

**Aluminum-based Material Fabrication by Friction Stir Processing:
Microstructural Evolution and Mechanical Properties**

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ABSTRACT

Friction stir processing (FSP) is an energy efficient solid-state material processing technique for microstructure modification of commercial high-strength Al alloys. Many variant techniques were developed in recent years that enabled light-weight and high-strength structure fabrication. Identifying relationship among process conditions, microstructures, and mechanical properties is of critical importance to facilitate the practical implementation of these new techniques. The research in the dissertation focusses on developing two main techniques of the FSP: a) friction stir back extrusion (FSBE) of 6063 aluminum alloy for tube making and b) FSP of 7075 aluminum alloy from powder feedstock. FSBE fabricated Al 6063 alloy tubes with refined grains in the inner walls and less orientation asymmetry, which is beneficial to the thin-walled light-wight structure building. The local concentrated precipitation and the grain-size gradient throughout the wall thickness illustrated the non-uniform straining applied by the current FSBE design. Such non-uniformity can be utilized for a selective microstructural modification in the extrusion process. FSP from premixed powder realized complete in-situ Al_3Ni formation in Al 7075- Al_3Ni composite. Nano-scale Ni additive in the start material produced fine-sized Al_3Ni , which generated more effective hardness enhancement than the micron-scale Al_3Ni reinforcement by the Orowan strengthening effect. The Ni addition also introduced precipitation kinetics change in Al 7075 alloy including Cu depletion from Al matrix and promoted T- $\text{Al}_2\text{Mg}_3\text{Zn}_3$ precipitation. The current FSP set up on powder enabled fabrication of large-scale consolidated composite with homogenous microstructure. The FSP on Al 7075 powder produced fully consolidated, highly recrystallized grain structure comparable to the solid pieces after FSP. The microhardness was mainly governed by the resultant morphology and content of the strengthening intermetallics. However, the excessive Fe-rich intermetallics ($\text{Al}_7\text{Cu}_2\text{Fe}$ and $\text{Al}_{23}\text{Fe}_4\text{Cu}$) were introduced possibly by the tool's wearing. The Fe-rich inclusion as well as the other possible residue features in powder triggered further grain refinement and reduction of main strengthening η'/η phases in the post heat treatment. The hardness reduction of the material from powder in the post heat treatment indicated the necessity of modifying material preparation and the post-process for the perfection of this FSP techniques.

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Chapter One. Introduction

1.1. Background: Friction Stir Processing (FSP) of Aluminum Alloy

Aluminum alloys are of the main structural materials in automotive and aerospace industry (Figure 1.1) because of their high strength-to-weight ratio, ductility, toughness, machinability, and other performances like corrosion resistance [1]. The strengthening of the aluminum alloy is an extensively studied topic since the strength is usually the top consideration in structural design [1, 2]. The strength enhancement is achieved by either modifying microstructure of the existing alloys or developing new materials with compositional change. The friction stir processing, in which non-consumable tools apply intensive frictional heat and plastic deformation into the workpiece, enables both microstructure modification and compositional changes. Therefore, the friction stir processing has been recognized as an attractive strengthening technique, and it is expected to offer several advantages: a) energy-efficient solid-state process with no melting and solidification defects (e.g., hot cracks, segregation, etc.), b) grain structure modification with severe plastic deformation and thermal input, and c) capability of making aluminum-based composite by introducing additives in the process.

Friction stir processing (FSP) is derived from the friction stir welding (FSW), a solid-state joining technique invented at The Welding Institute (TWI) in 1991 [3]. The idea is inserting a non-consumable rotating tool into the workpieces and soften the material with localized frictional heat. Welding beam is created upon the plastic deformation in the track of tool's motion. The FSW effectively addressed the issue of hot cracking in conventionally welded high-strength aerospace aluminum alloys, because the joint is produced at solid state with refined grains. Mishra et al. then developed FSP [4, 5] to produce superplasticity in aluminum alloy with ultrafine grain and high-volume fraction of grain boundaries by the friction stir effect. In the case, the rotating tool produces the friction stir effect on a single piece of material for localized microstructural modification. Enhancement of multiple properties, such as grain refinement, homogenization and material densification, can be achieved in a single step [6, 7]. Furthermore, the microstructure and the shape of the processed region can be accurately controlled by varying the process parameters and tool design [8].

FSP mainly produced equiaxed grain structures due to the dynamic recrystallization in its unique thermal-plastic process. Micrometric grains are usually obtained [5, 7, 9, 10], and even the production of nanostructured aluminum grains in size of 20 - 100 nm is also possible by conducting rapid cooling in FSP [11, 12]. The grain refinement results in both yield strength (YS) and hardness increment following the Hall-Petch relationship [9, 10, 13-17]. The refined grain structure also introduces the superplasticity into the aluminum alloys, as Mishra [4] reported the superplasticity of the FSPed Al 7075 alloy at high strain rate tensile test due to the fine grains and high-volume fraction of high-angle grain boundaries (HAGB). The grain structure can be controlled by changing tool design and process parameters, cooling/heating conditions, etc. Modified microstructure with superplasticity can be obtained both along [18, 19] and transverse [8, 20] to the tool's translating direction.

Impressive studies also expand the potential of FSP by combining its principle with the geometrical and dynamical designs of other material processing techniques (Figure 1.2). Those inspiring variant techniques are developed and known as friction stir forming (FSF) [21-23], friction stir rolling (FSR) [24], friction stir extrusion (FSE) [25-31] and friction stir deposition (FSD) [32-34]. Many detailed technique issues like process design, end-product microstructure and properties in those novel techniques are not fully studied. The dissertation focused on the study of the technique named friction stir backward extrusion (FSBE).

The friction stir extrusion (FSE) combine the FSP principle with the hot extrusion process to produce rod, wire, and tubular structures. The rotating part that can created frictional heat and severe plastic deformation is integrated into the extrusion tool set. FSE produces refined and homogenized grain structure in one step. Both wire and tube structure can be extruded by appropriate tooling design. Conventional extrusion of aluminum alloys, on the other hand, usually requires post heat treatment or other homogenization process. Another advantage of the FSE is the significant extrusion load reduction (over 90%) with respect to hot extrusion because of the localized heating and softening nature at the extrusion exit in FSE tools [35, 36]. Feng et al [25] proved FSE as an energy-efficient technique for aluminum recycling by extruding aluminum alloy wires using wasted aluminum alloy chips and powders. The improvements of mechanical and electrical performances due to refined microstructure were confirmed. The FSE can characterized into two deviation based on the extrusion direction. One of the technique is called friction stir

direct extrusion (FSDE) [29, 36], because the material is extruded out along the same direction as the tools plunging direction. The other is called friction stir backward extrusion (FSBE) where the extrudate move in the reverse way to the tools plunging [26, 37]. Tang et al [37] produced defect-free Al 2195 alloy wire using machined Al alloy chips as raw material. The final product contains fully recrystallized grains. Tahmasbi et al [38] demonstrated better surface finish for Al wire extrusion can be obtained with higher rotation rate and lower plunging load. Preliminary studies on the tube extrusion with a 5~10 μm grain refinement from >100 μm origin grain structure [26-28]. Nazari Tiji et al [36] made thin-walled AZ31 magnesium alloy tubes with a direct extrusion setup, both grain refinement and relatively high extrusion ratio (~18.8) are accomplished. It is noticed that the studies on extruding Al alloy tubes using FSE techniques is still limited.

FSP can also fabricate fully dense material using powder, waste turnings and chips, and cast blocks as starting material [8, 37, 39, 40]. It is because its intensive thermal-plastic deformation can homogenize the microstructure and eliminate defects like porosity, cracks, particle segregation and coarse dendrite grains [6, 39, 41]. Thus, the FSP can turn into a powerful tool of making aluminum-based composite materials. Al-based metal matrix composites is another important way for obtaining high performance structural material. The idea is to blend reinforcing material (known as ‘additive’) into the Al alloy (known as ‘matrix’). Enhancement of strength, Young’s modulus, wear, fatigue resistance and thermal stability can be obtained. Because the reinforcement results in Al grain size refinement as well as multiple strengthening effects by dislocation-reinforcement interactions. Various additives like transition metal [42-46], ceramics [47-51], carbon material [52-55] can be applied in FSP. There are two methods of introducing additives in FSP composite making: a) placing additives into the pre-machined holes/slots of a solid Al matrix and b) mixing additive into Al/Al alloys powder as feedstock for FSP. The pre-mixed powder gives better chance of more uniform particle distribution but also the risk of porosity [56]. Such risk can be mitigated with appropriate process (sufficient temperature and pressure input). The reinforcement can be created either ex-situ or by in-situ reaction between additive and Al. In-situ reinforcement formation is more favorable because of its better metallurgical bonding and thermal stability [57-60]. FSP possess several advantages compared with conventional casting composite techniques: a) available of more strength enhancement using high volume fraction of fine sized additives which is hard for melting Al process [47, 49, 61-64], and b) able to fabricate large

dimension of composite by repeating tracks of FSP [8, 44]. Al_3Ni phase has been proved as a good candidate for Al reinforcement because of its high strength both at room and high temperature, good interfacial bonding with Al matrix [43, 44, 46, 65-68]. Al - Al_3Ni composites with strength improvement was fabricated by FSP route by several preliminary studies [43, 44, 69]. Al - Al_3Ni composite fabrication with nano-size Al_3Ni particles by FSP of mixed powder feedstock awaits more research although it should provide promising performance.

1.2. Research Goal and Objectives

It is of great importance to provide knowledge on FSP's effect on material microstructure and mechanical properties. The knowledge needs renewal as the process design is modified. The overarching goal of this research is to provide such understanding on two modified FSP techniques for the strengthening of the aluminum alloys. One is friction stir backward extrusion (FSBE) making Al alloy tubes. The other is multi-track FSP of the compressed powder feedstock for grain refined Al alloy and Al - Al_3Ni composite.

Figure 1.3 shows the overall structure of this research composed by the following 3 topics:

- a) Provide understanding of the microstructural evolution of Al 6063 alloys tubes fabricated by friction stir backward extrusion (FSBE).
- b) Demonstrate the feasibility in-situ Al_3Ni reinforcement formation in fabricating Al 7075- Al_3Ni composite by using mixed Al 7075 powder and Ni nano powder.
- c) Provide understanding of the microstructural evolution and strength differences between FSP fabricated Al 7075 alloy from powder and wrought Al 7075 alloy.

1.3. Thesis Organization

Chapter 2 presents the microstructural and mechanical properties evolution of the Al 6063 alloy tubes processed by friction stir back extrusion (FSBE). Chapter 3 introduces the fabrication of in-situ fine-sized Al_3Ni reinforcement in Al 7075 alloy composite using the multi-track FSP technique. The particle strengthening effect and phase change are discussed. FSP fabricated material from powder exhibited hardness reduction with respect to solid Al 7075 alloy after the T6

aging heat treatment. A comparative study of powder and solid Al 7075 start material in FSP was conducted to interpret such hardness change in chapter 4. Chapter 5 summarizes the conclusions and possible future works.

