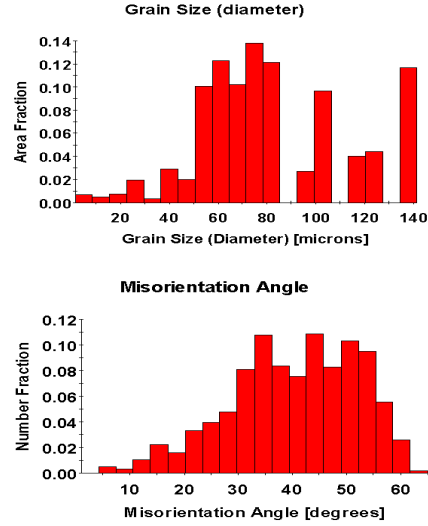


Figure 5.25: Grain size and misorientation angle distribution of as sprayed matrix in AlCuTi3.

5.9 Conclusions

A DACS powder injection pump was successfully integrated and commissioned on the spray forming facility at Oxford University. A series of powder flow studies were carried out using spherical gas atomised stainless steel and Ti-6Al-4V powder to calibrate flow behaviour and to assess safety aspects. Pump parameters including the volume of the powder chamber and the frequency of powder delivery were modified, along with length of delivery pipe to obtain the optimum powder flow rates. The frequency of powder delivery affected the flow rates more significantly than other parameters studied with a maximum flow rate recorded using a frequency of 5Hz and the best consistency of flow of $\sim 3\text{kg}/\text{min}$ was achieved at 7Hz.

An Al-4Cu alloy with co-injected Ti powder was co-spray formed for the first

time. Three Al-4Cu+Ti billets were processed at slightly different spray forming conditions and using Ti powder processed by mechanical milling, gas atomisation and the hydride-dehydride process. The resulting metal-metal composite billets were $\sim 40\text{kg}$, significantly larger than previous 100's of grammes produced by powder processing. Up to 20vol% Ti powder was incorporated into AlCuTi3. However, two problems endured. Firstly, at the centre region of the billets macroscopic voids developed usually indicative of a cold billet although dense regions of material were obtained along the billet sides and base. In such regions, prior to co-injection of Ti, the area fraction of porosity was 0.5% and in the regions of Ti injection the porosity reached 7% especially locally around groups of Ti particles. The second problem concerned variations in Ti fraction from place to place and was attributed to irregular flow of the Ti which was exacerbated when irregular particles were used.

The grain size of the Al-4Cu matrix in the co-injected region decreased by 65% relative to the matrix region due to the quenching effect of the injected particles. This quenching effect, followed by the billet slow cooling to room temperature led to the precipitation of Cu-rich precipitates, which were ascribed to θ' -Al₂Cu on the basis of their distinctive morphology. A slight Ti/Al-4Cu interfacial reaction was evidenced in AlCuTi1 and AlCuTi2. A more vigorous reaction occurred for AlCuTi3 that was co-spray formed at a higher temperature of 850°C. More studies are required to identify the optimum spray forming conditions that prevent excessive reaction but allows for sufficient liquid to reduce macro-voiding.

Chapter 6

Deformation processing of Al-4Cu+Ti

6.1 Introduction and objectives

In the second stage of processing metal-metal composites, the characteristic elongated filamentary morphology is achieved. Axisymmetric deformation processes are most commonly studied that include extrusion, swaging and wire drawing. Most previous work in the field explores hot extrusion followed by cold swaging or wire drawing as a means of deforming to high strains [9], because the original intent of the composites was to produce superconducting wires. More recently, rolling and equal channel angular pressing (ECAP) have been explored as new routes to downstream processing. Deformation processing by ECAP was carried out by the author at the University of Southampton on powder processed composites and the results were not very satisfactory. Only later it was discovered that the heavily work hardened nature of the minority phase resulted in its resistance to deformation. It has been suggested that processing by ECAP required 500 passes to produce nanometre filaments [122] but more importantly, ECAP is not considered a route to scale-up by industry. Rolling was the preferred choice since it is widely used in industry

to produce sheets, and as an established practice, it can be easily modified to allow for ARB. Although rolling restricts the size in one dimension, accumulative roll bonding, invented in 1999 by Saito *et al.* [10], alleviates this issue by providing a constant cross-sectional thickness regardless of the strain induced. Having processed the starting metal-composite material in large feedstock billets, the intention for obtaining scaled-up metal-metal composite sheet can be realised. Extruded composites were also studied in this work in order to assess and compare the microstructural evolution characteristic of both methods of deformation, although in extrusion, it is more difficult to accumulate very large strains.

6.2 Deformation behaviour of powders

30mm diameter sections 20mm in length were taken from each of the three billets (AlCuTi1, AlCuTi2 and AlCuTi3) and extruded at $\sim 520^\circ\text{C}$ to 2.5mm diameter wires at an extrusion ratio of 144:1 (equivalent true strain of ~ 5). The mechanically milled Ti powder injected into AlCuTi1 was heavily work-hardened and was somewhat resistant to further deformation despite the elevated temperature, as shown in Figure 6.1 (a). Spherical Ti powder that was processed by gas atomisation in AlCuTi2 did not undergo any measurable deformation as shown in Figure 6.1 (b), despite it being largely free from work. Ti powder processed by the hydride-dehydride route in AlCuTi3 readily underwent deformation as shown in Figure 6.2 (a). The convoluted ribbon morphology in the transverse direction, typical of axisymmetrically deformed composites [123], is shown in Figure 6.2 (b).

It may be the case that Ti powders of angular morphology more readily elongated during extrusion than spherical powders because spheres may be simply rotating in the resulting strain field during deformation, as also shown for undeformed spherical Nb in Cu-20vol%Nb composites [33]. Funkenbusch *et al.* [27] studied Cu-11wt%Mo composites processed to a strain of 7.2. The Mo minority phase was angular yet

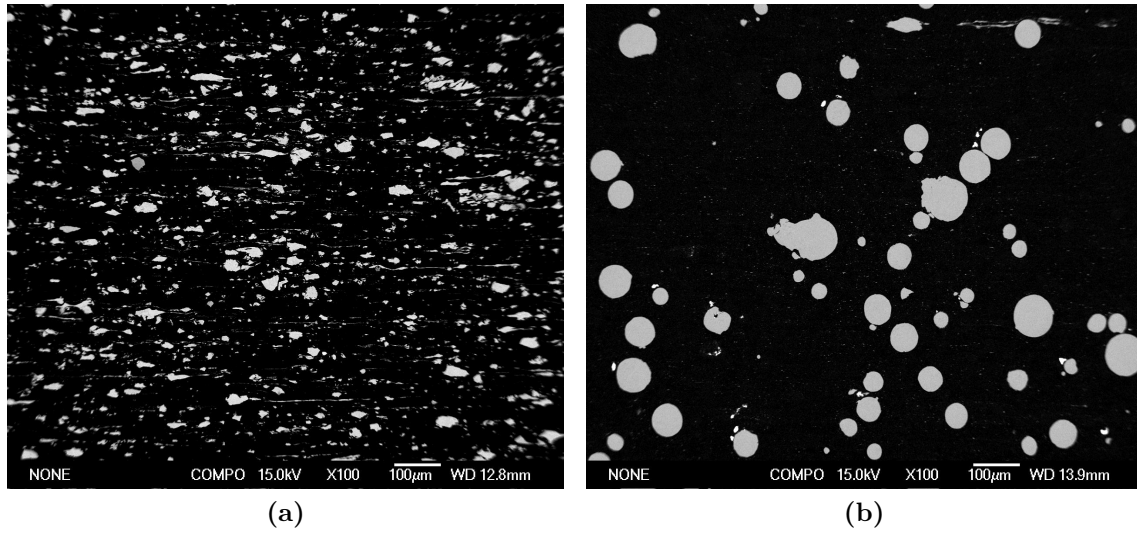


Figure 6.1: (a) Backscattered electron image of extruded AlCuTi1 in the longitudinal direction showing slightly mechanically worked elongated Ti and (b) backscattered electron image of extruded AlCuTi2 in the longitudinal direction showing undeformed spherical Ti.

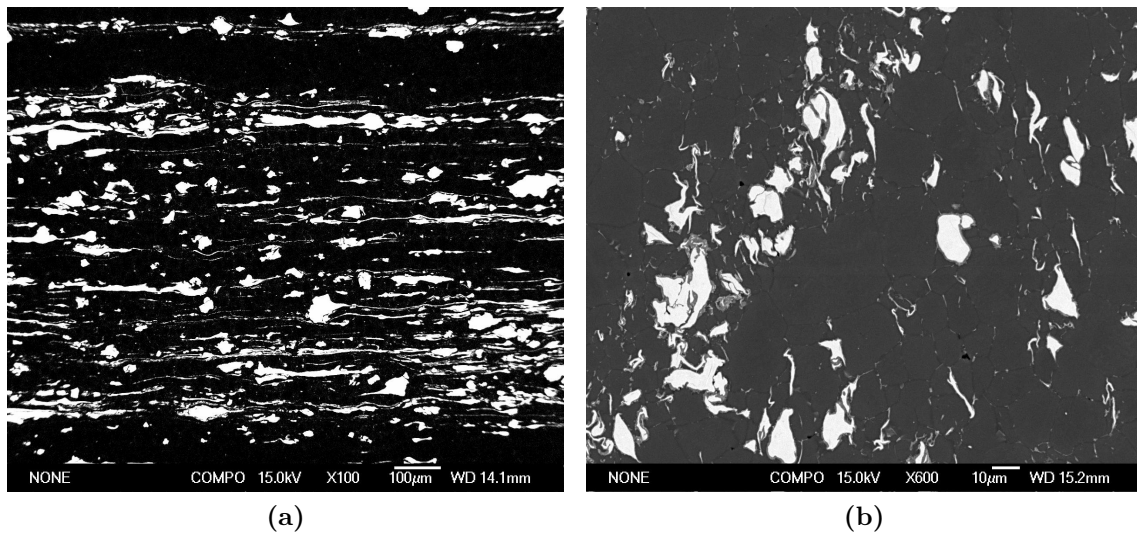


Figure 6.2: (a) Backscattered electron image of extruded AlCuTi3 in the longitudinal direction showing readily deformed hydride-dehydride Ti powder and (b) transverse direction of the extruded AlCuTi3 wire showing a convoluted Ti ribbon morphology in cross-section.

	Ti	O	Al,V,Fe,Cu	H	C	N	Hardness
Ti (mechanically milled)	95.92	0.86	0.5	-	0.18	0.06	333±34
Ti (gas atomised)	99.62	0.15	<0.5	21ppm	0.2	0.2	255±9
Ti (HDH)	99.7	0.45	-	0.015	-	-	189±20

Table 6.1: The hardness and chemical composition of Ti powders processed by mechanical alloying, gas atomisation and hydride-dehydride (HDH) all in weight percent unless otherwise stated. Note: Mechanically milled Ti composition does not add up to 100%.

some particles still retained an approximately equiaxed shape. Microhardness tests were carried out on individual Ti powders in cross-section in each of the as-sprayed billets prior to deformation. The average hardness across 25 particles is shown in Table 6.1, along with the chemical composition. For mechanically milled Ti, the chemical composition was analysed using induction coupled plasma-optical emission spectrometry (ICP-OES) at London and Scandinavian Metallurgical Co. Ltd, UK. The composition for the other Ti powders are according to the supplier nominal composition. As expected, the mechanically milled Ti had the highest hardness of $333\pm34\text{Hv}$. The spherical Ti powder had the lowest oxygen concentration but had an intermediate hardness. Despite its higher oxygen content, the HDH powder had the lowest hardness, but was not sufficiently hardened to prevent elongation during deformation.

The rest of this chapter considers billet AlCuTi₃, because despite residual problems of macro-pores and interfacial reaction, it had a reasonable volume fraction of Ti powders and these underwent deformation towards the filament morphology required for the class of metal-metal composite of interest here.

6.3 Extrusion of Al-4Cu+Ti

The majority of the Ti particles in Figure 6.2 (a) were deformed into fibres of thickness in the range $1\text{-}20\mu\text{m}$ and the majority of the fibres remained continuous, despite the extensive elongation. According to previous work, this behaviour is indicative

of recovery process in the Ti that is compatible with the rate of deformation under these conditions. Nonetheless some limited fibre “snapping” was evident and this was investigated further using sectioning and different types of imaging in the focus ion beam apparatus.

6.3.1 FIB studies

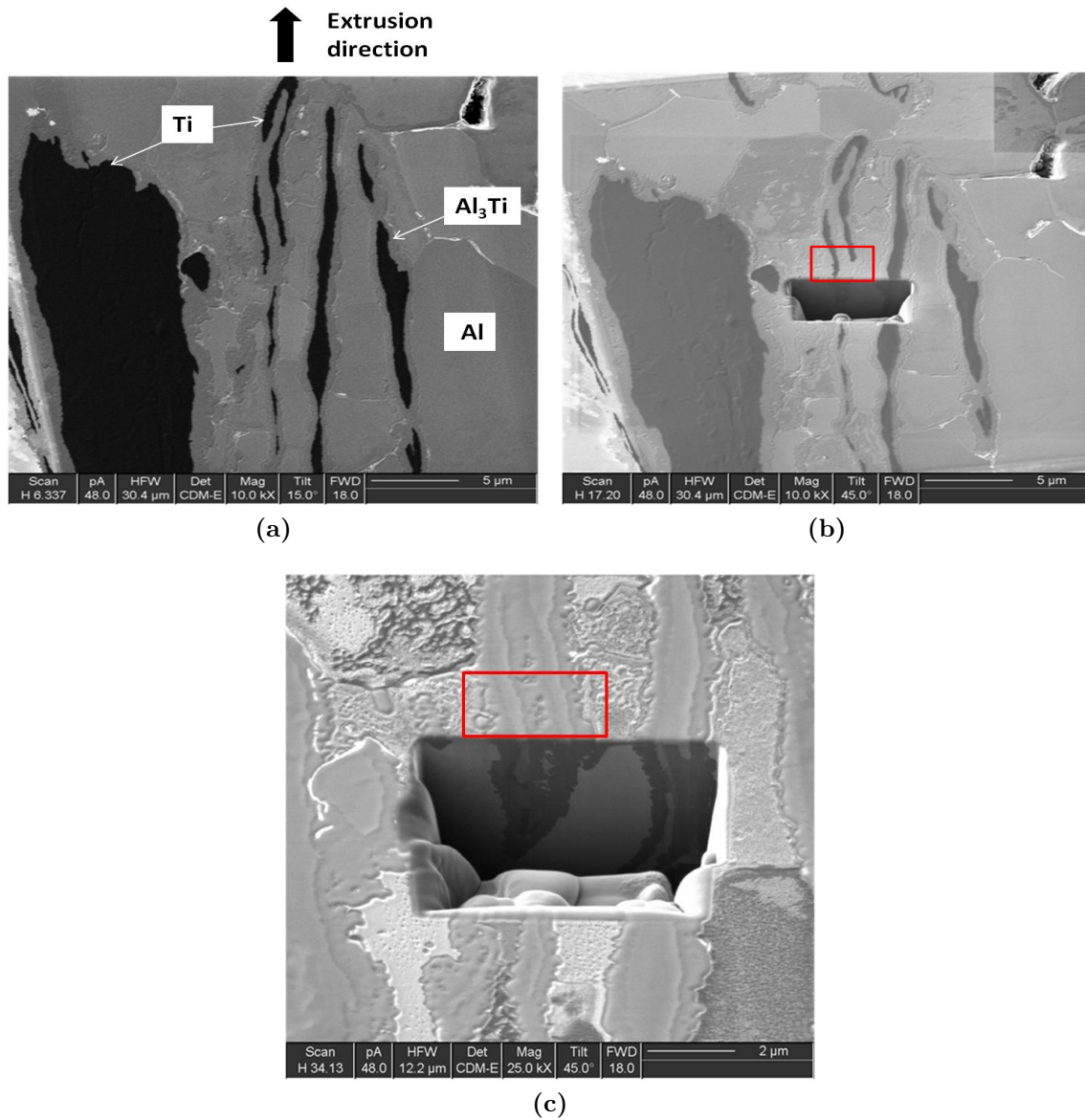


Figure 6.3: (a) Focused ion beam images of extruded Al-4Cu+Ti showing elongated Ti fibres (dark regions), α -Al matrix grains (light regions) and the interfacial reaction layer between the matrix and fibres. The red boxes show the regions (b) before milling and (c) after milling.

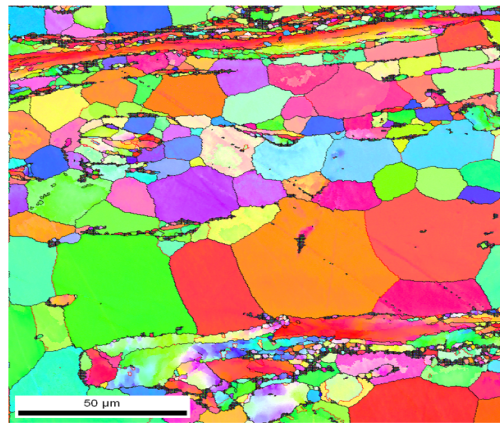
Figure 6.3 (a) shows a FIB cross-section of a Al-4Cu+Ti 2.5mm wire obtained

using ion induced secondary electrons showing apparently broken Ti fibres. A third phase at the α -Al/Ti interface was discerned and was almost certainly Al_3Ti previously detected by XRD and TEM, and ascribed to the relatively high melt temperature used for the production of AlCuTi_3 . Figure 6.3 (b) shows a section of the material removed by milling in the area of fibre breakage. Figure 6.3 (c) shows the same region after the surface has been cleared by using the ion beam to reveal that the apparently broken fibres were continuous to the sides of the milled trench (note the change in contrast of the various phases once the surface was cleared of oxide and polishing debris/damage).

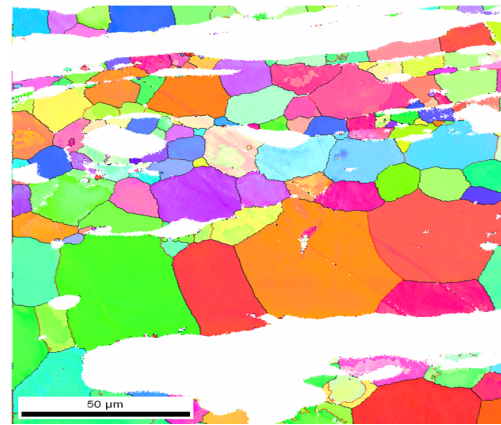
The cross-sectional view of the fibres also suggested that instead of breaking, many fibres were simply bending below the cross-section surface. Somewhat surprisingly, the interfacial Al_3Ti which was of varying thickness from Ti particle to particle, and around an individual particle, did not have a strong adverse effect on deformation behaviour. In most cases as in Figure 6.3 (a), the Al_3Ti deformed with the fibre and maintained contact along the deformed interface. This may be facilitated by the fine grain structure in the Al_3Ti .

6.3.2 EBSD studies

EBSD studies and accompanying tensile tests were carried out on the extruded 2.5mm Al-4Cu+Ti wire and the extruded 2.5mm Al-4Cu wire (matrix) to investigate any effect of the elongated Ti on the evolution of the α -Al microstructure and final mechanical properties. Figure 6.4 (a) is an EBSD orientation map along the extrusion direction of Al-4Cu+Ti 2.5mm wire showing a few highly elongated polycrystalline Ti particles and largely polygonal Al-Cu grains. In this case, EDS data collected during the EBSD scans was used to partition the Ti-rich regions from the Al-rich regions, as shown in Figure 6.4 (b). The corresponding orientation key is shown in (c). While some α -Al grains show signs of residual work, most were free of any internal crystallographic rotation (strain). Overall, the grain size was refined.



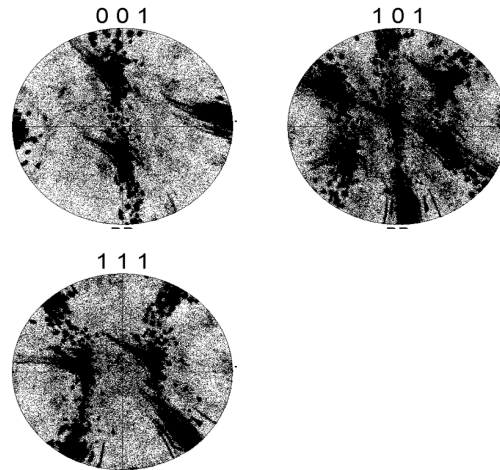
(a) Extrusion direction



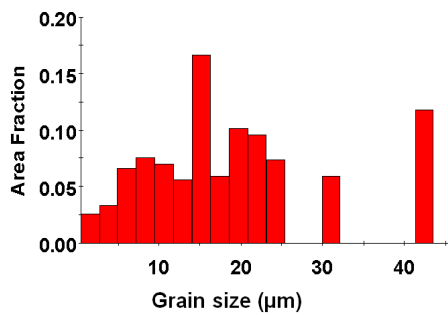
(b) EDS used to remove Ti data



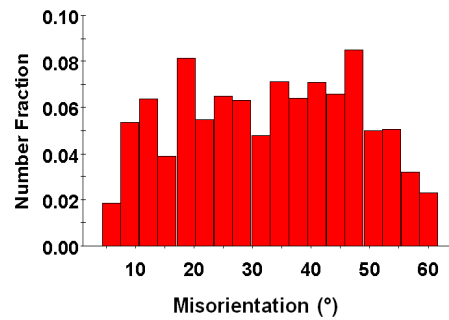
(c) Orientation Key



(d) Pole figures (radial direction at the center)



(e) Grain size distribution



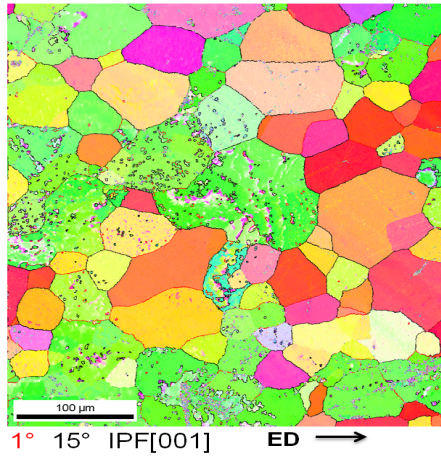
(f) Misorientation angle distribution

Figure 6.4: (a) EBSD orientation map of extruded Al-4Cu+Ti 2.5mm diameter wire showing elongated Ti grains and equiaxed Al-Cu grains in the longitudinal direction; (b) Al-rich only data points partitioned from (a) on the basis of EDS data; (c) Pole figure maps showing double fibre texture in the α -Al; (d) Grain size distribution of Al-Cu matrix; (e) Corresponding misorientation angle distribution chart of the Al-Cu matrix.

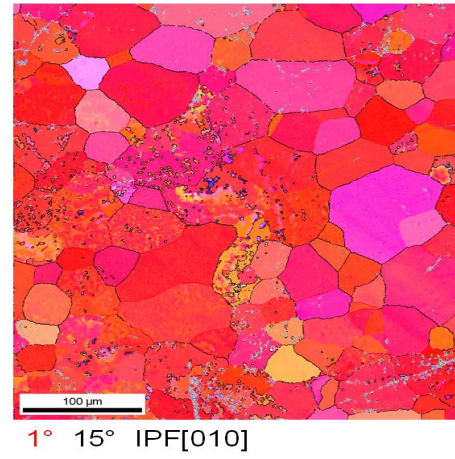
According to the pole figure maps in Figure 6.4 (d) a dual fibre texture ($\langle 100 \rangle$ and $\langle 111 \rangle$) existed in the extruded Al matrix which is commonly found in axisymmetrically deformed Al [12]. Figure 6.4 (e) shows that on the basis of EBSD, the average grain size of the Al-4Cu matrix was reduced from $51\mu\text{m}$ to $\sim 20\mu\text{m}$, while the corresponding misorientation distribution chart in Figure 6.4 (f) showed a broad spread of high angle grain boundary orientations, supportive of recrystallisation.

EBSD orientation maps of the as-extruded Al-4Cu matrix are shown in Figures 6.5 (a-b) with polygonal grains qualitatively similar in morphology to the as-sprayed morphology. The microstructure recrystallised either during or soon after deformation, removing high aspect, heavily deformed grains that were otherwise expected. Some unresolved small areas were attributed to the presence and/or precipitation of Al_2Cu -type particles. The sample taken along the extrusion direction was analysed in the EBSD. To get a complete analysis of texture, orientation maps were taken in the extrusion direction (a) and the radial direction (b) using OIM software to manipulate the data in (a). The corresponding orientation key is shown in (c). Pole figure maps were taken of (b) such that the centre of the pole figure represented the extrusion direction and are shown in Figure 6.5 (d). The pole figures, again as with Al-4Cu+Ti, show a dual fibre texture ($\langle 100 \rangle$ and $\langle 111 \rangle$) which is commonly found in axisymmetrically deformed Al [12]. A grain size distribution chart is shown in Figure 6.5 (e). The average grain size was reduced from $\sim 82\mu\text{m}$ in as-sprayed condition to $\sim 54\mu\text{m}$ after extrusion. The corresponding misorientation distribution chart is shown in (f). The majority of the grain boundaries were greater than 15° , supporting a largely recrystallized microstructure.