Appendix. Figures and Tables

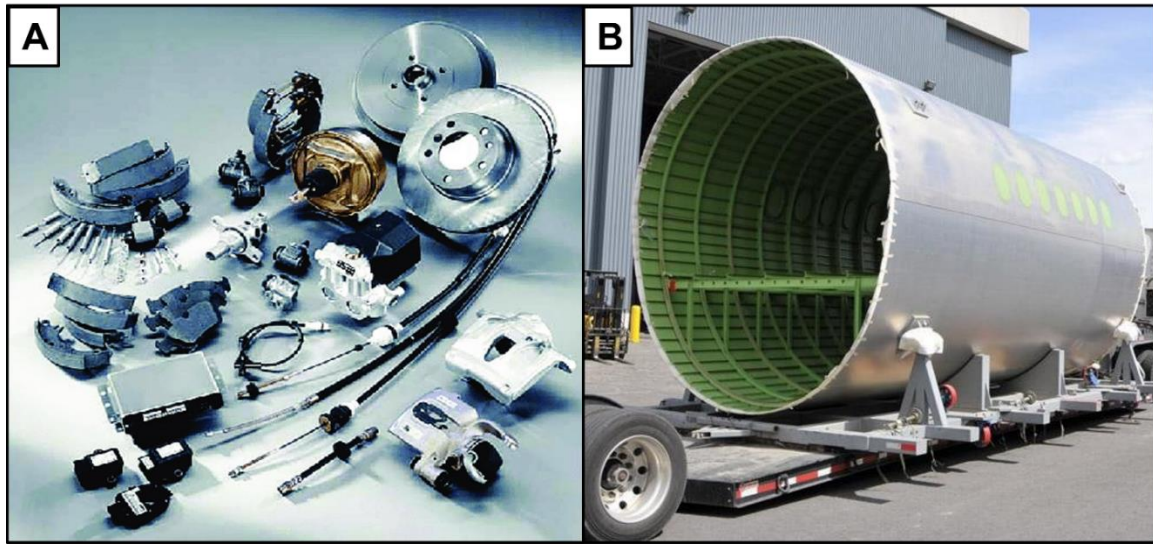


Figure 1.1 A) Automotive parts and B) aircraft frame structures as representative of aluminum alloy structures used in industry [70, 71].

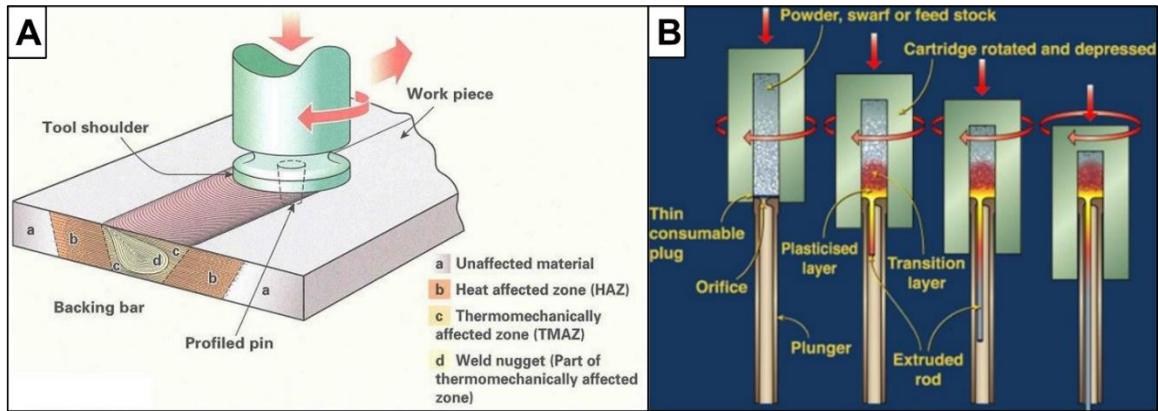


Figure 1.2 Schematic drawings of A) FSP [72] and variant technique of B) friction stir extrusion (FSE) [25].

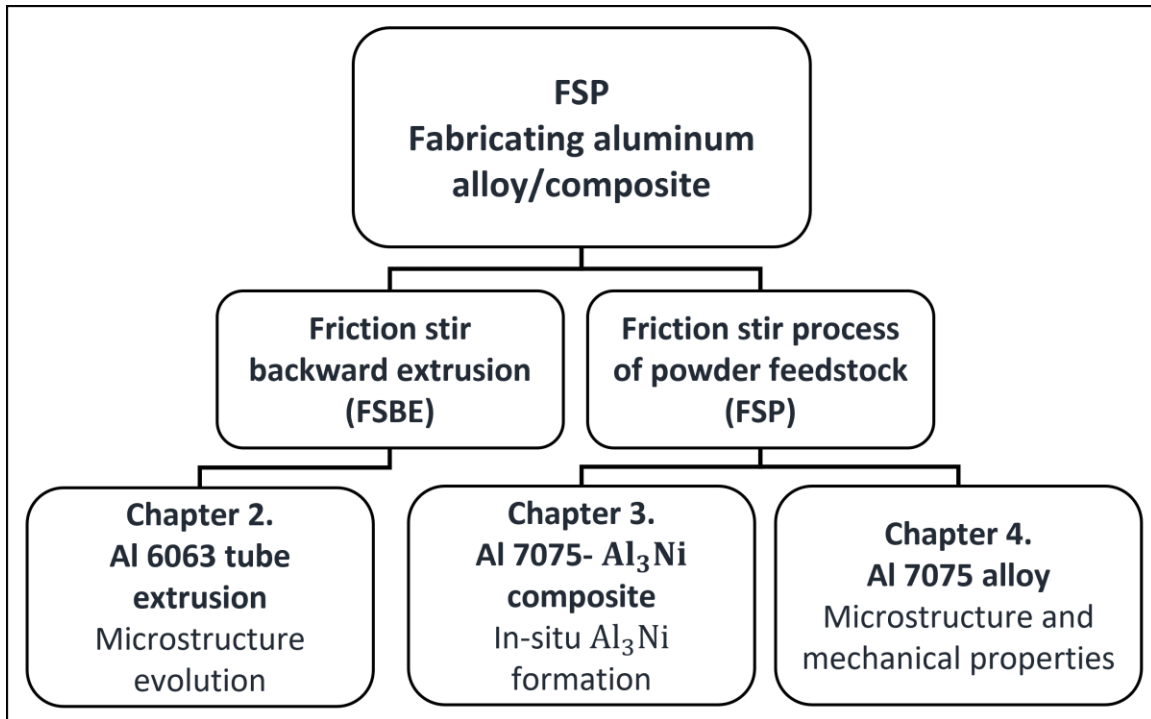


Figure 1.3 Diagram of the overall structure of the research in this dissertation.

**Chapter Two. Mechanical Property Characterization and
Microstructure Evolution of 6063 Aluminum Alloy Tubes Processed
with Friction Stir Backward Extrusion**

2.1. Disclosure

The chapter contains a published journal article titled: “Microstructure evolution and mechanical property characterization of 6063 aluminum alloy tubes processed with friction stir back extrusion” [73]. Suhong Zhang contributed to the writing of the manuscript and implementation of FSBE, metallography, hardness measurement and analysis of the characterization results. Alan Fredrick helped with FSBE trials. Yiyu Wang performed EBSD test on the material. Paul McGinn contributed to characterization of Al 7075 alloy processed by FSBE (recorded in supplementary material with the article). Zhili Feng, Wei Tang and Anming Hu supervised the project.

2.2. Abstract

Friction stir extrusion (FSE) is a novel technique for light-weight metal extrusion. The frictional heat and severe plastic deformation of the process generate the equiaxed refined grain structure because of dynamic recrystallization. Previous studies proved that the fabrications of the tube and wire structures are feasible. Limited studies on FSE hinder the industrialization of the process. This research is to build up the understanding of the microstructure evolution in the friction stir back extrusion (FSBE). 6063 aluminum alloy tubes are extruded. The process force and temperature are recorded during the processes. Microstructure of the extruded tubes is characterized using optical microscope, electron back scattered diffraction (EBSD). The experiment realized a grain size reduction from 58.2 μm to 20.2 μm of the friction-stir-processed inner wall. The FSBE process also created a non-uniform distribution of Mg_2Si and $\beta\text{-AlFeSi}$ precipitation in the material. Microhardness of the processed material was reduced from 100 HV to 60~75 HV due to the precipitation formation affected by the process thermal cycle.

2.3. Introduction

The metal extrusion process has been widely used for light-weight alloys for more than 80 years. It provides most of the semi-finished bar, wire and tube structures for various applications [74]. The friction stir extrusion (FSE), on the other hand, is emerging extrusion technique derived from the friction stir welding (FSW), which is first patented for aluminum alloy joining [75]. They

share common ideas, which is using frictional heating to soften and plasticize the material. The frictional heat and severe plastic deformation produce quasi-axed refined grains in the structure by dynamic recrystallization, which made the friction stir extrusion an attractive process to improve the extrusion microstructure and properties. Feng et al [25] proved FSE as an energy-efficient technique for aluminum recycling by extruding aluminum alloy wires using wasted aluminum alloy chips and powders. The improvements of mechanical and electrical performances due to refined microstructure were confirmed. The grain refined tube structure is of great interest as well because of its potential in aerospace and automotive industries. Several preliminary studies [26-28] on friction stir extrusion of tube structures were conducted with a primary tool setup: a rotating tool drill into solid material billets placed in the die to make reversely growing tube extrusions. They realized a 5~10 μm grain refinement from >100 μm origin grain structure. Whalen et al. [29] made thin-walled AZ31 magnesium alloy tubes with a direct extrusion setup, both grain refinement and relatively high extrusion ratio are accomplished. It also reported that product properties depend on process condition, tool design and materials. Non-ideal coarse grains can be created with too much heat input [28]. The technique of the friction stir extrusion is still premature for industrial applications due to limited understanding of the process mechanism. As for wire extrusion, finite element models of the wire extrusion from both material flow and heat transfer aspects are built [30, 31, 76] because the earlier start of wire extrusion provided more accumulation of process conditions. While the tube extrusion is in even more pre-mature stage, current studies of the tube extrusion microstructure were mainly conducted with the tool setup proposed in the preliminary research [26-28]. Increasing of the tool design and knowledge on process conditions are beneficial to the industrialization of the friction stir tube extrusion process.

In this research, a new tools setup of friction stir back extrusion was developed for tube extrusion. Aluminum 6063 alloy tubes with thinner wall were extruded by plunging tools into hollowed billet and enlarged their inner diameter. Grain refinement from 58.2 μm to 20.2 μm of the tubes' inner wall was observed. While hardness reduction and a non-uniform distribution of secondary phases of the extruded tubes were also obtained. The phenomena were tried to be explained by microstructural characterization and analysis.

2.3. Experimental

2.3.1. *Experimental Setup of the Friction Stir Backward Extrusion (FSBE)*

The essential features of the FSBE process are schematically shown in the Figure. 2.1A The tools set consist of two parts: friction stir tool made from MP159 superalloy, and the die made from 17-4 PH steel. The rotating tool is plunged into a hollow aluminum billet. It softens the billet material with frictional heat and force material to flow through the die while applying severe plastic deformation on the billet inner wall. For this experiment, AA6063-T6 aluminum alloy was used. The initial hollow aluminum billets had a 21.34 mm outer diameter (OD), 16 mm inner diameter (ID). The inner diameter of the extruded tube was the same as outer diameter of the tool's working part which had a length of 25.4 mm and maximum diameter of 16.76 mm. The billet was deformed into a tube with thinner wall and extruded out of the die in a way opposite to tool's plunging direction. The die was made of two halves to form a circular hole for tube extrusion. This setup makes it easy to remove the extruded tubes after the experiment and allowed embedding thermocouples to measure the temperature during the extrusion process.

K-type thermocouple wires were embedded in the channels and attached to the end of the channel near the inner surface of the die hole to measure the process temperature. The channels were 2.54 mm in diameter 1.25 mm depth. Temperature data were collected from positions at 7.62 mm, 22.86 mm, 50.8 mm, 76.2 mm (0.3'', 0.9'', 2.0'', 3.0'') beneath the top surface of the die. At each depth, the distance away from the billet outer wall is 1.5 mm for the left side and 1 mm for the right one.

The tools are designed to connected with the ISTIR PDS friction stir welding machine built by MTS Systems Ltd., which can generate 88.96 kN (20,000 lbf) plunge force and 180.78 N·m (1600 lbf·in) rotation torque at maximum. The tool rotated at 500 RPM with plunging rate of 63.5 mm/min in the first 31.75 mm plunge and 76.2 mm/min in the later 86 mm to make sure the tool's working part completely exit from the bottom of extruded tube.

2.3.2. Microhardness Tests and Microstructure Characterization

The hardness test and microstructure characterization of the extruded tubes are performed on 2 different cross-sectional views. One of the views is perpendicular to the tube axis (denote as ‘CS’ in Figure. 2.4A) and the other is along the tube axis (denote as ‘AS’ in Figure. 2.4A). Mapping tests of microhardness was conducted both on CS and AS in a direction from outer diameter (OD) to inner diameter (ID) using LECO LM100 AT microhardness tester. Vickers hardness tester with 10 grams load is used to apply an array pattern on 2 cross sections. The distance between the indentation is 75 μm along x and y directions. The cross-sectional surfaces were grinded and polished properly for optical and electron microscope tests. After appropriate polishing and etching with Keller’s reagent, optical images were taken to reveal the grain structure before and after the extrusion using Nikon MA700 Eclipse metallurgy microscope. Electron backscatter diffraction (EBSD) tests were performed using JEOL JSM-6500F scanning electron microscope on the materials before and after the extrusion to collect more information about grain orientation, strain and secondary phases distribution. 1 μm step scan operating at 30 kV is used.

2.4. Result and discussion

2.4.1. Temperature and Process Condition

Three trials were performed in the same condition mentioned in section 2. The initial hollowed billets were 82.55 mm (3.25’’) long with 21.34 mm (0.84’’) OD and 16 mm (0.63’’) ID. The extruded tubes were 95.25 mm (3.75’’) long with 21.34 mm (0.84’’) OD and 16.75 mm (0.66’’) ID. The extrusion ratio of the tube is about 1.15. Some aluminum is extruded out of the hole from the bottom side and become a 6.35 mm long part with 20.32 mm (0.8’’) OD at the end of the tube. Both actual extruded torque and the process load plotted as a function of tool position are displayed in Figure 2.2. After the initial spikes, the plunge force and torque stabilized at 1200N and 110 N·m, respectively.

The process temperature data were collected at a rate of 5 Hz with a dedicated temperature acquisition system. The motion and force data were collected by the friction stir welder. The relationship of the temperature with respect to tool’s position is plotted in the Figure 2.3. Closer measuring points that are 1 mm to hole reach peaks $\sim 50^\circ\text{C}$ higher than the further points (1.5 mm)

at the same depth. The maximum temperature that material ever experienced is 550.7 °C acquired at 22.86 mm and 50.8 mm depth, which is over solubilization temperature (521 °C) but below the melting point (616~654 °C) of the 6063 [77]. The material was at the peak temperature for ~20 sec and naturally cooled down to room temperature.

2.4.2. Optical Microscope Imaging (OM)

The optical microscope images of the etched material surfaces are shown in Figures 2.4 and 2.5. Figure 2.4 shows the grain structure of a billet before FSBE process. grain size and morphology are similar on AS and CS sections. Most of the grains are in size of 50 - 120 μm . The grain sizes from OM images is characterized by measuring and calculating the average grain diameter from the AS view using ImageJ software [78]. The average grain diameter of the original billets is 53.72 μm .

Figure 2.5 shows the grain structure of the extrudate at different locations. Figure 2.5A-C are the AS view at 1) outer diameter zone (ODZ) 2) half wall thickness zone to ID (denote as 'HWTZ') and 3) inner diameter zone (IDZ). Figure 2.5D - F are the CS view at corresponding locations of Figure 2.5A-C. The extruded tube structure shows high continuity without obvious porosity. The average grain diameter of the extrudate from AS view are 103.96 μm , 45.51 μm and 18.70 μm at zones 1) ODZ 2) HWTZ and 3) IDZ. It depicts that the grain growth at ODZ and grain refinement at IDZ with a relative smooth transition of grain diameter from OD to ID. The ID grain size and morphology is similar to the recrystallized grain structure in the friction stir weld nugget zone reported by Sato et al [10]. More detailed analysis is performed using EBSD images because of the need of a more distinct grain structure.

2.4.3. Electron Back Scattering Diffraction (EBSD)

Figure 2.6 displays EBSD pattern of both the original billets. Data like grain diameter and phase fractions are collected using OIM analysis 7 software from EDAX Inc. 3 phases are detected in the EBSD scan of 6063 alloy: α -aluminum phase, Mg_2Si precipitation and β -AlFeSi precipitation [79, 80]. Figure 2.6A is the orientation map based on the [001] inverse pole figure

(IPF) of the 3 phases from AS view, where most of the aluminum grains in the displayed zone oriented to direction [001], and the precipitation particles have orientation distinct from the aluminum. Inverse pole figure (IPF) indicate the local crystal direction (expressed as the Euler angle in the maps) that aligned to normal direction of the maps. Figure 2.6B shows the phase map with grain boundaries of the same area. The precipitate particles distributed both in grain and along the grain boundaries. 3.4% and 1.1% volume fractions of Mg_2Si (orange color particles in Figure 2.6B) and $\beta\text{-AlFeSi}$ (blue color particles in Figure 2.6B) are calculated from Figure 2.6. Low angle boundaries ($2^\circ\text{-}15^\circ$) and high angle grain boundaries that above 15° (denoted as LAGB and HAGB) are plotted out with green and black lines in Figure 2.6B. LAGB are considered as sub-grain structure and the average grain diameter are calculated by the software using HAGB to identify the grains. The average grain diameter is $59.18\text{ }\mu\text{m}$ with a $27.33\text{ }\mu\text{m}$ standard deviation.

Figure 2.7.A - C display the orientation maps based on [001] inverse pole figures at IDZ, HWTZ and ODZ from the AS view. Figure 2.7D - F are the phase maps with grain boundaries of the same zones. The orientation map of IDZ (Figure 2.7A) indicate a texture varied between directions [111] and [101]. The grain numbers in other zones are not enough for texture analysis currently. The parameter used to characterize the grain elongation direction: average grain angle [81] are 12.1° , 11.7° and 13.2° at the IDZ, HWTZ and ODZ zones respectively. Small average grain angle indicates that the grains' major axis preferably aligns to the images' horizontal direction which is also the tubes' circumferential direction. Because material undergo shear strain along the circumferential direction (denoted as 'CD' in Figure 2.9) as well as compressive strain along the radial direction (denoted as 'RD' in Figure 2.7 - 9). All the strain creates grain elongation along the CD and axial direction (denoted as 'AD' in Figure 2.7).

No severe elongated grain which was commonly seen in other FSBE studies [26, 27, 82] was witnessed in all regions. Globular-shaped grains are dominant in the extrudate microstructure. The average grain diameters are $20.6\text{ }\mu\text{m}$, $58.5\text{ }\mu\text{m}$ and $89.1\text{ }\mu\text{m}$ at IDZ, HWTZ and ODZ, which depicts the same tendency of the grain size in the OM images. The tube ID grain refinement can be attributed to the dynamic recovery (DRV) and dynamic recrystallization (DRX). During the plastic deformation under high enough temperature ($>0.4t_m$, t_m : melting point), dislocations distributed inside the grain will be permanently annihilated or rearranged to form low angle grain boundaries (LAGB) by dislocation glide, climb, cross-slip. Globular-shaped sub-grain structure are formed

with LAGB separation of the grain [83, 84]. As the deformation continuous, sub-grains will become individual smaller grains via possibly 2 mechanism: continuous dynamic recrystallization (CDRX) and geometric dynamic recrystallization (GDRX) [85, 86]. In CDRX, the sub-grain will rotate to maintain the lattice consistency and the LAGBs continuously turn into HAGBs as the misorientation exceed the critical angle. Globular refined grains are generated by this mechanism. In GDRX, deformation make the initial grain fragments by forcing HAGBs to serrate at LAGBs. Separate small grains with identical orientation along the material flow line are generated by this mechanism. Discontinuous dynamic recrystallization (DDRX) is not likely to happen in aluminum and its alloys because of the high mobility of dislocations induced by high stacking fault energy [87]. The transition of the grain diameter may be due to varying deformation history in different area. As the rotating tool expanding the tubes inner wall. Shear deformation was introduced to the material and the amount of which reduced from ID to OD, on the other hand, radial compressive deformation forces the tubes to extend along the axial direction (AD). In IDZ displayed in Figure 2.7, strain input was large enough to produce refined grains by CDRX (typical grains are highlighted in the circle A), while there are still grains in initial size with sub-grains inside via DRV process in IDZ (highlighted in the circle B). Large fractions of LAGBs (0.209 from AS view and 0.237 from CS view) and sub-grains in IDZ indicates that grain refinement in this area is incomplete.

Moreover, IDZ in Figure 2.9 displays serrated elongated grains with LAGBs inside right to the CD (highlighted in the circle C). Circle D highlights small grains that may generated from GDRX. It may indicate the presence of GRDX mechanism. In HWTZ only grains in comparable size with original material and LAGB by DRV present because of the insufficient strain input in the area. ODZ experienced a grain growth (89.1 μm) compared with initial microstructure. While the material undergoes an elevated temperature, least shear deformation was applied to this zone, and the constraint from die wall to the tubes' OD make the material less movable along the axial direction. Similar condition is created in the dead material zone in conventional extrusion where the same coarse grain structure is produced [88, 89]. Compared with current FSBE studies and other state of art friction stir processes [7, 25-27, 29]. Grain refinement in the FSBE process is limited because of the insufficient deformation induced to the material. Further grain refinement

may be achieved by using larger diameter tool or other modifications to create more plastic deformation.

Figure 2.8 displays misorientation distribution at IDZ from AS view with 1) the grain average misorientation (GAM) and 2) kernel average misorientation (KAM) maps. The grain average misorientation is the average misorientation angle within individual grains which can be used as a measurement of LAGB and dislocation density in grains. The kernel average misorientation represent for the misorientation angle of one measure point with respect to a set of neighboring points, which is used for evaluating local misorientation [90, 91]. Area with higher misorientation are darker colored. The precipitate concentration of the extrudate becomes non-uniform compared with original material. In the IDZ from AS view (Figure 2.8) two ‘belt-like’ precipitation concentrated zone along the axial direction (AD) (denoted as PCZ) are seen. This may result from inhomogeneous material flow along the circumferential direction (CD). As mentioned above, both material circumferential and axial deformation varies from tubes’ ID to OD in the FSBE process. Banded structure due to layered material flow likely to form in such an inhomogeneous strain distribution in friction stir process and conventional extrusion [92-95]. As displayed in Figure 2.8 and calculated by OIM analysis software, KAM and GAM between 1-15° in PCZs have fractions of 0.319 and 0.342, which is higher than that of area of IDZ other than PCZs (0.275 for KAM and 0.291 for GAM). Precipitation in Figure 2.8 (black dots) distribute along grain boundary and KAM rich region. Because higher density of misorientation (blue color in Figure 2.8A and B) indicate higher density of dislocation and LAGB (red lines in Figure 2.8A and B), which provide more nucleation sites for Mg_2Si precipitation [96].