Using EBSD to draw strong conclusion of the texture in Al can be suspect because a large number of grains should be sampled. Here, the heterogeneous nature of the two-phase structure (three phase if $\theta\text{-Al}_2\text{Cu}$ is considered) and the high magnification used to resolve the Ti undermines the integrity of texture measurements being representative. XRD was used for bulk qualitative texture analysis. XRD



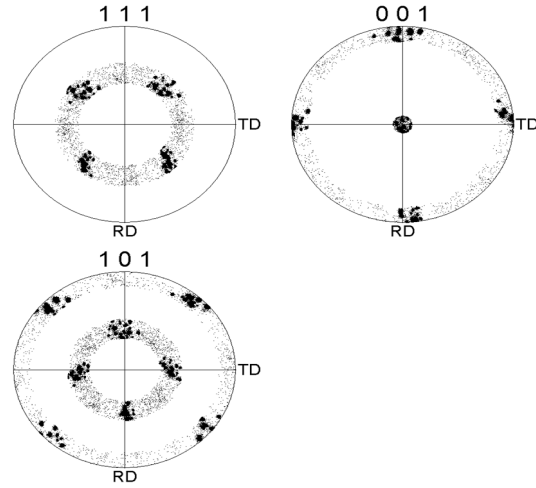
(a) Extrusion direction (ED)



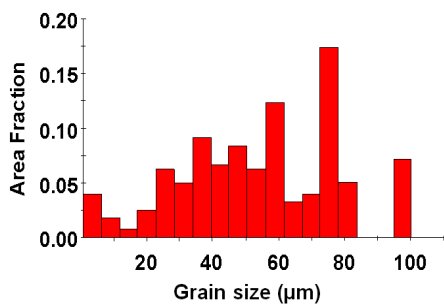
(b) Data re-oriented to show information normal to ED



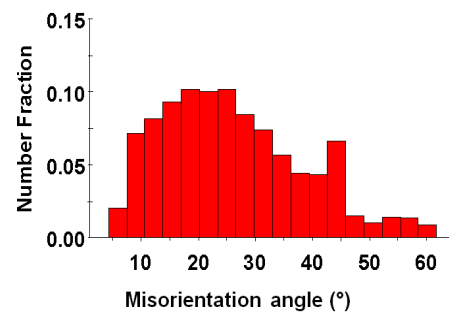
(c) Orientation Key



(d) Pole figures with ED at center



(e) Grain size distribution



(f) Misorientation angle distribution

Figure 6.5: (a) EBSD orientation maps of extruded Al-4Cu with the orientation key shown in (c); (b) Orientation map in (a) orientated to show information normal to ED; (c) pole figure maps taken from (b) showing $\langle 100 \rangle$ fibre texture and $\langle 110 \rangle$ cube texture; (d) grain size distribution chart of extruded Al-4Cu; and (e) corresponding misorientation angle distribution.

traces were taken of as-spray formed Al-4Cu+Ti, and extruded wires of Al-4Cu+Ti and Al-4Cu in the longitudinal direction as shown in Figure 6.6. Due to the small 2.5mm diameter wire only traces from sections taken along the longitudinal direction were studied by XRD. The relative intensities of certain diffraction peaks were compared to a non-textured reference trace of Al in the XRD database [101]. An Al-4Cu trace from a database could not be sourced, but Al is within close agreement for the purposes intended. Both XRD and EBSD used to analyse texture in this work determined the preferred orientation in one macroscopic direction only and thus do not provide a complete description of texture, but were considered sufficient to provide satisfactory analysis.

The ratio of peak intensities in extruded wire for the α -Al (200) and (311) reflections according to $I_{(200)}/I_{(311)}$ in Figure 6.6 were compared with that of non-textured Al from the database [101]. The α -Al peaks of as-spray formed Al-4Cu+Ti closely matched those of a non-textured sample from the database which has been added to Figure 6.6 for comparison purposes. The ratio of Al peak intensities indicated a $\langle 100 \rangle$ texture in extruded Al-4Cu, ~ 4 times stronger than random. Similarly the ratio of peak intensities for the α -Al (220) and (311) reflections indicated a $\langle 220 \rangle$ texture, ~ 3.5 times stronger than random. Combining the XRD studies with EBSD pole figure analysis in Figure 6.5 (d), there is strong evidence of fibre texture in the α -Al, and a $\langle 110 \rangle$ recrystallisation cube texture. As with Al-12Si+Ti in Chapter 4, the extruded matrix without Ti showed stronger texture. Similar findings were reported by Brokmeier for deformation processed Al-Pb composites where the majority α -Al grains developed a $\langle 111 \rangle$ fibre texture that decreased as the volume fraction of Pb increased [124].

Deformation textures in wire extruded materials are fibre textures. For fcc metals, the most commonly observed fibre texture is $\{111\}$ and $\{100\}$. It is widely known that other slip systems operate at high temperatures and particularly in metals with high stacking fault energy. Hazif observed slip on $\{110\}$, $\{112\}$ and $\{122\}$

planes [125]. The fact that Al was extruded at 520°C, might explain the $\langle 110 \rangle$ recrystallisation cube texture that existed in addition to the dual fibre texture.

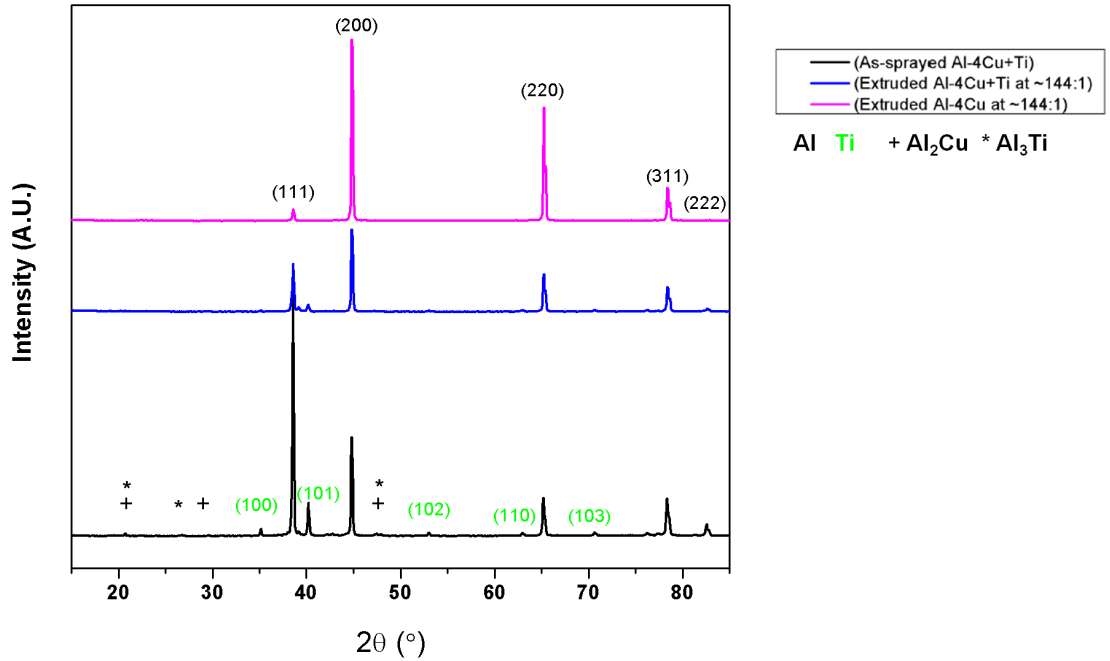


Figure 6.6: XRD traces for as-sprayed Al-4Cu+Ti, extruded Al-4Cu+Ti and Al-4Cu 2.5mm diameter wires.

FIB was used to seek more information on the microstructure of extruded Al-4Cu+Ti. Figure 6.7 (a) is an ion induced secondary electron image showing a region containing elongated Ti fibres of different thicknesses shown as near black. The Al_3Ti reaction layer appears intermediate grey along the edge of the fibres. After a minute of slow scanning of the gallium ion beam at a current of 300pA, to remove sample surface oxide and/or mechanical damage, more of the grain structure of the Ti fibres was revealed, as shown in Figure 6.7 (b). Most of the Ti grains within a single fibre were highly elongated particularly in the thinnest fibres. Again there was evidence of sub-structure development that supported recovery processes were operating.

Room temperature tensile properties of the extruded Al-4Cu+Ti 2.5mm wires are shown in Figure 6.8. Al-4Cu+Ti had a yield strength and ultimate tensile strength (UTS) of 150MPa and 315MPa respectively, with the yield strength showing a 66% increase over the unreinforced alloy and an increase in UTS of 37%. The elongation

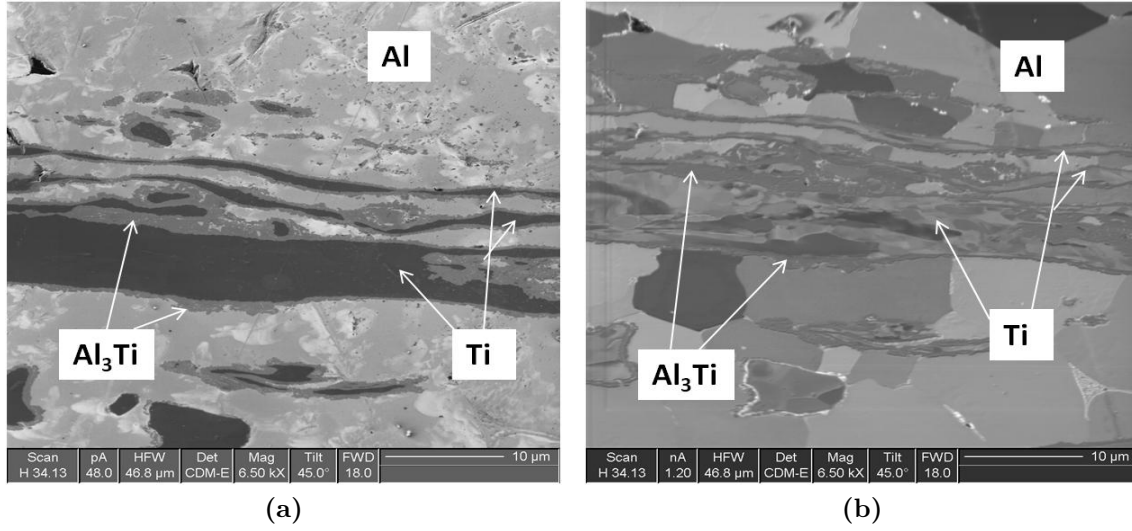


Figure 6.7: (a) Secondary electron image of extruded 2.5mm dia wire taken in the FIB microscope and (b) Secondary electron image of the same sample showing sub-surface structure after ion beam milling.

at failure was unobtainable because the wires broke in the grips during the testing, but the elongation to fracture was $\sim 15\%$ for Al-4Cu and $\sim 10\%$ for Al-4Cu+Ti.

To assess whether the strengths were similar to those predicted by a rule of mixtures (ROM) as shown in Equation 2.1, appropriate strengths for the monolithic Al-4Cu and Ti were required. Hyun *et al.* [112] studied the mechanical behaviour of commercially pure Ti at different degrees of deformation by ECAP at 410°C . After 6 ECAP passes, the Ti UTS had work-hardened to 669MPa, and this deformation extent was approximately equivalent to a strain of 4.6, close to a strain of 5 induced in the Al-4Cu+Ti composites by extrusion in this work. The Al-4Cu strength was taken as the monolithic extruded equivalent at 243MPa, and the volume fraction of Ti was assumed to be 20%. According to a rule of mixtures, the Al-4Cu+Ti UTS should be $\sim 318\text{MPa}$, which is in good agreement with experiment at $\sim 315\text{MPa}$. Therefore no “anomalous” strengthening beyond ROM was implied. However, such effects are proposed to be insignificant below a strain of ~ 7 [37]. Above this level of strain, the primary cause of strengthening is the difficulty in transmitting plastic flow between the matrix and minority phase [76]. However it should be noted that the Ti UTS used in the ROM estimate from [112] is at the top end of what might be

expected since deformation in [112] was carried out at a lower temperature and the extent (if any) of recovery was unclear, and likely to be lower than that experienced here.

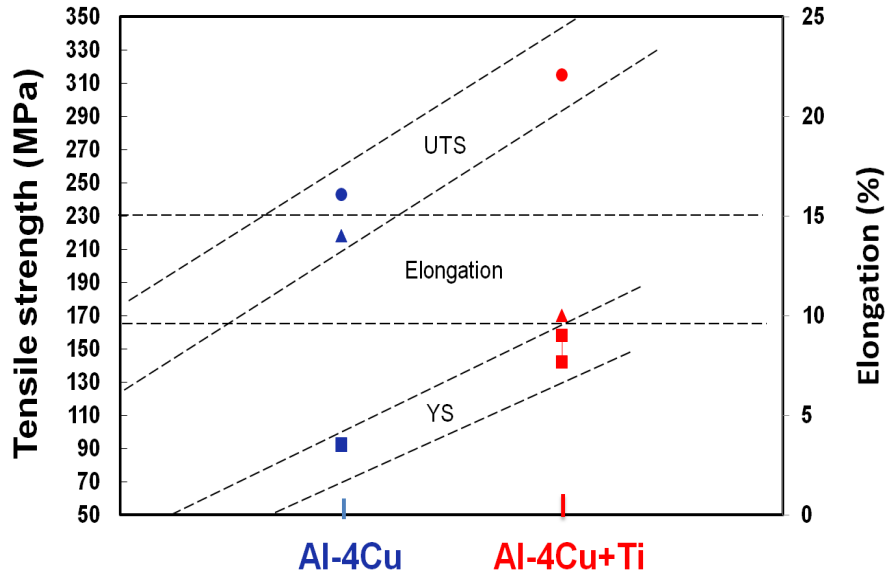


Figure 6.8: Mechanical properties of spray formed billet AlCuTi3. Sections were extruded in regions with and without Ti injection under the same conditions.