Figure 2.9A - F are the [001] inverse pole figures and phase-boundaries maps at IDZ, HWTZ and ODZ from the CS view. No significant texture can be seen from the orientation map of IDZ from CS view (Figure 2.9A). The precipitation fractions in volume calculated from all the measured CS images are 9.6% and 3.1% for Mg_2Si and $AlFeSi$, which are much higher than that of AS view (Figure 2.7, 2.3% for Mg_2Si and 0.96% $AlFeSi$). This again demonstrate a non-uniform precipitate distribution in the extrudate. Because the CS and AS section are at different axial location of the tube, the density of precipitation of 2 section are not necessarily the same. Noted that the 6063-aluminum alloy has 0.45-0.9 wt% Mg and 0.2-0.6 wt% Si, respectively [97]. The alloy can have 1.92% Mg_2Si in volume at maximum assuming all the Mg and Si turn into

precipitation form. From temperature measurement shown in Figure 2.3A. The peak temperature (550 °C) exceeded the solubilization point (521 °C) and maintained for 20 seconds. Original precipitation (at least most of them) may dissolved into the solid solution during FSBE process [98]. Precipitation in the processed material formed in the slow cooling. In addition, there are inevitable instability in current process due to assembly tolerance and machine vibration. Non-uniform plastic deformation was applied to the material. Therefore, non-uniform distribution of the secondary phases would be formed.

2.4.4. Effect of Plastic Strain Rate on Grain Size

Both recrystallization and recovery happened to Al alloys in the thermal-mechanical process. The grain size is altered by temperature, strain and strain rate. The relationship can be expressed in the equations below [73, 99]:

$$\log \left(\frac{d}{D_0} \right) = a + b \log(Z) \quad (2.1)$$

$$Z = \dot{\epsilon} \exp \left(\frac{Q}{RT} \right) \quad (2.2)$$

Where d and D_0 are the grain size before and after thermal-mechanical process, the average grain size of the start material 59.2 μm is used as D_0 . a and b are material-related parameters estimated as -0.259 and -0.113 from the previous studies [10, 73, 100]. Z is the Zener-Hollomon parameter as a function of strain rate $\dot{\epsilon}$ and temperature T . Fast heat transfer in the ~ 2 mm tubes side wall caused limited temperature gradient from ID to OD. It is reasonable to assume much less grain size change caused by temperature than the straining variation at different locations. The identical temperature of 550 °C throughout the wall thickness is then used for the estimation. Q and R is the activation energy for the dislocation mobilization (180.2 kJ/mol) [10, 73, 101] and gas constant.

Figure 2.10 shows the calculated equivalent strain rate as a function of material location along the wall thickness direction. The equivalent strain rate at IDZ, HMTZ and ODZ were estimated as 1.7, 2.6×10^{-3} and $5.1 \times 10^{-6} \text{ S}^{-1}$ from the average grain size. The blue line is the linear regression of the strain rate change in the wall thickness. The sufficient plastic deformation at the ID resulted in grain refinement by DRX. While the low plastic straining with the elevated temperature at OD

resulted in grain growth due to the stationary die fixture. The PCZs in the EBSD imaging at IDZ (Figure 2.8) depicted localized concentration of plastic strain. Therefore, strain rate didn't reduce monotonically following the linear trend from ID to OD.

2.4.4. Microhardness Mapping

The result of microhardness tests is shown in Figure 2.11. The measurement of the original billet gets an average microhardness of HV 90-95, which is T6 aging condition. The hardness of the extruded tube is in a range of 60-75, which equals to T4-T5 aging condition [102]. The material hardness agrees with the result of the friction stir process with similar thermal cycles [10, 101].

It is well known in the previous research that grain size has little effect on 6063 aluminum alloy hardness [9, 103]. The precipitate distribution strongly affect the material hardness in the friction stir process of aluminum alloy [79, 104]. Previous research states that quench sensitivity, which is the effect of the cooling rate from solubilization temperature affect strengthen precipitation formation and then the material hardness [100, 105, 106]. Meta-equilibrium β'' -Mg₂Si and β' -Mg₂Si precipitations are the main strengthen phases in 6063 alloy, because their coherent and semi-coherent structure can better hinder motion of dislocations, While the equilibrium β -Mg₂Si phase with non-coherent interface with base material contribute little to the hardness and strength. Therefore, it requires fast-enough quenching (~ 10 °C/sec) of the aluminum solid solution before artificial aging treatment. 20 °C/sec cooling rate during the critical temperature range of 300 - 410 °C to avoid equilibrium β phase formation [107, 108].

In the FSBE process, material undergoes a short period of solubilization and then slowly cooled down to room temperature. The average cooling rate of the tube is about 3.7 °C/sec. A low cooling rate gives opportunities of equilibrium β phase formation and reduce the hardness. Figure 2.7 and 2.9 show the sign of Mg₂Si particles growth next to the AlFeSi precipitates, which confirmed that β phase particle is prior to nucleate on the AlFeSi dispersoids in the critical temperature range [100]. Rapid growth of β -Mg₂Si phase leads to low Mg and Si concentration of the solid solution and reduces concentration of main strengthen phases β'' -Mg₂Si and β' -Mg₂Si.

2.5. Conclusion

A new FSBE process is setup and trialed for 6063 alloy tubes extrusion. A small amount of plastic deformation was induced to the material because of the conservative tool design, which leads to small extrusion ratio (~ 1.15) and limited grain refinement ($\sim 20.2 \mu\text{m}$ at ID). Furthermore, grain growth at OD and non-uniform distributed precipitation are found because of unideal tool's setup and process condition. Low cooling rate after the process caused undesired $\beta\text{-Mg}_2\text{Si}$ phase formation and material hardness reduction. Improved cooling condition and more aggressive tool design may be needed to make extrusion with better properties. This research provided reference for improving tool design and material performance control.

Appendix. Figures and Tables

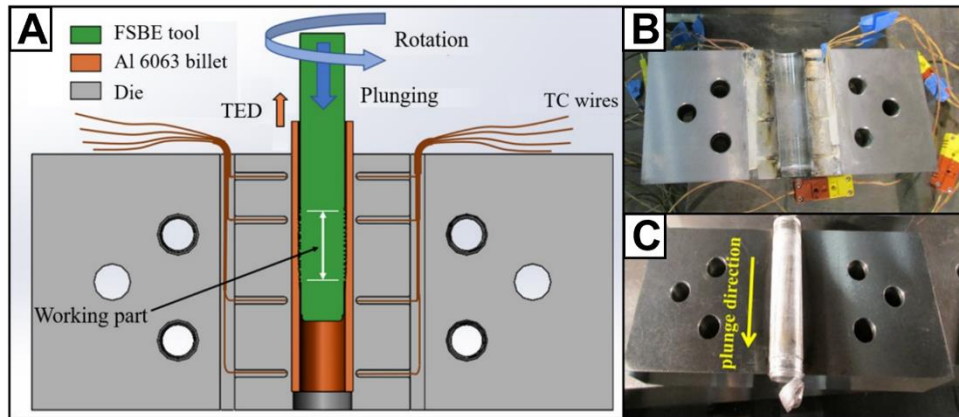


Figure 2.1 A) A schematic drawing of the tools for FSBE process, thermocouple wires (TC wires) are welded to the end of the channels notched on the die part surface. The aluminum tube (orange part) extrusion direction is denoted as orange arrow 'TED'. Actual photos of B) die half embedded with TC wires and C) the other die half with an extruded tube.

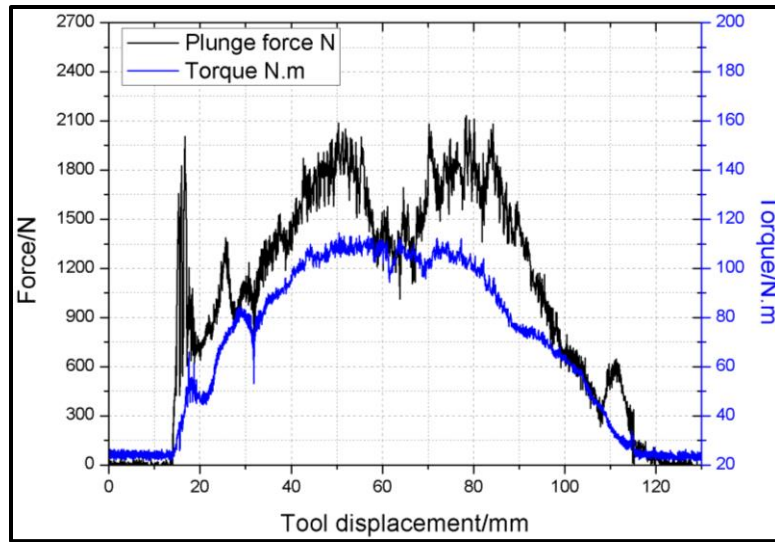


Figure 2.2 Plunging force and torque of the FSBE process as a function of tool's motion.

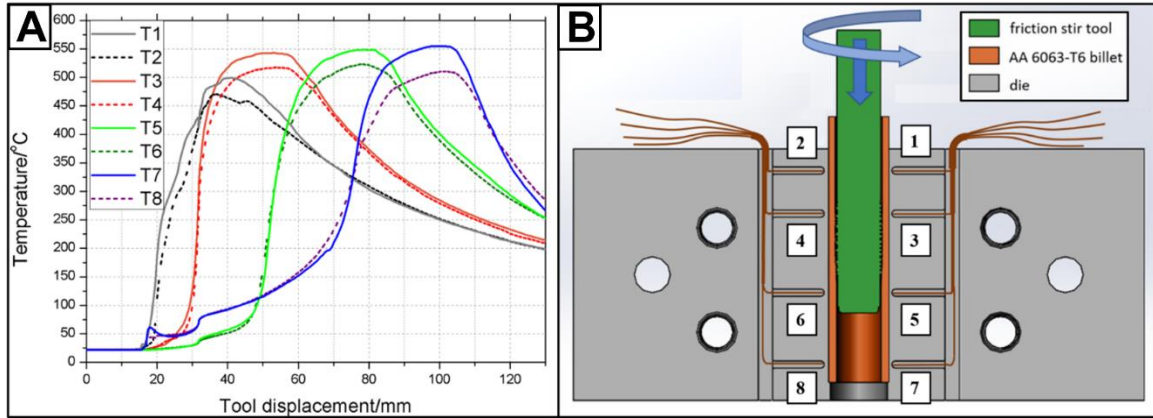


Figure 2.3 A) the temperature data from different position as functions of tool's motion in the process, where T1-8 represent for temperature at positions 1-8. B) displays numbering of the temperature measuring position, those 8 positions are placed in 4 depths (1,2 at 7.62 mm, 3,4 at 22.86 mm, 5,6 at 50.8 mm, 7,8 at 76.2 mm). Positions 1,3,5,7 were 1 mm away to tubes' OD and position 2,4,6,8 are 1.5 mm far from tubes' OD.

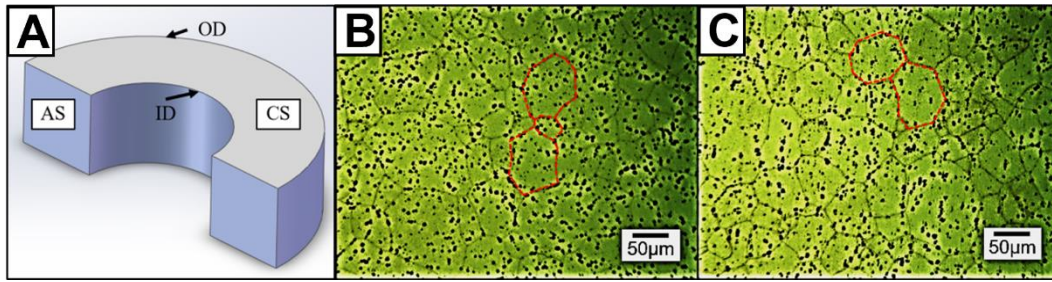


Figure 2.4 OM images of original billets before FSBE process, A) schematic of cross-sectional views of the material, etched grain structure of B) AS view, C) CS view. Typical grains are highlighted with red dash lines.

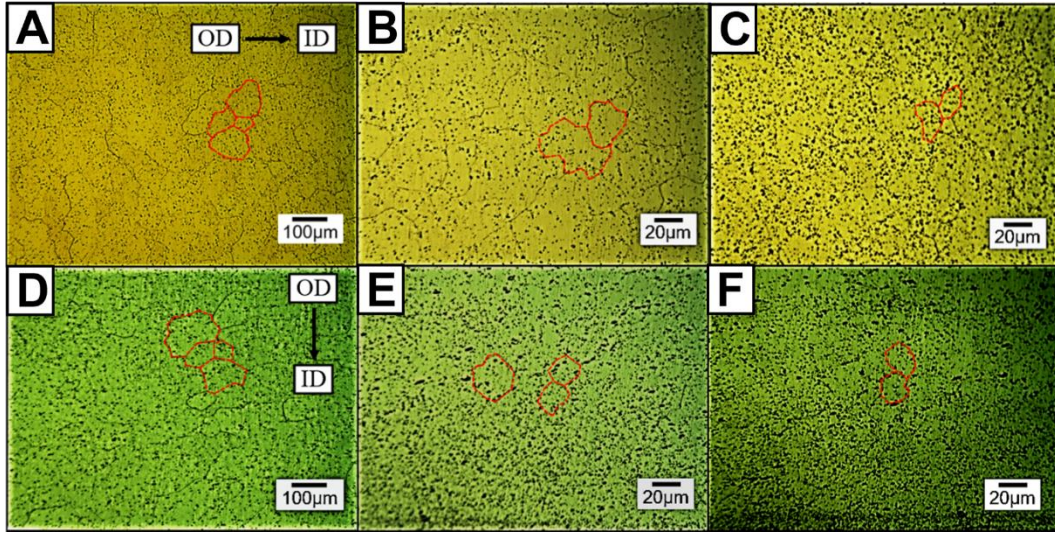


Figure 2.5 OM images of the extruded tubes on AS view at positions: (A) ODZ (B) HWTZ, (C) IDZ, and on CS view at positions: (D) ODZ, (E) HWTZ, (F) IDZ, the direction from OD to ID is from left to right in image A-C and from up to down in image D-F. Typical grains are highlighted with red dash lines.

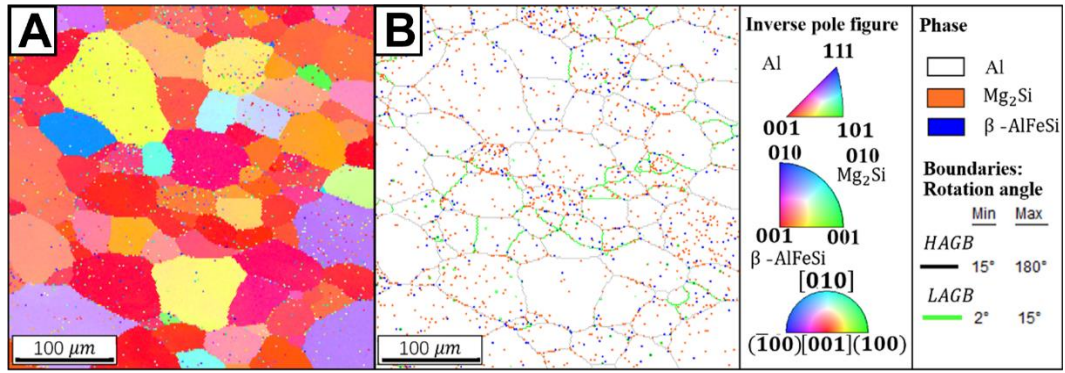


Figure 2.6 EBSD image of the original billet A) orientation map colored by [001] inverse pole figure (IPF) B) phase distribution and grain boundaries. Right legends list the color code of IPFs and phase-boundary maps.

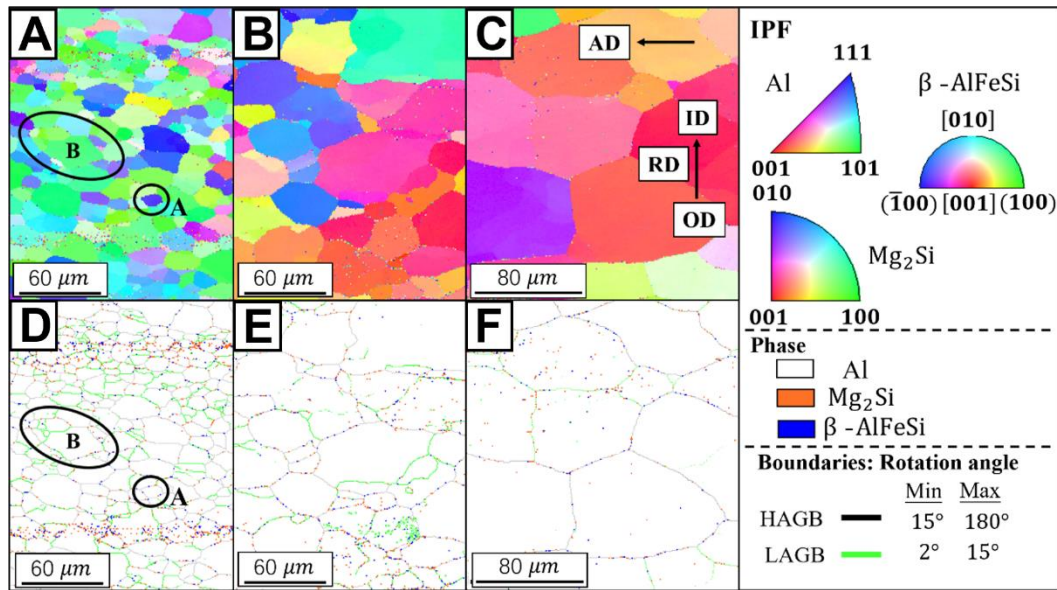


Figure 2.7 EBSD images of extruded tube on AS section: [001] inverse pole figure (IPF) image of different zones on A) IDZ, B) HWTZ, C) ODZ and phase maps of different zones on D) IDZ, E) HWTZ, F) ODZ. Circle A highlights a recrystallized grain; circle B highlights a grain with LAGB from DRV. The directions are noted in the (C): AD: axial direction, RD: radial direction.

The RD arrow point at the direction from OD to ID.

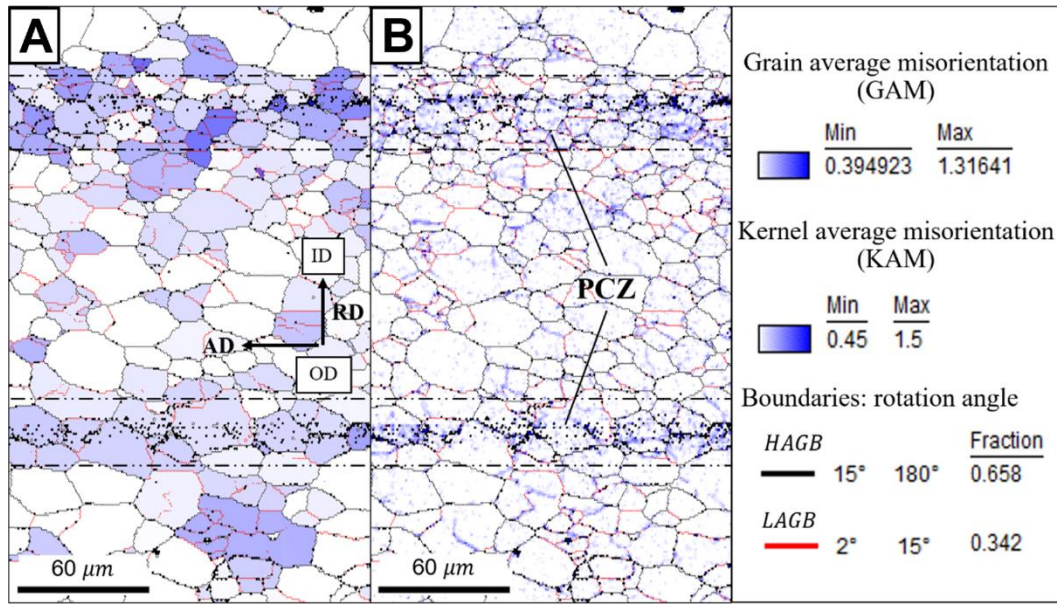


Figure 2.8 Misorientation image at IDZ from the AS view: A) grain average boundaries (GAM). B) kernel average misorientation (KAM) of the material. two precipitation concentrated zones (PCZ) are highlighted with black dashed lines.

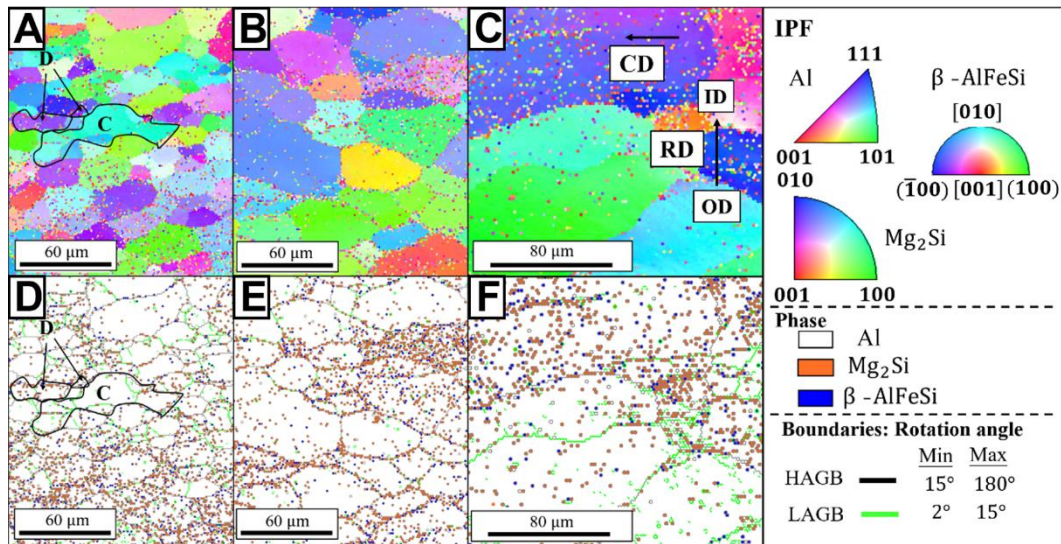


Figure 2.9 EBSD images of extruded tube on CS section: orientation maps based on [001] inverse pole figure (IPF) images at A) IDZ, B) HWTZ, C) ODZ zone and phase maps at D) IDZ, E) HWTZ, F) ODZ. Circle C highlights an elongated grain that undergoes serrating of GDRX. Circle D highlights small grains may come from GDRX. The directions are noted in the (C): AD: axial direction, RD: radial direction. The RD arrow point at the direction from OD to ID.