The fracture surfaces of the failed tensile specimens are shown in Figure 6.9 (a), showing necking and ductile failure in Al-4Cu. A dimpled structure was revealed at higher magnifications in Figure 6.9 (b). The fracture surface of Al-4Cu+Ti is shown in Figures 6.10 (a) with markedly less necking, while at higher magnifications in (b), the surface was less dimpled with more earing of the α -Al matrix and some limited Ti fibre pull-out and Ti/ α -Al debonding.

The Al-4Cu+Ti fracture surface was mounted in Wood's metal in cross-section and polished so that the Ti fibres in the transverse direction could be observed. Figure 6.11 (a) shows the Ti fibres (running in and out of the page) suggesting some clustering that may indicate drawing together into a spiral arrangement as the fibre rotated during extrusion and much as a rope is drawn together from fibres, and/or the clustering may reflect inhomogeneity and banding of Ti distribution obtained in

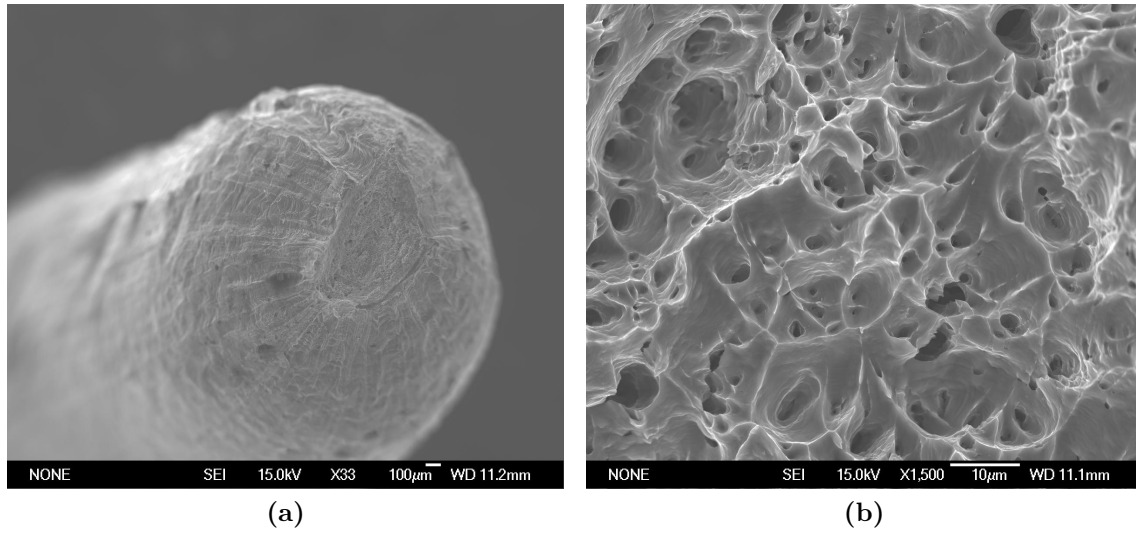


Figure 6.9: Secondary electron images of the fracture surface of extruded Al-4Cu 2.5mm diameter wire at low magnifications (a) and at higher magnifications (b).

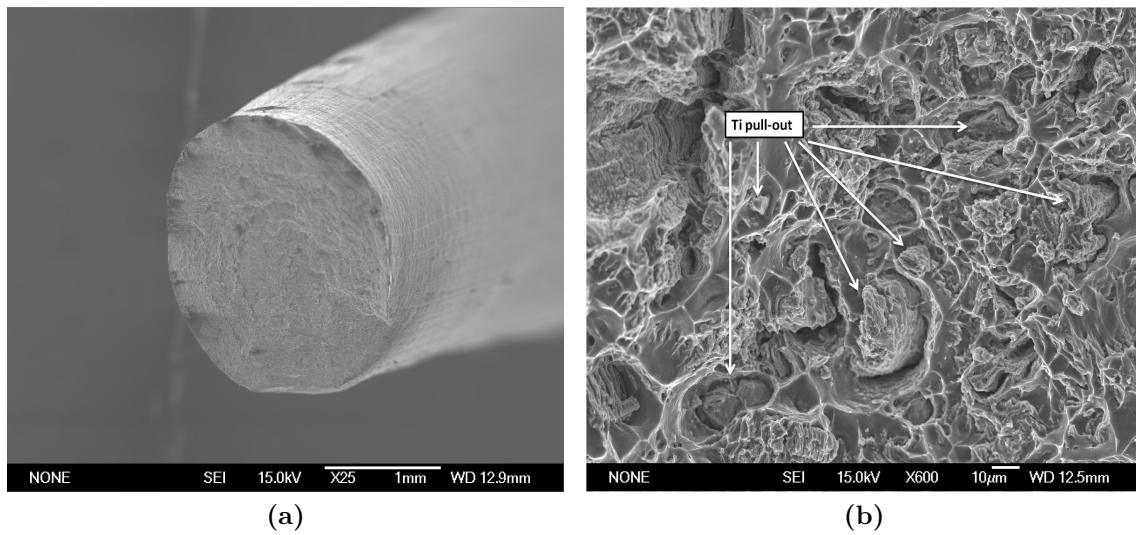


Figure 6.10: Secondary electron images of the fracture surface of extruded Al-4Cu+Ti 2.5mm diameter wire (a) and at higher magnifications (b).

the spray formed billet.

A second fractured Al-4Cu+Ti wire was investigated in the longitudinal direction, as shown in Figure 6.11 (b). There were many transverse small cracks, almost exclusively in the Al_3Ti interfacial reaction zone. These cracks were almost always arrested once they reached the Ti fibres or the α -Al matrix. However in some cases for the thinnest fibres $<5\mu\text{m}$, the cracks propagated through fibres/ribbons completely. Therefore where interfacial reaction existed or was unavoidable, fibre thickness should not approach the nano-scale since these would not provide enough resistance to propagating transverse cracks. There were few cracks in the α -Al although some pores were occasionally present that may be due to pre-fracture internal rupture in regions of inhomogeneous strain accumulation, or may simply reflect as-sprayed porosity that was not closed by extrusion because of shielding by a local high fraction of Ti.

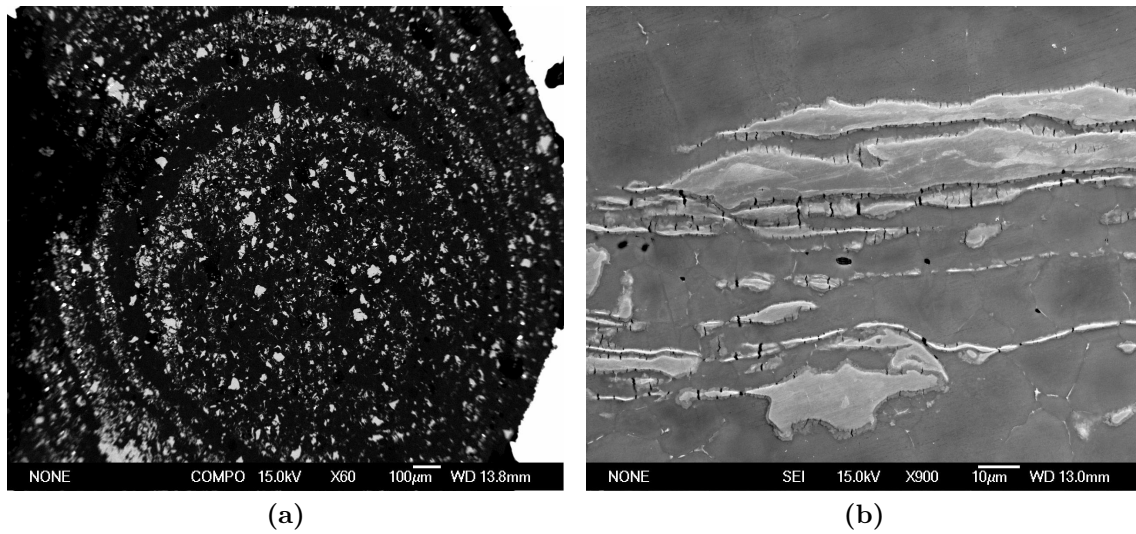


Figure 6.11: (a) Backscattered electron image in the transverse direction beneath the fracture surface of extruded Al-4Cu+Ti 2.5mm diameter wire and (b) Secondary electron image of a longitudinal section beneath the fracture surface of extruded Al-4Cu+Ti 2.5mm diameter wire.

6.4 Rolling

Rolling was carried out at the University of Warwick, with the help of Richard Keyte, using a Farmer Norton rolling mill shown in Figure 3.13. The tangential speed of the mill ranged from 0 to 23m/min and the roll diameter was 254mm, as shown in Figure 6.12. The samples for rolling were taken from the base of billet AlCuTi3 below the region of macro-porosity and were $\sim 90\text{mm}$ wide and $\sim 200\text{mm}$ long, and the associated rolling parameters are shown in Table 6.2. Each sample was heated to $\sim 370^\circ\text{C}$ for 20mins prior to rolling and at intermediate stages of rolling when cracks at the strip edges started to appear. A lubricant was used to guide the sample through the mill and every so often the rollers were cleaned to remove oxide from the surface. Rolling was carried out at slow speeds of $\sim 1\text{m/min}$ and at gradual reductions in thickness of $\sim 1\text{mm}$ per pass in an attempt to prevent any edge cracking.



Figure 6.12: The roll mill showing accumulative roll bonding of Al-4Cu+Ti.

Figure 6.13 (a) shows samples 1 and 2 (Al-4Cu without and with injected Ti) of identical dimensions prior to rolling. They were rolled under the same conditions of rolling reduction, temperature and speed so that the effect of the Ti minority phase on microstructure and mechanical properties could be assessed. Figure 6.13

Sample	Label	Initial thickness (mm)	Final thickness (mm)	Strain
Sample 1	Al-4Cu	11	1.38	2.3
Sample 2	Al-4Cu+Ti	11	1.38	2.3
Sample 3	Al-4Cu+Ti	23	0.3	6.5
Sample 4	Aged sample 3	23	0.3	6.5

Table 6.2: The basic rolling procedure for different spray formed materials. Each sample was heated to $\sim 370^\circ\text{C}$ prior to rolling and at intermediate stages of rolling. Sample 4 was aged after rolling. Sample 1 to 3 were all taken from different regions of billet AlCuTi3.

(b) shows the final length of sample 1 and 2 after accumulated rolling reductions.

A final strain ϵ of 2.3 was estimated according to [76]:

$$\epsilon = \left[\frac{2}{\sqrt{3}} \ln \left(\frac{t_0}{t} \right) \right] \quad (6.1)$$

where t_0 and t were the initial and final sample thickness respectively.

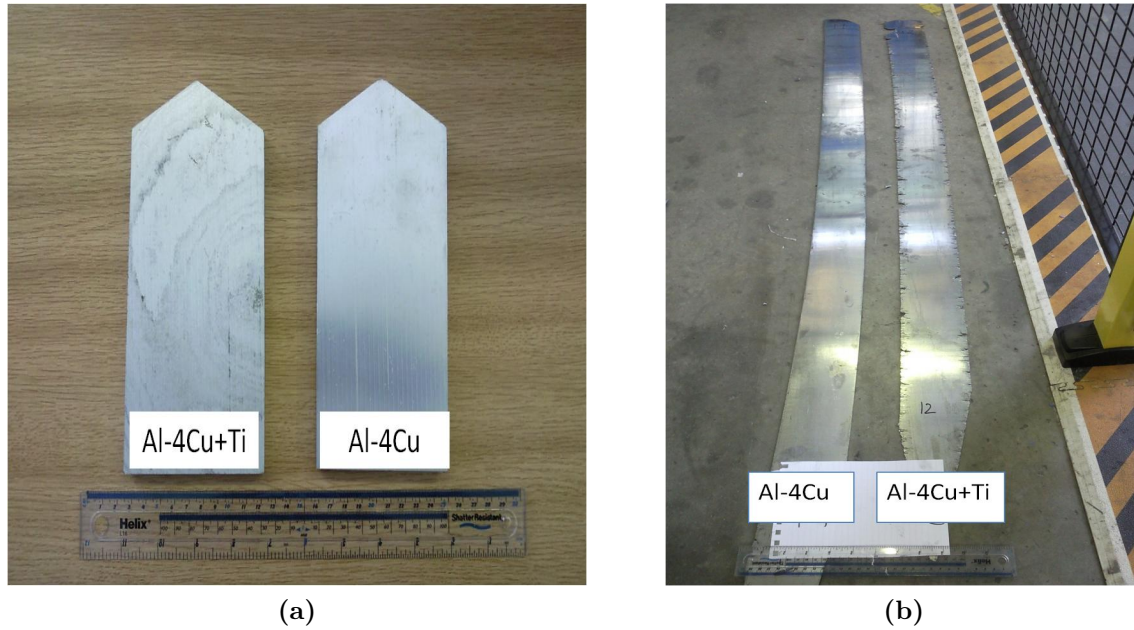


Figure 6.13: (a) As-spray formed Al-4Cu (sample 1) and Al-4Cu+Ti (sample 2) machined from the least porous basal region of billet AlCuTi3 and (b) The materials in (a) after rolling from 11mm to 1.4mm thickness in gradual reductions resulting in a final length of $\sim 1.5\text{m}$.