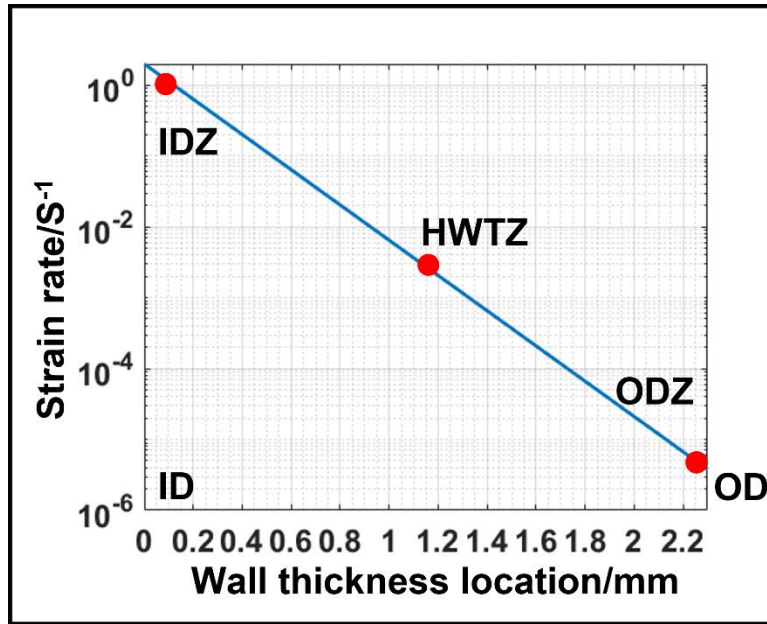


Figure 2.10 Equivalent strain rate calculated from the average grain size at IDZ, HWTZ, ODZ (red dots) with the linear regression (blue line) showing the trend of the strain rate change.

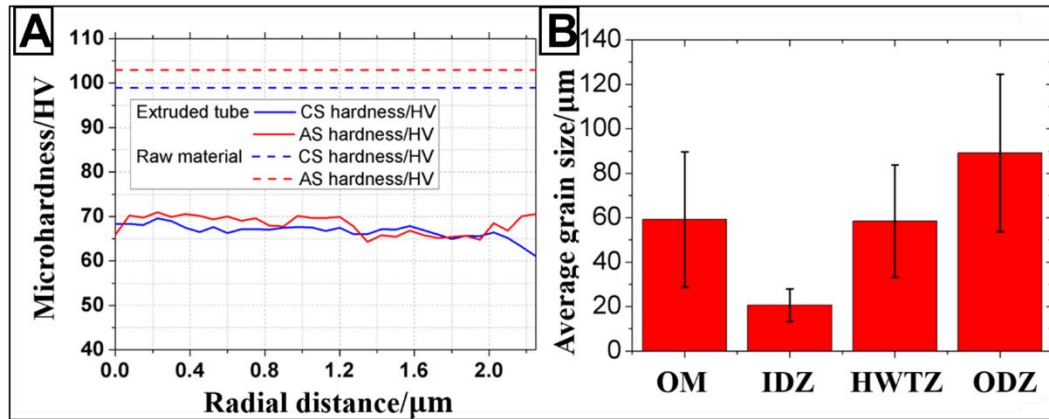


Figure 2.11 A) Microhardness value along the radial distance of the cross-sections. B) Histogram of the average grain size (red bar) and the standard deviation (error bar) from AS view calculated by EBSD analysis software at different positions. OM: original material; IDZ, HWTZ and ODZ of the extrudate.

**Chapter Three. Nickel and Intermetallic Particulate Reinforced
Composite of 7075 Aluminum Alloy Fabricated by Friction Stir
Processing**

3.1. Disclosure

The chapter contains a manuscript submitted for publication that titled: “In-situ Formation of Al-Ni Intermetallic Particulates and Property Improvement in 7075 Aluminum Alloy by Friction Stir Processing using Ni nano powders”. Suhong Zhang conducted design and implementation of the FSP experiment and characterization with the support from Alan Frederic. Yiyu Wang and Yuan Li contributed to specimen preparation as well as SEM, hardness measurement and XRD tests. Yanli Wang made the start materials for FSP by hot compression. Lawrence Allard Jr. provided TEM results and professional suggestions on the analysis. Zhili Feng supervised the project. The manuscript is revised by Zhili Feng, Seungha Shin and Anming Hu.

3.2. Abstract

Al-Ni composite material was fabricated by friction stir process (FSP) using Al 7075 alloy powder mixed with 10 wt% Ni nano powder as feedstock (denoted as ‘10Ni’). The hot-compressed pure Al 7075 (denoted as ‘7075p’) is fabricated with the same process for comparative study. Scanning electron microscopy (SEM), and X-ray diffraction (XRD) indicate the in-situ transformation of most Ni addition to Al_3Ni particles in the matrix solely by the FSP. The composite ‘10Ni’ presents Vickers hardness of 109.6 HV and 145.2 HV in as-processed (AP) and T6 aged conditions, which achieves 19.0 % and 14.6 % hardness increment than that of ‘7075p’. ‘10Ni’ shows tendency of promoting T- $\text{Al}_2\text{Mg}_3\text{Zn}_3$ and inhibiting η - MgZn_2 precipitation with respect to ‘7075p’ in XRD tests with ramping temperature (50 - 500 °C). The Orowan strengthening effect of the Al_3Ni reinforcement is evaluated for the ‘10Ni’ material. This work displays the potential of FSP as a facile and effective tool to process the materials for surface enhancement.

3.3. Introduction

7xxx series Al alloys (Al-Zn-Mg-Cu) are widely used in automotive and aerospace structures due to its high strength, strength-to-weight ratio, fracture toughness, and corrosion resistance [109, 110]. As for the Al 7075 alloy, the high strength is mainly attributed to the nano-scale metastable η and η' - MgZn_2 precipitation and their precursory Guinier-Preston (GP) zones. A maximum yield

strength above 500 MPa can be achieved in top aged T6 temper. However, strength enhancement by improving thermal-mechanical process on the current alloy composition has a limitation. While escalating usage of strong light-weight structures call for materials beyond such limitation. Furthermore, those precipitation suffers coarsening and dissolution at temperatures above 300 °C, which results in the degradation of the mechanical properties in service especially at elevated work temperatures such as automotive engine parts [111-113].

One of the main approaches to address the above challenges is making Al-based metal matrix composites (MMCs) [114-116]. Thermally-stable additive materials (ceramic, carbon allotropes and refractory metals) are introduced into Al and its alloys for the improvement of mechanical properties at both room and high temperatures. Ni is one of the attractive candidates of the reinforcements, because Ni possess a high mechanical strength and corrosion resistance even at high temperatures above 350 °C [117, 118]. Ni addition in the Al matrix below 25 % of molar fraction exists in the form of thermally-stable Al_3Ni intermetallic phase [46, 119]. Al_3Ni can form an eutectic structure with Al that is stable at temperatures above 500°C [120]. Al_3Ni significantly strengthens the Al matrix more than pure Ni phase given the same amount of Ni addition because of its higher hardness (Al_3Ni : 841 HV and pure Ni: 80-100 HV) and relatively lower density (Al_3Ni : 4 g/cm³ and pure Ni: 8.9 g/cm³) [43, 121, 122]. Al- Al_3Ni composites have been fabricated using casting [67, 117, 123] and powder metallurgy technique [124, 125]. Tiwary et al. [123] produced Al cast alloy with 3.5 at% Ni addition and achieved 400 MPa of yield strength at room temperature and 150 MPa at 300 °C. Also, Yang et al. [126] reported 90.3 MPa of yield strength at 350 °C for Al-Cu-Mg cast alloy with 1.83 at% Ni. However, casting and mechanical alloying process requires high energy consumption, sophisticated process and may result in undesired microstructures like cast dendrite, and sintering porosity [66, 127-129].

Friction stir process (FSP) has been proved as a competitive technique for fabricating Al-based composites [7, 130, 131]. In FSP, a non-consumable rotating tool is plunged into workpiece and generates friction heat to soften the surrounding material. The material microstructure is then modified by the heat input and severe plastic deformation without being melted. Therefore, the powdered reinforcements (particulate or fabric ceramic/carbon/metal) can be readily added into the workpiece and uniformly dispersed in the workpiece by the friction stir effect, and defect-free composites with refined grains can be fabricated in a single step [43, 46, 130, 132, 133].

Multiple studies have been conducted on fabricating Al-Al₃Ni composite via FSP due to its promising mechanical potential. Ke et al. [43] embedded ~100 µm sized Ni powder in Al 1060 plate and successfully produced defect-free Al-Ni intermetallic composites through FSP. Coarse Ni particles were broken into fine pieces in vigorous stirring, and Al₃Ni and Al₃Ni₂ phases were also formed due to thermal exposure. Qian et al. [44] achieved in-situ synthesis of Al₃Ni reinforced composite by introducing Ni powder into the FSP zone of Al 1100 alloy. Increasing number of FSP passes resulted in 140 % microhardness and 50 % ultimate tensile strength (UTS) increase at maximum because of grain refinement and more Al₃Ni production. Shahi et al. [46] demonstrated the feasibility of in-situ Al₃Ni synthesis without additional heat treatment, and the effect of rotational and transverse speed of the tool on the microstructure and hardness was investigated. Golmohammadi et al. [134] significantly improved the hardness and wear resistance of cast Al-Si alloy A413 by introducing in-situ Al₃Ni formation in FSP.

Starting materials of FSP in those studies were prepared by filling Ni powder in the pre-machined holes/grooves of the solid Al pieces [43, 44, 46]. Because the initial Ni feedstock is placed in narrow gaps/grooves in the workpiece, it is challenging to create homogenous composite microstructures in a large scale. An option to amend the issue is to prepare starting material by mixing Al alloy powder with powdered additive (Cu, Ti, Mo. etc.) through powder metallurgy (P/M) route [42, 62, 135]. However, it has not been used for Al-Al₃Ni composite yet. In most of previous studies, micron-scale Ni-rich reinforcements were created within a limited area no more than the tool diameter, and Ni powder with particle size less than 10 µm was not used as starting feedstock somehow. It is anticipated that sub-micron size [130] or nano size [135-137] particles can provide more remarkable strengthening effect the Al matrix due to the increased particle interaction with dislocations [137-139]. Thus, nano-sized Al₃Ni reinforcement in Al 7075 alloy using mixed powder feedstock can provide promising strength enhancement.

The studies on metallurgy of Al-Zn-Mg-Cu-Ni systems indicate that Ni contained intermetallics like Al₃(Cu, Ni)₂ and Al₇Ci₄Ni changed Cu content available for other precipitates like T-Al₂Mg₃Zn₃ and η-MgZn₂, which still play important roles in strengthening [118, 126, 140]. Such effect in the composite made by FSP route is not well understood. Therefore, it is also important to investigate the possible phase change of Al 7075 alloy caused by Ni.

In this research, we studied the fabrication of Al-Ni composites with in-situ Al₃Ni formation via FSP route, focusing on the precipitate mechanism of Al-Ni phase in Al 7075 alloy and its relations with the mechanical properties. Hot-compressed mixed powder of Al 7075 alloy and nanosized Ni powder were employed as start materials, and solid solution heat treatment and T6 aging heat treatment were conducted on the processed materials.