Sample 3 of Al-4Cu+Ti underwent the largest rolling reduction from 23 to 0.3mm at a strain of 6.5. A backscattered electron image taken along the rolling direction is shown in Figure 6.14 (a) with elongated Ti particles along the rolling direction.

Somewhat disappointingly, the extent of Ti deformation was rather low, and much less than achieved by extrusion to a similar overall strain. The reason for the lower extent of Ti deformation may be related to the deformation temperature. Extruded composites were processed at a higher temperature of 520°C that may have facilitated deformation by softening the Ti. At higher magnifications in Figure 6.14 (b) there was occasional evidence of spherical θ -Al₂Cu particles interacting with the Ti, although this was much less frequent than that observed for Si interacting with Ti in Al-12Si+Ti in Chapter 4.

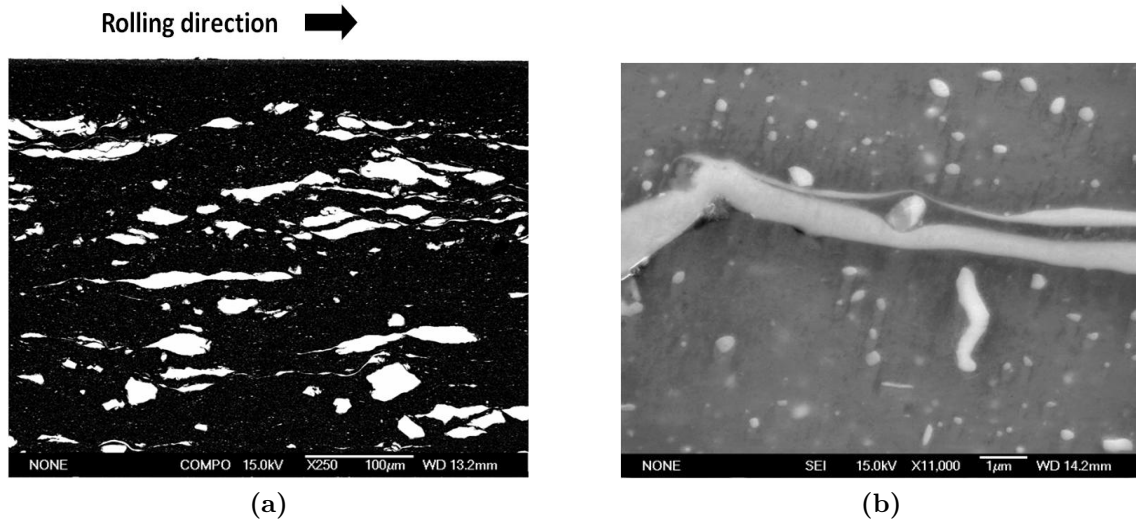


Figure 6.14: (a) Backscattered electron image of Al-4Cu+Ti rolled to a strain of 6.5, showing elongated Ti particles along the rolling direction and (b) Secondary electron image of rolled Al-4Cu+Ti showing spherical θ -Al₂Cu particles possibly playing a role in Ti deformation.

6.5 Ageing

Al-4Cu was chosen because its age hardening response provided an extra variable in optimising the transfer of load from the Al to the Ti, where it has been suggested that flow stresses should be as similar as possible. Ageing studies were performed on the as-spray formed Al-4Cu matrix using microhardness measurements. Cubes from the as-sprayed Al-4Cu matrix were firstly solutionised at 540°C for 2 hours to dissolve any θ -Al₂Cu-based precipitates, quenched and then aged at 190°C for

different periods of time.

SEM investigations confirmed that the solutionised matrix was largely free of Al_2Cu -based precipitates after a solid solution formed at 540°C . Samples were aged at 190°C for 18, 24, 44 and 72 hours. The resulting ageing response is shown in Figure 6.15, and was broadly similar to the ageing response of Al-4wt%Cu in [119]. The peak hardness was $113 \pm 8\text{Hv}$ after 190°C for 24 hours. After 44 hours ageing, the hardness gradually decreased and at this stage the material was overaged. According to Silcock, precipitation hardening would completely disappear after 100 days [119]. The original hardness of the as-spray formed Al-4Cu prior to ageing was $\sim 75\text{Hv}$, which is $\sim 15\text{Hv}$ higher than reported in literature [119]. This was because Al-4Cu was partially heat treated during spray forming. First the billet was solutionised, then quenched by the addition of significant volume fraction (20%) of room temperature Ti powder, and then the billet maintained a level of heat for a period of time that could replicate ageing.

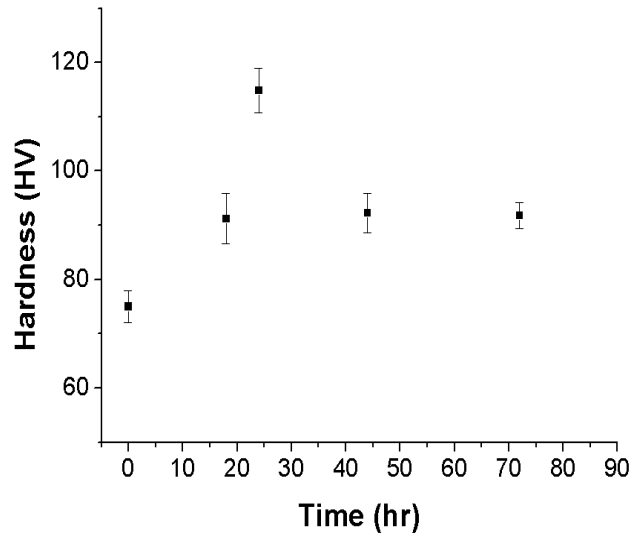


Figure 6.15: Ageing response of spray formed Al-4Cu from billet AlCuTi3 that was solutionised at 540°C for 2 hours, quenched and then aged at 190°C for 18, 24, 44 and 72 hours.

Figure 6.16 is a back-scattered electron image of the peak aged sample showing plate-like precipitates with average lengths of $\sim 1\mu\text{m}$ and thicknesses of $\sim 100\text{nm}$

aligned at right angles to each one another. This is the classic θ' -Al₂Cu precipitate peak hardness microstructure, with the tetragonal precipitates growing on the (001) faces of the Al unit cell [119,126]. There was also a weak precipitate free zone formed where precipitates coarsened on grain boundaries.

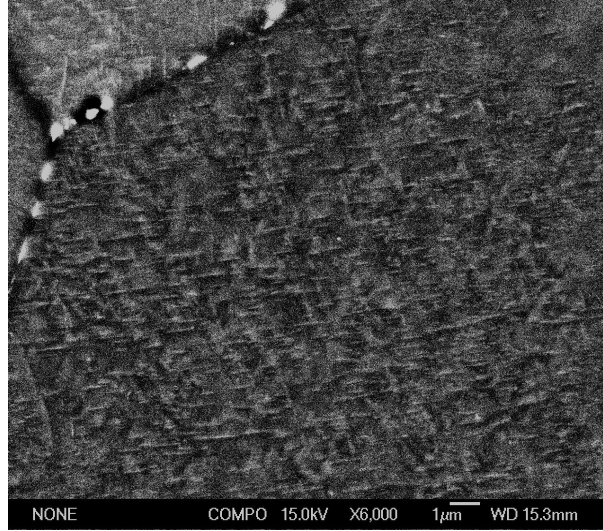


Figure 6.16: Backscattered electron image of peak aged Al-4Cu at 190°C for 24 hours showing θ' precipitates.

A section of Al-4Cu+Ti for rolling was heat treated as described above with the intention that the resulting less deformable α -Al matrix would encourage Ti deformation. However due to time constraints and restricted access to the rolling mill, it was not possible to roll peak aged material. Nevertheless the findings on peak hardness of Al-4Cu were useful for ageing material *after* rolling.

Figure 6.17 shows the mechanical properties of rolled Al-4Cu+Ti compared to the identical sample that was solutionised, quenched and aged at 190°C for 24 hours after rolling. The rolling conditions were outlined in Table 6.2. The unaged alloy broke in the grips during testing so that elongations may have been underestimated. The yield and ultimate tensile strength after ageing reduced by 41% and 9% respectively. Hardness measurements confirmed a deterioration from 119 ± 10 Hv unaged (and significantly higher than as-spray formed at 75 ± 3 Hv) to 107 ± 2 Hv.

Precipitation behaviour has been shown to be different in severely deformed Al-2wt%Cu compared with undeformed material [86] where Al-2Cu deformation

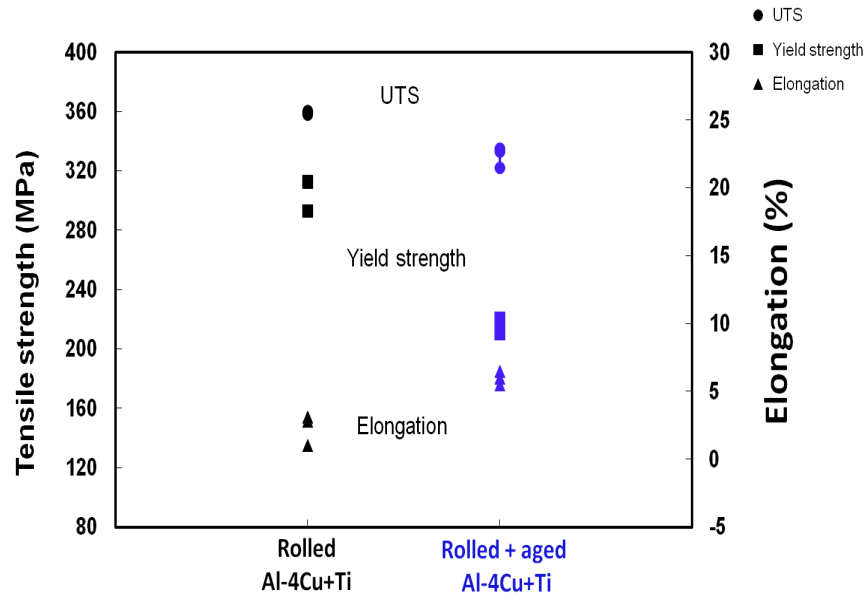


Figure 6.17: A comparison of the mechanical properties of Al-4Cu+Ti rolled to a strain of 6.5, without and with post-roll peak ageing.

processed to 6 ARB cycles had a hardness of 115Hv; then after ageing at 190°C, hardness decreased to 75Hv. In this case the relief of work-hardening and reduction in strength by annealing was more dramatic than the increase in strength due to precipitation hardening. In addition, the kinetics of hardening can be dramatically altered by the presence of work, so that the target peak aged condition from the ageing studies was actually an overaged condition when the starting alloy is heavily worked.

According to Tsuji [86], precipitation is also enhanced in ultra fine grained materials processed by ARB due to the increased number of grain boundaries that act as nucleation sites and provide high speed diffusion paths in the material. It is very likely that additional ageing studies on severe deformation processed Al-Cu is required to identify optimum time-temperature combination for precipitation of θ' -Al₂Cu under these conditions.

6.6 Accumulative roll bonding

Many ARB trials were carried out initially using Al-4Cu from billet AlCuTi2 in an attempt to develop roll conditions for bonding. The roll mill gauge was set to provide 50% reduction at each pass. After surface preparation, the sheets were heated in the oven at 100°C for ten minutes, but bonding between sheets was not achieved, probably because the rolling mill speed of 8m/min was too fast to provide sufficient time for bonding. However a speed of 1m/min worked well for preliminary bonding studies of Al-12Si+Ti at the University of Buenos Aires, and was then adopted here. That rolling procedure used preheating at 200 °C for 10min, but also did not improve bonding on the Warwick mill. However, using a pre-heat at 300°C for 10min worked well, and was then applied to Al-4Cu from billet AlCuTi3 (sample 1). However, the surfaces to be bonded pulled apart on exiting the rollers. Although the Al-4Cu did not bond between sheets, it nonetheless underwent deformation as Al-4Cu+Ti similarly deformed under 1 preliminary ARB cycle. Again, due to time constraints on the rolling mill, it was not possible to continue working on Al-4Cu from billet AlCuTi3 despite successful bonding already achieved for AlCuTi2.

To make the best of available rolling time, efforts were subsequently focused on Al-4Cu+Ti from billet AlCuTi3. Using a preheat of 300°C for 25 minutes and a ~50% reduction per pass, bonded sheet was produced, as shown in Figure 6.18. The underlying reason for more ready bonding in the presence of the Ti particles could not be deduced. A possible explanation might be that Ti has a lower thermal conductivity and a higher specific capacity than Al and it retained heat for longer and made bonding easier. After each roll cycle, the bonded sheets were chopped in half and prepared as outlined above, and stacked ready for re-rolling. The estimated load of the rolling mill during ARB was ~60 tonnes. After 2 ARB cycles, the sample was trimmed along the edges to remove cracks. During the 3rd ARB cycle, the sheets pulled apart laterally as shown in Figure 6.18 so no further ARB cycles were carried out. The exact same ARB procedure was repeated on a second set of rolled AlCuTi3

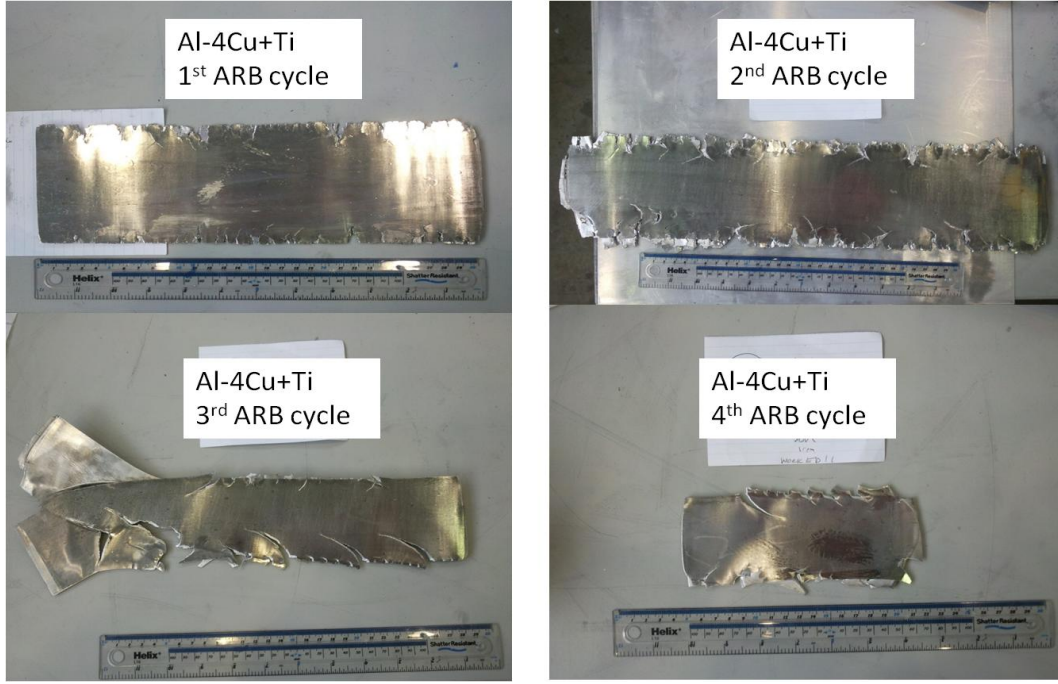


Figure 6.18: Al-4Cu+Ti was accumulative roll-bonded to 1, 2, 3 and 4 cycles.

sheets. Prior to the 4th ARB cycle, the sheets were heated for a longer duration of 40 minutes in order to relieve some of the accumulated plastic strain so as to increase chances of bonding. Bonding was successful but now the resulting sheet as shown in Figure 6.18 was too small for further ARB processing.

Based on Equation 6.1, the degree of deformation ϵ is calculated by the following equation [76]:

$$\epsilon = \left[\frac{2}{\sqrt{3}} \ln(2) \right] \times n = 0.8n \quad (6.2)$$

where n is the number of ARB cycles. The equivalent plain strain calculation assumes no lateral spreading and a reduction of 50% per ARB cycle ($(t_0/t)=2$). Table 6.3 shows the resulting calculated total reduction and strain corresponding to each ARB cycle.

Figure 6.19 (a) shows a backscattered electron image of Al-4Cu+Ti after 1 ARB cycle ($\eta \sim 3.1$) at low magnification. The Ti minority phase was only slightly deformed along the extrusion direction, and there were many undeformed near-

Sample	Label	Total reduction (%)	True strain	Total true strain (+2.3*)
1 ARB	5	50	0.8	3.1
2 ARB	6	75	1.6	3.9
3 ARB	7	87.5	2.4	4.7
4 ARB	8	93.8	3.2	5.5

Table 6.3: The total reduction and strain after each ARB cycle applied to Al-4Cu+Ti material. *2.3 is the strain previously induced from rolling prior to ARB.

spherical Ti particles: spherical particles have already been shown not to deform readily into fibres. Perhaps Ti in the extruded wires more readily deformed into fibres because the extrusion temperature of 520°C softened the reaction layer and speeded up recovery in the Ti so that the flow stresses of both phases were similar enough to allow co-deformation. Although pre-heating was also used in the rolling studies, the section thickness was sufficiently small that by the time the sheet was transferred to the cold, room temperature equipment - including the rolls - it is certain much of the preheat temperature will already be lost.

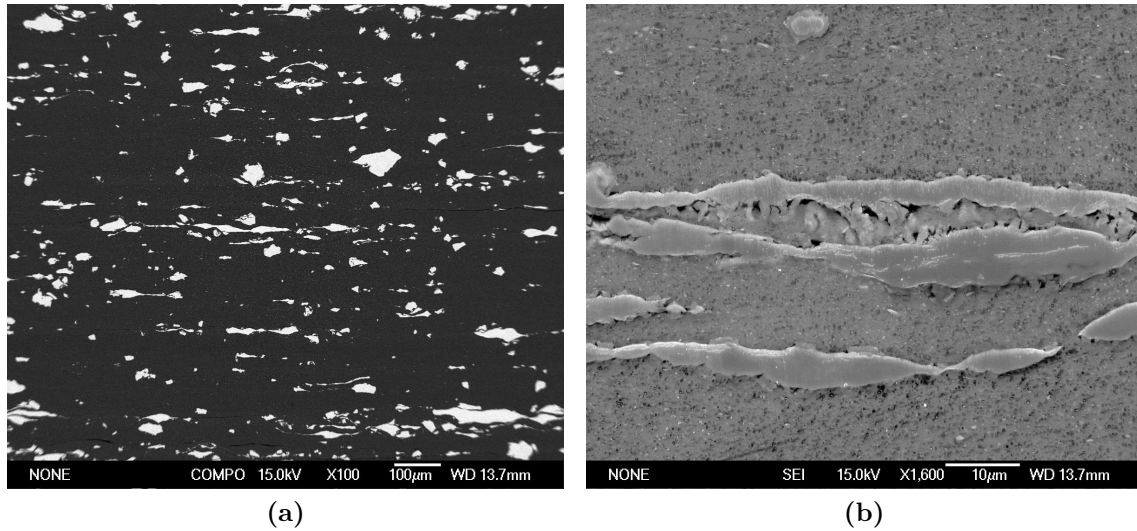


Figure 6.19: (a) Backscattered electron image of Al-4Cu+Ti after 1 ARB cycle and (b) Secondary electron image at higher magnifications of Al-4Cu+Ti after 1 ARB cycle showing elongated fibres and cracking of the Al_3Ti interfacial reaction layer.

Figure 6.19 (b) is a secondary electron image at higher magnifications of Al-4Cu+Ti after 1 ARB cycle showing elongated Ti particles and cracking of the Al_3Ti interfacial reaction layer leaving some micro-porosity.

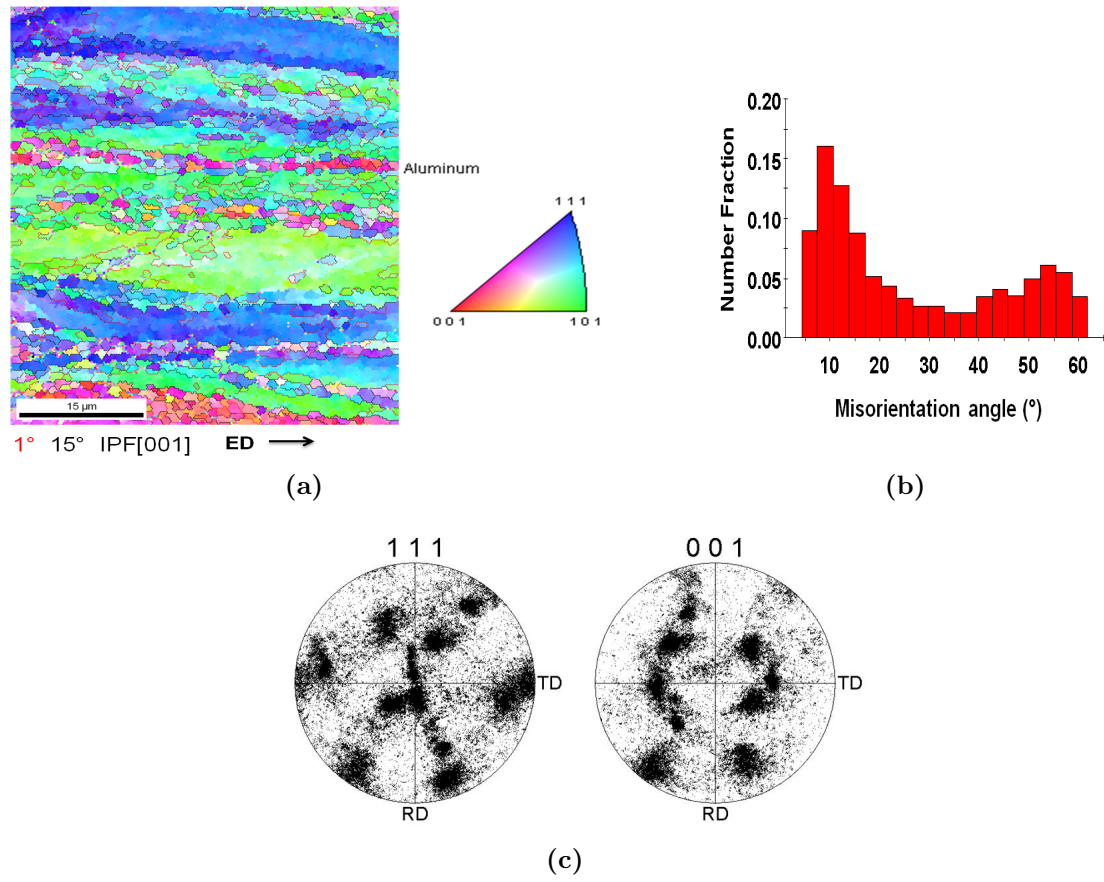


Figure 6.20: (a) EBSD orientation map of the α -Al matrix in Al-4Cu after 1 cycle of ARB; (b) corresponding misorientation angle distribution of Al-Cu after 1 ARB cycle for the grains in (a) and (c) corresponding pole figure maps showing a preferred orientation in Al-Cu matrix grains for the grains in (a).

EBSD was carried out on a longitudinal section of the Al-4Cu matrix in Al-4Cu+Ti that underwent 1, 3 and 4 ARB cycles. Figure 6.20 (a) shows an EBSD orientation map of the α -Al matrix after 1 ARB cycle, with the rolled Al-4Cu microstructure very different to the recrystallised polygonal microstructure after extrusion. Low angle grain boundaries were defined as those between 1° and 15° (coloured red) and high angle grain boundaries were those above 15° (coloured black). The microstructure comprised a mixture of highly elongated α -Al grains (5-10 μ m thickness) with substantial internal sub-structure (strain) decorated in many cases by more equiaxed grains as small as 1 μ m. The matrix microstructure was typical of ARB processed Al-based materials [127]. The majority of the grain boundaries had relatively low angle misorientations as shown by the distribution in Figure 6.20 (b) with a bimodal distribution and peaks at $\sim 10^\circ$ and 55° . The corresponding pole figure map in Figure 6.20 (c) shows evidence of texture in the Al-4Cu grains. By measuring the angles between clusters of points (representing planes) and by careful comparison to pole figures found in [128], the pole figures in (c) represented a $\{110\} \langle 211 \rangle$ brass texture, but there may well be other textures present in this material as well. An ODF using XRD is necessary to identify whether other rolling textures are present.