3.4. Experiment

Feedstock materials used in this work included Al 7075 alloy powder in 10-44 μm size (Valimet Inc), and Ni nanopowder in 80-150 nm size (99% purity, Skyspring Nanomaterial Inc). Solid blocks of Al 7075 (McMaster-Carr) were also used for support and facilitating FSP of powder materials. 10 wt% Ni nanopowder was mixed with the Al 7075 powder (denoted as ‘10Ni’) for friction stir processing. For comparison, 100% Al 7075 alloy powder (denoted as ‘7075p’) was also processed. Table 3.1 summarizes the chemical composition of the selected powder materials. Ni powder and 7075 alloy powder were mixed using the Glison LC-92 low-speed jar mill at 120 RPM for 6 hours. The powders were first cold-compressed into blocks under 210.6 MPa of pressure, achieving approximately 80% relative density of the solid Al 7075 alloy. The blocks were further consolidated by a hot compression at 400 °C and 40 MPa for 40 min, to achieve a final 93% relative density (denoted as ‘HP’ condition).

Figure 3.1 is the schematic drawing of the material layout for friction stir processing trials. The hot-compressed blocks were cut into $(18 \times 18 \times 5) \text{ mm}^3$ rectangular blocks, and eight rectangular blocks were placed into a pre-machined $(36 \times 72 \times 5) \text{ mm}^3$ opening in the 5 mm thick solid Al 7075 alloy plate (Figures 3.1B and 3.1C). Another 6 mm-thick Al 7075 alloy plate was placed beneath the powder blocks as the bottom support. The consolidated powder blocks and the plate were first welded into one piece by spot-wise FSP on the top surface using the pin-less $\phi 19$ mm H13 steel tool. The multi-track FSP swept through the powder block region using a $\phi 19$ mm H13 steel tool with a $\phi 6 \times 4.4$ mm threaded pin. The rotational speed of the tool was 550 RPM, and the linear travel speed is 25.4 mm/min. The tool tilt angle is 2° with 0.05 mm shoulder depth beneath the surface. The processed materials were naturally cooled down by air (denoted as as-processed or ‘AP’ condition). The friction stir processed materials were post heated. They were solution heat treated at 475 °C for 1 hour and water quenched (denoted as condition ‘SS’). Some

were further aged at 120 °C for 24 hours to achieve the T6 condition (denoted as condition ‘T6’) [141].

The phases in the processed materials were identified by the X-ray diffraction (XRD) analysis using a Malvern Panalytical Empyrean diffractometer with Cu K- α radiation (45 kV, 40 mA, 0.05°/sec). High-temperature XRD tests (HTXRD) with continuous heating of the material was conducted using the same machine. The X-ray diffraction signal of solution heat treated material was collected between 15° and 50° of 2 θ angle, increasing temperature from 50 °C to 500 °C at a heating rate of 1 °C/min. The XRD results were quantitatively analyzed by GSAS-II software [142].

In addition, the microstructures in processed materials were characterized by electron microscopy on grinded and polished specimens. A MIRAS3 TESCAN scanning electron microscope (SEM) was used to reveal the microstructure. The specimen for transmission electron microscopy (TEM) was prepared by electrolytic polishing using the methanol solution with 25% nitric acid under -40 °C following the literature [143]. A JEOL JEM 2200FS TEM equipped with an energy dispersive X-ray spectroscopy (EDS) system was employed for the TEM characterization (210 kV, 20 nA) for the fine structure characterization and crystal structure determination. Elemental distribution was obtained by EDS in both SEM and TEM. Microhardness of the material was measured by microhardness tester (LECO LM100 AT) with a 25 g load. Measurement of particle size and area fractions in SEM and TEM micrographs were performed with the ImageJ software and in-house MATLAB code.

3.5. Results and Discussion

Figures 3.2A and 3.2B show the SEM micrographs of the as-received Al alloy powder and Ni nanopowder blended and mounted in the epoxy resin. Particles of both Al 7075 and Ni powder have spherical shapes, and their average particle sizes (diameters) are $21.8 \pm 13.4 \mu\text{m}$ and $0.66 \pm 0.61 \mu\text{m}$, respectively. The larger average size of Ni (660 nm) than the specification (80 - 150 nm) is attributed to the nanoparticle agglomeration.

The cross section of the hot-compressed ‘10Ni’ mixed powder block in Fig. 2C presents that the dark-colored Al particles were compacted together and slightly deformed. Ni particles are in bright color in the figure, with large ones (5 - 20 μm) residing at the corner of Al particles, and the smaller Ni particles distributed along the Al particle interfaces. Voids at particle interface was apparent, indicating incomplete consolidation during the hot compression prior to friction stir processing. Such distributions of Ni particles were attributed to the size difference between the Al 7075 powder and the Ni powder. Ni nanopowder was filled into the gap during powder mixing and compression and agglomerated in the gaps between spherical Al particles.

Figure 3.3A shows a cross-section view of the ‘10Ni’ material after FSP. The darker-colored top region was approximately 4.8 mm thick, as a result of severe thermal deformation by the stirring effect of the 4.4 mm long tool pin. The dash-dotted line between the dark and bright regions delineates the boundary between the friction stir processed powder region and the supporting solid block of 7075 alloy at the bottom. The distinct bright flow lines indicate that a small portion of the bottom 7075 plate was stirred up and blended into the powder region. Figures 3.3B-D show the magnified sections of the locations corresponding to ‘B’, ‘C’, and ‘D’ in Figure 3.3A, that were in the AP condition. The bright Ni-containing particles are uniformly distributed in the Al matrix. The crack or porosity from the hot compression step (Figure 3.2C) disappeared after FSP, suggesting the FSP fully consolidated the powder materials together. Several bulk particles (‘retained Ni’ marked by the arrows) were observed, possibly from the agglomerated Ni at Al particle intercepts. Most of the particulates smaller than 2 μm have dark gray color in the figures in contrast to the bright color of the retained Ni. Figures 3.3E-G presents that all particles turn into the same gray color regardless of size after the solution heat treatment and T6 aging. However, the centers of large-size particles remain relatively bright color and form core-shell structures (Fig. 3G). This indicates further transformation of the large-size Ni particles’ interiors to nickel aluminide during the post-process heat treatment.

The SEM/EDS analysis of the particles revealed the Al and Ni element composition and their spatial distribution (Figure 3.4). Figure 3.4A shows element quantification of locations 1-3 in the AP material. The bright-colored core region of particle 1 is pure Ni phase, while particle 2 and particle 3 in a darker color are estimated as Al_3Ni phase by EDS. Figure 3.4B shows $\sim 10\ \mu\text{m}$ core-shell particles close to the region in Figure 3.3G. Line scanning across the particle from point ‘a’

to ‘b’ identifies decreasing Al: Ni atomic ratio inside out. The bright-colored core region Al: Ni ratio close to 1: 3 implies AlNi_3 phase, followed by a steep transition to 3: 1 ratio to the exterior shell region that corresponds to Al_3Ni phase. Previous studies of solid-state Al-Ni diffusion [144, 145] concluded that multiple Al-Ni intermetallics can form at Al-Ni boundary with decreasing Al concentration into the Ni region. Al_3Ni is a predominant phase in Al matrix with a minor Ni addition due to the higher diffusivity of Al into Ni [146, 147]. FSP transforms Ni particles smaller than 3 μm into Al_3Ni intermetallics. Since the solid-state reaction to form Al_3Ni is available at 270 °C [44, 73, 146], the temperature during FSP thermal cycle is sufficient for the formation of Al_3Ni , including full transformation of small Ni particles into Al-Ni intermetallics. However, the relatively short time at temperatures above 270 °C during FSP, which is in a range of 10-100 second, does not allow for a full transition of coarser Ni particles into nickel aluminide. The post-process heat treatment (475 °C for 1hr plus 120 °C for 24 hrs.) leads to further Al diffusion into the inside of large Ni particles, to transform into additional intermetallics within the large Ni particles. This indicates that the usage of fine Ni particles facilitates the full in-situ transformation of Al_3Ni with no additional heat treatment.

The in-situ formation of Al-Ni intermetallics during FSP and subsequent heat treatment was further confirmed by XRD diagrams as shown in Figure 3.5. Typical precipitations in Al 7075 alloy, including $\eta\text{-MgZn}_2$, $\eta'\text{-Al}_4\text{Mg}_2\text{Zn}_3$, $\text{T-Al}_2\text{Mg}_3\text{Zn}_3$ and $\text{S-Al}_2\text{CuMg}$ were observed. Ni-containing phases are comprised of Ni, Al_3Ni_2 , Al_3Ni , and small fraction of $\text{Al}_7\text{Cu}_4\text{Ni}$. The weight fraction of Ni-containing phases calculated by the Rietveld quantification [142, 148] were 7.1 wt% Ni and 1.5 wt% Al_3Ni in hot-compressed material (‘10Ni-HP’). Using the same quantification process, the composition of as-processed ‘10Ni’ material (‘10Ni-AP’) was also identified as 0.5 wt% Ni, 0.5 wt% Al_3Ni_2 , and 13.6 wt% Al_3Ni . As for the T6-aged 10Ni (‘10Ni-T6’), the results were 0.3 wt% Ni, 0.2 wt% Al_3Ni_2 , and 14.7 wt% Al_3Ni . This analysis reconfirmed the that the majority of Al_3Ni was formed in-situ by FSP. Assuming the Ni constituents strictly follow the phases’ stoichiometry (usually not the real case), the total Ni contents in ‘10Ni’ material are estimated as 7.5, 6.1, and 6.3 wt% for HP, AP, and T6 conditions, respectively. The difference can be attributed to the quantification uncertainty, and the variability of Ni contents in certain phases depends on the equilibria. However, lower Ni contents in AP and T6 condition than the HP may be due to the material mixing between powder feedstock and surrounding Al 7075 solid plates.

The chemical composition of Al 7075 solid alloy and powder are almost identical as shown in Table 3.1.

Figure 3.6 shows the HTXRD spectrum of A) 7075p-SS and B) 10Ni-SS materials from 50 to 500 °C. Both materials are solution heat treated (475 °C, 1hr) and water quenched in prior to the test. The bright yellow vertical bands represent for diffraction peaks of certain phases. The intensity of Al_3Ni phase peaks in ‘7075-Ni’ changed little from 50 to 500 °C, which is because the Al_3Ni remains thermally stable till the Al matrix is melt [149]. The peaks corresponding to η - MgZn_2 precipitate (marked by ‘+’) only appeared from 200 to 350 °C in both materials. The η phase intensity in ‘7075p’ is stronger than that of ‘10Ni’. In addition, ‘10Ni’ exhibits peaks of T- $\text{Al}_2\text{Mg}_3\text{Zn}_3$ phase (marked by ‘stars’) between 300 and 450 °C whereas ‘7075p’ material has no evident peaks of the T phase. Figure 3.7 further shows the weight fractions of the two phases as functions of temperature, which were quantified from HTXRD analysis. Maximum 3.8 wt% of η precipitate was measured in ‘7075p’ while only 2.2 wt% was observed from ‘7075-Ni’ at the same temperature. It is noted that the T phase in ‘7075-Ni’ began to precipitate at 300 °C, reached the maximum weight fraction at 400 °C, and completely dissolved when the temperature reached 450 °C.