Again, XRD was used for bulk qualitative indications of texture. XRD traces were taken of as-spray formed Al-4Cu+Ti, and extruded wires of Al-4Cu+Ti and Al-4Cu in the longitudinal direction as shown in Figure 6.6. The XRD traces in Figure 6.21 compare the relative intensities of as-sprayed Al-4Cu+Ti and rolled to 1 ARB cycle. The as-sprayed trace was inserted to provide a visual comparison for a largely non-textured trace, however the Al trace from the database [101] was used to quantify the degree of texture. A ratio of peaks intensities for the α -Al reflections according to $I_{(220)}/I_{(311)}$ indicated a $\langle 220 \rangle$ texture in the α -Al, ~ 2 times stronger than random. Therefore, XRD supported evidence from EBSD of a $\{110\} \langle 211 \rangle$ brass rolling texture in Al-4Cu. There may be a mixture of textures in rolled Al-

4Cu+Ti. Trybus *et al.* processed Cu-20vol%Nb metal-metal composites by rolling up to strains of 7, and similarly reported $\{110\} \langle 211 \rangle$ texture in fcc Cu [76].

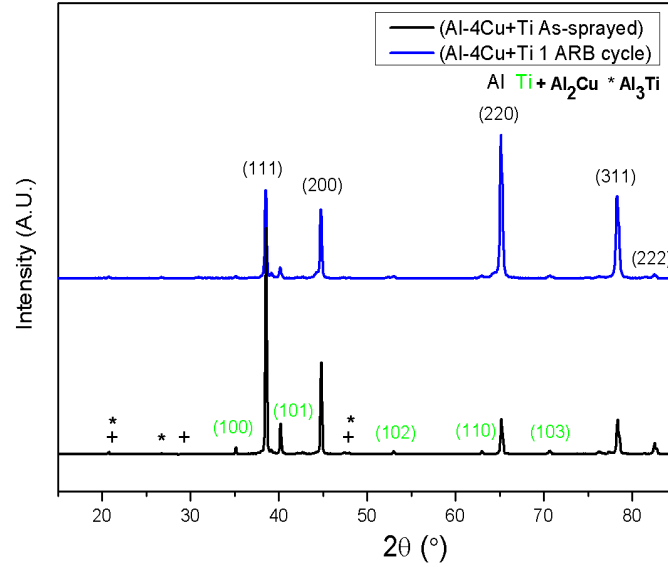


Figure 6.21: XRD traces of Al-4Cu+Ti after 1 ARB cycle compared to randomly orientated as-sprayed Al-4Cu+Ti.

Figure 6.22 (a) is a backscattered electron image of the longitudinal section from Al-4Cu+Ti after 3 ARB cycles. The Ti phase did not noticeably elongate further with respect to the first ARB cycle, and rolling was not as efficient as extrusion in providing fibrillar minority phase under the conditions so far explored. Residual porosity remained after ARB, and became elongated as shown in Figure 6.22 (b). It was sometimes difficult to distinguish interfacial de-bonding between sheets. While some Ti particles were heavily elongated to fibres, many others were much less deformed. Possible explanations for this include the near spherical morphology of these particles, that are unfavourable for deformation processing.

Figure 6.23 (a) shows an EBSD orientation map of the Al-4Cu matrix after 3 ARB cycles. The region scanned was the same area as for 1 ARB cycle so the area fraction of grains and their misorientation distribution could be compared. Low angle grain boundaries were again defined as those between 1° and 15° (coloured

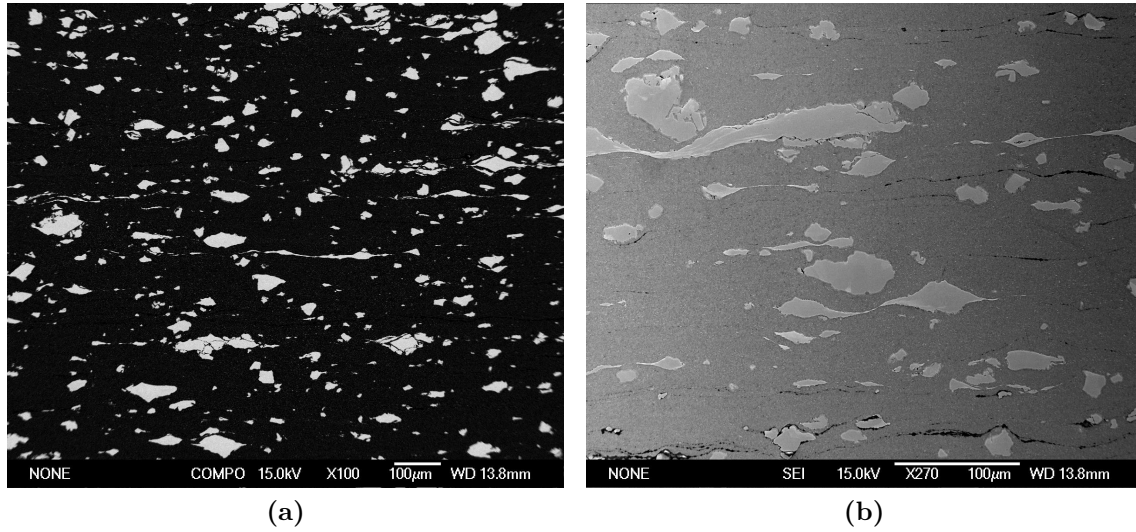
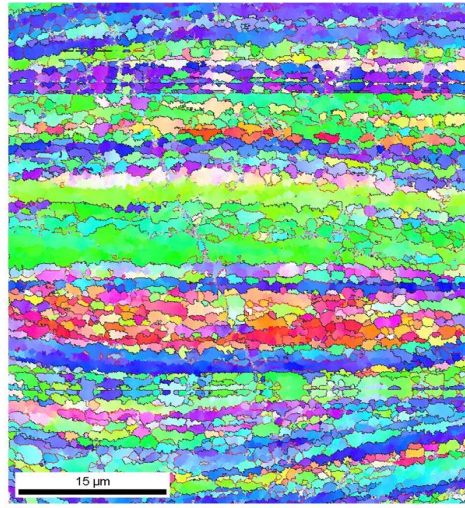


Figure 6.22: (a) Backscattered electron image of Al-4Cu+Ti after 3 ARB cycles and (b) Secondary electron image at higher magnifications of Al-4Cu+Ti after 3 ARB cycles showing some elongated Ti fibres and pores.

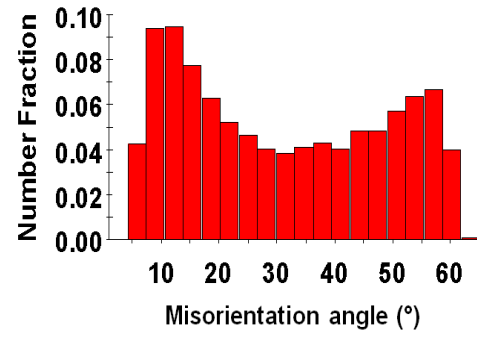
red) and high angle grain boundaries were those above 15° (coloured black). The elongated microstructure was again evident after 3 ARB cycles, and had become further refined at $1\text{-}5\mu\text{m}$ thickness. Again, many of the grains recrystallised to produce a higher fraction of higher misorientation grain boundaries as shown in Figure 6.23 (b). Figure 6.23 (c) shows an EBSD orientation map of the Al-4Cu matrix after 4 ARB cycles showing that even after a longer pre-heat time of 40 minutes the microstructure was not further recrystallised beyond that shown after 3 ARB cycles. Figure 6.23 (d) shows the corresponding misorientation angle distribution for the grains in (c) that was again similar to the chart in (b).

6.7 Mechanical properties

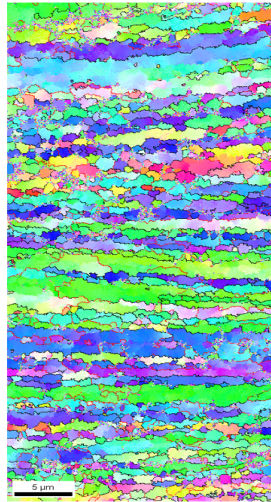
Figure 6.24 shows the mechanical properties of accumulative roll bonded Al-4Cu and Al-4Cu+Ti after 1ARB, 3ARB and 4ARB cycles. All specimens were machined to flat dog bone type according to the ASTM E8M standard. Both Al-4Cu and Al-4Cu+Ti experienced equivalent deformation after 1 ARB cycle although bonding was not successful for Al-4Cu and the specimen was therefore 50% thinner. Figure



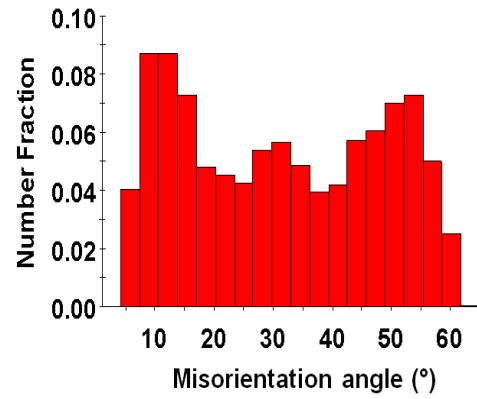
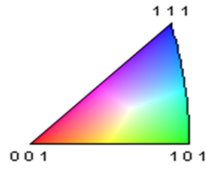
(a)



(b)



(c)



(d)

Figure 6.23: (a) EBSD orientation map of the α -Al matrix in Al-4Cu after 3 cycles of ARB; (b) corresponding misorientation angle distribution of Al-Cu after 3 ARB cycles; (c) orientation map taken of Al-4Cu after 4 ARB cycles, with the orientation key to the right; and (d) is the misorientation angle distribution after 4 ARB cycles.

6.24 shows the yield strength and the ultimate tensile strength were increased from 220MPa and 235MPa to 329MPa and 339MPa respectively. The elongation of both composites was lower than expected and was due to the embrittling interfacial reaction phase. The yield strength and tensile strength was 50% and 43% respectively higher relative to the unreinforced composite.

To assess whether strength was similar to that predicted by the rule of mixtures shown in Equation 2.1, appropriate strengths for the monolithic Al-4Cu and Ti were required. Hyun *et al.* [112] studied the mechanical behaviour of commercially pure Ti at different degrees of deformation by ECAP at 410°C. After 4 ECAP passes, the Ti UTS had work-hardened to 669MPa, and this deformation extent was approximately equivalent to a strain of 3.04 compared with ~ 3 induced in the Al-4Cu+Ti composites by accumulative roll bonding in this work. The Al-4Cu strength was ~ 226 MPa, taken as the monolithic accumulative roll bonded equivalent, and the volume fraction of Ti was assumed to be 20%. According to a rule of mixtures, the Al-4Cu+Ti UTS should be ~ 288.5 MPa, whereas ARB Al-4Cu+Ti had a tensile strength of ~ 339 MPa. At low strains of 3.1, the Ti was not heavily elongated and cannot be ascribed to interfacial effects normally restricted to strains > 7 . One obvious source of error is the assumed UTS for Ti deformed by ECAP, but a more realistic Ti UTS is likely to be *lower* than that assumed here because the Ti was not generally deformed. Alternatively, the rate of work-hardening in the Al-Cu may be enhanced by the Ti, or the matrix is readily ageing even at low temperature due to the very small matrix grain size and substructure increasing effective Cu diffusion rates.

The strength of Al-4Cu+Ti was significantly reduced after 3 ARB cycles. As shown in Figure 6.18, larger visible cracks were initiated in the sheet after 3 ARB cycles. Although the most dramatic cracks at the edges were milled away, cracks rippled through the whole of the sheet, and probably explain the deteriorated mechanical properties. In other words and as shown by the difficulties in bonding, the

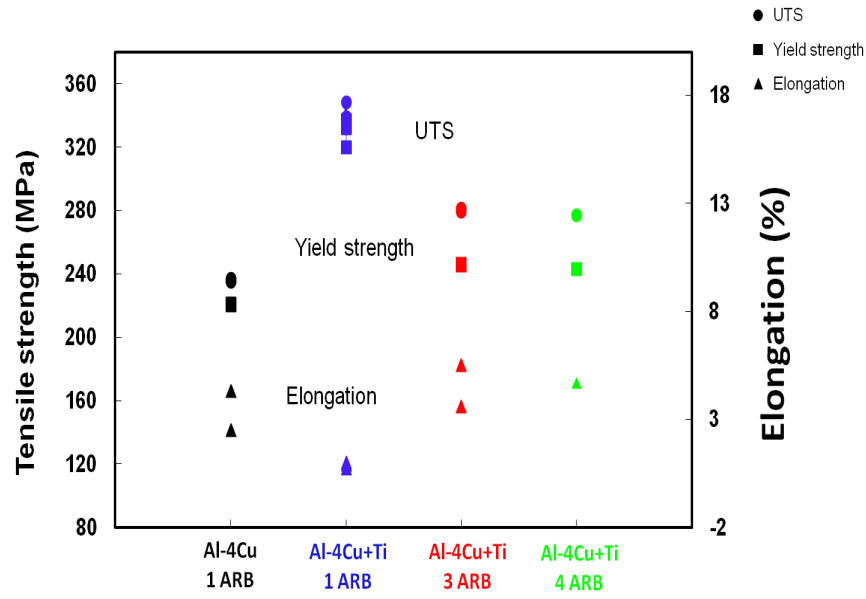


Figure 6.24: Mechanical properties of accumulative roll bonded Al-4Cu and Al-4Cu+Ti up to 4 ARB cycles. The Al-4Cu strips did not always bond and were 50% thinner than Al-4Cu+Ti after 1 ARB cycle.

ARB process was far from optimised for this material. Additionally, after 3 ARB cycles there would be 16 sheets and consequently 16 macro-planar defects for failure where bonding may not be complete. SEM studies indicated de-bonding between layers as shown in Figure 6.22 (b). The complex nature of bonding mechanisms have been studied extensively and the primary factors affecting bonding include the amount of deformation, the type of metal and its purity, lattice structure, temperature of bonding, pressure induced, time for bonding to occur and surface preparation [85]. The strength of composites after 3 and 4 ARB cycles were similar as shown in Figure 6.24. The strength may have reached a point of saturation after 3 ARB cycles ($\eta \sim 4.7$). Saito *et al.* carried out studies on commercially pure Al deformed by ARB and discovered that after $\eta = 4.8$, the strength no longer increased and attributed this to homogeneous saturation of fine grains processed to 6 ARB cycles and beyond [87]. Hoppel *et al.* reported a similar finding in the strength of pure Al deformed by ARB that plateaued in strength and hardness after a strain of 6 [129]. Similarly, the Ti did not continue to provide continuous strengthening

for similar reasons, and the strengthening effect of nano-scale Ti/Al interfaces at very high strains had yet to be reached. Considering the strength deteriorated after 1ARB cycle indicated that there was insufficient bonding after the 3rd and 4th ARB pass leading to inferior properties.

6.7.1 Comparison of deformation mode

Extruded composites contained more heavily elongated Ti fibres than rolled composites. The most likely explanation relates to the difference in temperature during deformation processing. Wire composites were preheated for 30 min at 520°C and retained temperature during extrusion, compared with cold rolled material preheated to 370°C for 25 minutes. Whilst this softened the α -Al matrix, it also similarly softened the Ti and enhanced recovery so that work hardening was avoided. In rolling, a lower preheat was used, and heat was very quickly lost from the thin, highly conductive Al sheet during transport to the mill from the furnace, and due to the large cold rolls. Evidence of cold rolling is shown in the microstructure where recrystallisation was much more restricted compared with extrusion. The twist or “roping” effect in extrusion may also play a minor role in encouraging Ti deformation.

An attempt was made to compare the strengthening mode of extrusion versus rolling. At a strain of 5, the extruded Al-4Cu+Ti wire had a UTS of 315MPa, whereas at a lower strain of 3, rolled Al-4Cu+Ti sheets (1ARB) had a tensile strength of 340MPa. The results are rather unusual particularly since according to microscopy, extruded wires contained more heavily elongated Ti fibres. However, the wires were extruded at 520°C compared with the rolled material, preheated to 370°C, but which was probably considerably colder during the rolling itself, suggesting that unrelieved cold work is playing a larger role in the overall strength. Trybus *et al.* compared deformation processed Cu-Nb composites that were wire drawn and rolled and suggested substructural features such as dislocation cell walls in the matrix were controlling the strength in rolled composites. Evidence in this

thesis for substructure contribution to strength came from EBSD investigations that showed textured, elongated grains; rolled Al-4Cu had much stronger texture than extruded Al-4Cu that was generally recrystallised, indicating the primary cause for increased strength in rolled Al-4Cu was texture strengthening. In addition, rolled and accumulative roll bonded materials showed differences in strengthening mechanisms. The ultimate tensile strengths of rolled ($\eta=6.5$) and 1 ARB material ($\eta=3.1$) were similar at $\sim 344\text{MPa}$ and $\sim 340\text{MPa}$ respectively. It is likely that the increased strength of 1 ARB material was due to the effect of shear deformation below the surface introduced by friction between the material and the rollers under dry conditions (i.e. without lubrication) which is a necessary constraint for ARB as opposed to rolling [10].

6.8 Conclusions

The morphology of the minority phase is an important factor in deformation processing of metal-metal composites. Angular shaped powder particles are the optimum morphology while spherical powders rotate and resist deformation. The processing route to powder manufacture plays an important role in determining deformation behaviour because each route of mechanical alloying, gas atomisation and hydride-dehydride produced Ti powder that varied in hardness and morphology. The hardness of spherical gas atomised Ti powder was 35% higher than angular Ti processed by the hydride-dehydride process. Relatively impure mechanically milled Ti powders had the highest hardness and were heavily work hardened. Co-deformation of the minority Ti phase was inhibited if the Ti hardness was substantially higher than the matrix.

Spray formed Al-4Cu+Ti was extruded to a strain of ~ 5 at a temperature of 520°C . Ti elongated into fibres along the extrusion direction. SEM, EBSD and FIB were used to analyse the microstructure. FIB studies confirmed that most fibres were

elongated despite the appearance of breaking in 2-D sections. EBSD studies showed recrystallised grains after extrusion in the Al-4Cu matrix and evidence of $\langle 100 \rangle$ fibre texture that was also supported by XRD studies. Mechanical properties of the extruded Al-4Cu+Ti were compared with extruded Al-4Cu alone. The composite had a tensile strength of 315MPa and did not show strengthening beyond that predicted by a rule of mixtures, due to the relatively low total strain. Fracture surfaces revealed that many cracks were initiated at the Al_3Ti interfacial reaction layer, although both Ti and $\alpha\text{-Al}$ were effective in blunting crack growth.

Rolling was carried out up to a strain of 6.5 and accumulative roll bonding was carried out up to 4 ARB cycles, equivalent to a strain of 5.5. Elongation of the minority Ti phase was more modest for rolled composites compared with the extruded composites, as previously found by Trybus [76]. The most likely explanation for this was proposed to be related to the temperature difference during deformation processing: a higher deformation processing temperature of 550°C for extruded composites compared to 370°C for rolling was shown to facilitate Ti elongation. Rolling induced a $\{110\} \langle 211 \rangle$ brass texture in Al-4Cu according to XRD and EBSD analysis.

The UTS of rolled Al-4Cu+Ti exceeded a simple rule-of-mixtures prediction based on estimates of constituent strength, whereas the extruded composites largely agreed with simple predictions. The extra strengthening in the rolled composite over the monolithic material may arise from a stronger texture or the shear deformation induced in roll bonding without lubrication as opposed to conventional rolling, differences in the extent of work-hardening in either the $\alpha\text{-Al}$ or the Ti when both were present; differences in the age-hardening behaviour with the composite showing more ready natural ageing due to its more defective nature, or finally, the beginning of anomalous strengthening in which the $\alpha\text{-Al}/\text{Al}_3\text{Ti}/\text{Ti}$ interfacial areas begin to contribute significantly to inhibited dislocation motion.

The ultimate tensile strength of Al-4Cu+Ti was highest at 339MPa after 1 ARB

cycle ($\eta=3.1$) but decreased after 3 ARB cycles to ~ 280 MPa. The deterioration in strength was attributed to edge cracks that may have rippled through the entire sheet.

Chapter 7

Conclusions

Spray forming with co-injection has been established as a feasible route to the manufacture of metal-metal composites at large scale. The Al-12Si+12Ti industrial scale billet comprised refined equiaxed α -Al grains ($\sim 5\mu\text{m}$), spherical Si particles ($\sim 1\mu\text{m}$) and uniformly distributed Ti particles ($D_{50}=80\mu\text{m}$), and was free from measurable interfacial reactions or oxides. Deformation processing was carried out to a true strain of ~ 8.4 , providing elongated Ti fibres/ribbons of sub-micron thickness. Microstructural insensitivity of the α -Al grains to maintain a fine, near-constant grain size irrespective of total strain was attributed to either geometric dynamic recrystallization or particle stimulated recrystallization, but stronger evidence for the latter was supported by powder processed composites. It was suggested that during deformation, the Si particles played a role in imparting stress to the Ti particles to produce fibres/ribbons of sub-micron thickness, but powder processed composites could not reproduce this behaviour because the Ti powder used in this case was already heavily work hardened. The morphology of the minority phase was also shown to be important in controlling the extent of its deformation. Accumulative roll bonding showed encouragement as a deformation processing route to scale-up.

A DACS powder injection pump was successfully integrated and commissioned on the spray forming facility at Oxford University. A series of powder flow studies

were carried out using spherical gas atomised stainless steel and Ti-6Al-4V powder to calibrate flow behaviour and to assess safety aspects. Pump parameters including the volume of the powder chamber and the frequency of powder delivery were modified, along with length of delivery pipe to obtain the optimum powder flow rates. The frequency of powder delivery affected the flow rates more significantly than other parameters studied with a maximum flow rate recorded using a frequency of 5Hz and the best consistency of flow of $\sim 3\text{kg/min}$ was achieved at 7Hz.

An Al-4Cu alloy with co-injected Ti powder was co-spray formed for the first time. Three Al-4Cu+Ti billets were processed at slightly different spray forming conditions and using Ti powder processed by mechanical alloying, gas atomisation and the hydride-dehydride process. The resulting metal-metal composite billets were $\sim 40\text{kg}$, significantly larger than previous 100's of grammes produced by powder processing. Up to 20vol% Ti powder was incorporated into AlCuTi3. However, two problems endured. Firstly, at the centre region of the billets macroscopic voids developed usually indicative of a cold billet although dense regions of material were obtained along the billet sides and base. In such regions, prior to co-injection of Ti, the area fraction of porosity was 0.5% and in the regions of Ti injection the porosity reached 7% especially locally around groups of Ti particles. The second problem concerned variations in Ti fraction from place to place and was attributed to irregular flow of the Ti which was exacerbated when irregular particles were used.

The grain size of the Al-4Cu matrix in the co-injected region decreased by 65% relative to the matrix region due to the quenching effect of the injected particles. This quenching effect, followed by the billet slow cooling to room temperature led to the precipitation of Cu-rich precipitates, which were ascribed to θ' -Al₂Cu on the basis of their distinctive morphology. A slight Ti/Al-4Cu interfacial reaction was evidenced in AlCuTi1 and AlCuTi2. A more vigorous reaction occurred for AlCuTi3 that was co-spray formed at a higher temperature of 850°C.

The morphology of the minority phase is an important factor in deformation

processing of metal-metal composites. Angular shaped powder particles were the optimum morphology while spherical powders rotated and resisted deformation. The processing route to powder manufacture plays an important role in determining deformation behaviour because each route of mechanical alloying, gas atomisation and hydride-dehydride produced Ti powder that varied in hardness and morphology. The hardness of spherical gas atomised Ti powder was 35% higher than angular Ti processed by the hydride-dehydride process. Relatively impure mechanically milled Ti powders had the highest hardness and were heavily work hardened. Co-deformation of the minority Ti phase was inhibited if the Ti hardness was substantially higher than the matrix.

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texture in Al-4Cu according to XRD and EBSD analysis.

The UTS of rolled Al-4Cu+Ti exceeded a simple rule-of-mixtures prediction based on estimates of constituent strength, whereas the extruded composites largely agreed with simple predictions. The extra strengthening in the rolled composite over the monolithic material may arise from a stronger texture or the shear deformation induced in roll bonding without lubrication as opposed to conventional rolling, differences in the extent of work-hardening in either the α -Al or the Ti when both were present; differences in the age-hardening behaviour with the composite showing more ready natural ageing due to its more defective nature; or finally, the beginning of anomalous strengthening in which the α -Al/ Al_3Ti /Ti interfacial areas begin to contribute significantly to inhibited dislocation motion. The ultimate tensile strength of Al-4Cu+Ti was highest at 339MPa after 1 ARB cycle ($\eta=3.1$) but decreased after 3 ARB cycles to ~ 280 MPa. The deterioration in strength was attributed to edge cracks that may have rippled through the entire sheet.

Chapter 8

Future work

(1) It remains an open question if there exists a processing window in which a co-spray formed metal-metal billet can be produced that offers both minimum interfacial reaction (“cold” conditions) and absence of macro-voids (“hot” conditions). Further experiments, perhaps guided by modelling studies to reduce the amount of expensive experiments, should be undertaken to fully explore process parameter combinations.

(2) The mechanical pump system studied here provided many advantages over conventional fluidised bed and Archimedian screw powder systems including independent control of mass flow rate and carrier gas flow rate and pressure. However flow rate variability endured. Given the system here was effectively a prototype, further work with suppliers should be undertaken to improve flow regularity under spray forming conditions.

(3) Further ARB studies should be undertaken since it offers the only scalable route for metal-metal composite fabrication and is well matched to spray forming in terms of scale and maturity. Only very few, off-site experiments were undertaken here, but there was sufficient encouragement to suggest spray forming plus ARB could produce attractive strong plate and sheet material. Important parameters not so far studied are the toughness, high strain rate and blast resistance of these

materials where they may offer some intriguing properties.

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