The difference in the precipitation mechanisms caused by the Ni addition to Al 7075 may be interpreted as follows. The formation and dissolution of the η and T phase agree with the precipitation sequence of the 7075 alloy [1]: GP zone $\rightarrow \eta' \rightarrow \eta \rightarrow T' \rightarrow T$ phase. The relative fraction between η and T phase depends on Zn/Mg ratio and Cu content in 7xxx series Al alloys. Zn/Mg ratio in Al matrix should be hardly affected by Ni addition because Mg and Zn has a very low solubility in Ni and nickel aluminide phases [150]. Cu behaves synchronously with Zn in the Zn containing phases. Nickel contained phases like $\text{Al}_3(\text{Cu}, \text{Ni})_2$ and $\text{Al}_7\text{Cu}_4\text{Ni}$ reduce the remaining Cu in Al matrix, thus increasing T phase formation rather than η . The simulation and experimental observation of Belov et al. [118, 140] demonstrated the affinity of T formation with higher Ni and lower Cu content in an Al-Cu-Zn-Mg-Ni alloy system.

Both the size and volume fraction of Ni-containing intermetallic particles play important roles in the particle reinforcement of the Al matrix. The particle sizes and distribution were determined by image processing of the SEM micrographs. Figure 3.8A shows volume fractions of Ni-

containing phases from the mass fraction quantification from XRD. The densities of Ni, Al₃Ni₂, and Al₃Ni used for the volume fraction calculation are 8.9, 4.8, and 4.0 g/cm³, respectively [68, 151]. Figure 3.8B shows the volume fractions of Ni and nickel aluminide intermetallic under the HP, AP and T6 conditions by processing SEM images of a total 2.08×10⁵ μm² area. It is noted that distinguishing Al₃Ni₂ from Al₃Ni is difficult in this study, since only small volume fraction of Al₃Ni₂ was formed in large-size particles. Similar volume fraction results were obtained from two methods. The results are used for the calculation of Orowan strengthening effect in the composite.

The minimum resolution of SEM imaging in this study was approximately 2-3 nm [152]. It is difficult to identify feature smaller than 90 nm (dimension per image pixel) in the analysis of the SEM micrographs. TEM was used to observe more detailed microstructure and possible defects (with a resolution down to 0.06 nm). Figure 3.9A shows a TEM micrograph of the 7075-Ni composite in the AP condition. Al₃Ni (white arrows) are mainly in size of 100-200 nm. The lath-like η precipitate (yellow arrows) are in size of ~20 nm, which is in a good agreement with the 7075 wrought alloy in annealed condition [153, 154], annealed microstructure is anticipated since AP material is slowly air-cooled after FSP. Some micro-voids in size of 100 nm were shown at Al₃Ni particulate interfaces (red arrows), while SEM imaging under the 3000× magnification captured no such void due to the limited resolution. The elastic and thermal expansion mismatch between Al₃Ni and Al would cause interfacial straining during thermal cycles in FSP [151, 155], which makes the boundary material easier to be etched in electropolishing than that away from the particles [156]. Corresponding Al-Al₃Ni composite previous studies Figure 3.9B is the selected area electron diffraction (SAED) diagram of the particle 'B' along Al₃Ni<013> with 9.1° off the <110> direction of the surrounding Al grain. The SAED diagrams of other Al₃Ni particles present random orientations with no fixed relationship with the neighboring Al grains. This may indicate that Al-Al₃Ni interface in composite is non-coherent. One plausible argument would be that Al₃Ni was formed by solid state reaction between Al and Ni in FSP. Ni particles and nickel aluminides present random orientation with respect to the surrounding Al under the plastic material flow of FSP, the thermal-mechanical induced dislocation vacancies fall into the particle interfaces in the following recovering and recrystallization process. Incoherent orientation relationship between Al and Al₃Ni is finally formed. It shows a different precipitation mechanism from the Al-Al₃Ni cast alloy, where Al₃Ni precipitates are solidified from liquid first and cause heterogeneous nucleation

and growth of Al matrix phase from the Al₃Ni precipitates. In this case, a coherent Al matrix forms around the Al₃Ni with the boundary Al₃Ni<010>//Al<321> and Al₃Ni (102)//Al (111) [65-67, 69, 117].

Figure 3.10A shows the microhardness measurement results of the friction stir processed region at the 2 mm depth beneath the top surface. There is no significant hardness change observed across the path of measurement. Figure 3.10B shows the average microhardness of four materials: ‘7075p’ and ‘10Ni’ under as-processed (‘AP’) and T6 aged (‘T6’) conditions. Both the FSP-processed ‘7075p’ and ‘10Ni’ material, which started from the mixed and compressed powders, showed lower hardness than wrought 7075-T6 Al alloy after T6 aging. The wrought 7075 alloy in T6 condition usually has microhardness of 185 HV (red dashed line in Figure 3.10A and 3.10B) [141]. The average hardness of ‘7075p’ material is 92.1 HV and 126.7 HV in AP and T6 conditions, respectively, and that of Al-Ni material is 109.6 HV and 145.2 HV in AP and T6 conditions, respectively. The increment of 7075-Ni with respect to the 7075 at both heat treatment conditions can be attributed to the particle reinforcement of Ni and nickel aluminide. The Ni addition results in 17.5 HV and 18.5 HV increment than the Ni-free ‘7075p’ material in AP and T6 condition.

Most of the Ni addition presents in the form of Al₃Ni particles, and thus, only the strengthening contribution of Al₃Ni is discussed. The reinforcement particles strengthen the matrix by either the dislocation shearing mechanism or the Orowan dislocation bypassing mechanism [157, 158]. The Orowan mechanism is dominant in the studied material because no lattice coherency between Al₃Ni and Al is found, and the dislocations prefer bypassing the Al₃Ni particles. The yield strength increment $\Delta\sigma$ by the Orowan mechanism is [158, 159]:

$$\Delta\sigma = \frac{2.48Gb}{2\pi\sqrt{1-\nu}(D-d)} \ln\left(\frac{d}{r_0}\right), \quad (3.1)$$

where G and b are the Al matrix shear modulus (26.9 GPa) and the magnitude of Burgers vector (0.286 nm) [14]. ν , D , and d are the Poisson ratio, average particle spacing, and average particle diameter, respectively. r_0 is a constant that is equivalent to $1.5b$. The average spacing D is given as [158]

$$D = \frac{2}{3} \cdot d \left(\frac{1}{V_p} - 1 \right), \quad (3.2)$$

where V_p is the volume fraction of the reinforcement. The volume fractions of Al_3Ni are determined as 10.20 vol% in AP condition and 11.25 vol% in T6 condition. The average particle diameter d for Al_3Ni is determined as 0.26 and 0.43 μm in AP and T6 condition, respectively. The relationship between Al alloy's yield strength σ_y (MPa) and Vickers hardness H_V can be estimated by [160]:

$$\sigma_y = 2.106H_V. \quad (3.3)$$

The yield strength increment estimated by the Orowan mechanism due to Al_3Ni are 43.5 MPa and 35.0 MPa in AP and T6 condition. The equivalent yield strength enhancement of '10Ni' estimated from the Vickers hardness measurement are 36.9 MPa and 39.0 MPa with respect to '7075p' in AP and T6 condition. Previous studies of FSP Al- Al_3Ni composite shows the usage of micron-scale Ni powder usually produces micron-scale and submicron-scale Al_3Ni reinforcement with wide range of particle size [43, 44, 46, 134, 161, 162]. Residue Ni particle sometimes in millimeter scale found in those FSP composite indicates insufficient Al-Ni reaction of coarse Ni particle [161]. The hardness enhancement achieved per wt% of Ni addition is 1.2-1.7 HV in the FSP Al-based composite with micro-Ni powder as feedstock [43, 44, 46, 134, 161, 162]. In contrast, the in-situ formed Al_3Ni in the current composite '10Ni' shows finer particle size with much less residue coarse particle (0.10 vol% coarse Ni from SEM image analysis) in AP condition. The '10Ni' composite achieves 2.2 HV and 2.3 HV hardness increment per wt% of Ni addition in AP and T6 condition with nano-size Ni feedstock. Apparently, the usage of nano-size Ni particle addition in the feedstock facilitates more homogeneous distribution of fine Al_3Ni formation with more efficient strengthening, even if Ni particle agglomeration between Al particles was not eliminated.

Figure 3.11 shows TEM images of the grain boundaries in '10Ni' material. Needle- and plate-like η' precipitates distributed in $\text{Al}\langle 110 \rangle$ grains are in size of 2-5 nm. The SAED diagram (Figure 3.11C) shows a semi-coherent relationship of $\text{Al}\langle 110 \rangle // \eta'\langle 1010 \rangle$, which is a common structure of T6 aged Al 7075 alloy [163]. The precipitation free zone (PFZ marked with the black dashed line) was observed at both Al-Al grain boundaries and Al- Al_3Ni boundaries. η phase particles are

seen at Al-Al boundaries but not at Al-Al₃Ni boundaries. Guinier-Preston (GP) particles and η' precipitates are not likely to form in PFZ due to the lower vacancy concentration in the vicinity of grain boundary region after the heat treatment [41]. PFZ is believed to negatively affect the strength and ductility of the precipitate hardening alloys [42, 43]. The width of the PFZ between Al grains measured from the TEM images are approximately 19 nm in 7075s material and 18 nm in Al-Ni material. The width of PFZ at Al-Al₃Ni boundaries is 20 nm.

3.6. Conclusions

Al-based composite material was fabricated using FSP with the hot-compressed 7075 powder as start material. 10 wt% nano-sized Ni powder was mixed into the start material as reinforcement of the composite. The research provides an alternative route of fabricating intermetallic reinforced Al-based composites. We comprehensively evaluated the microstructure and hardness of the materials.

1) XRD phase quantifications shows in-situ transformation of 93 wt% of Ni to Al₃Ni phase in as-processed material ('10Ni-AP'). This demonstrates the FSP as an effective way to make Al composite with in-situ Al₃Ni formation. Coarse Ni particles were formed during powder mixing and hot compression. Ni particles larger than ~3 μm had pure Ni phase in the core. The lack of Al-Ni interdiffusion in the coarse Ni particles has been found in other studies of Al-Al₃Ni FSP fabrication [43, 44, 46, 161]. The usage of fine size Ni addition aids to complete in-situ formation of Al₃Ni.

2) TEM observed nano-sized Al₃Ni particles in Al matrix with random orientations and non-coherent interfacial bonding, and this leads to the limited strengthening effect compared with the cast Al-Ni alloys. The average sizes of Al₃Ni particles are 96 nm and 151 nm in AP and T6 conditions, respectively.

3) Pure 7075 Al alloy made by FSP (7075p) and '10Ni' composite achieved 92.1 and 126.7 HV of Vickers hardness at AP condition, respectively. The hardness of 7075 and 7075 Ni reached 109.6 and 145.2 HV after T6 aging. The hardness increment of 7075-Ni than 7075 can be attributed to the Orowan strengthening effect of Al₃Ni particles.

4) Ni addition induces the affinity of T-Al₂Mg₃Zn₃ formation and inhibition of η -MgZn₂ precipitation due to the formation of Al₃(Ni, Cu)₂ and Al₇Cu₄Ni and resultant Cu depletion in Al matrix.

Appendix. Figures and Tables

Table 3.1 Chemical composition of the Al 7075 powder and Al 7075 plate used in FSP

Material	Al	Cu	Mg	Zn	Ni	Fe	O
7075 powder	90.32	1.57	2.22	5.68	0.01	0.10	0.10
7075 plate	90.23	1.60	2.11	5.95	0.01	0.10	<0.01

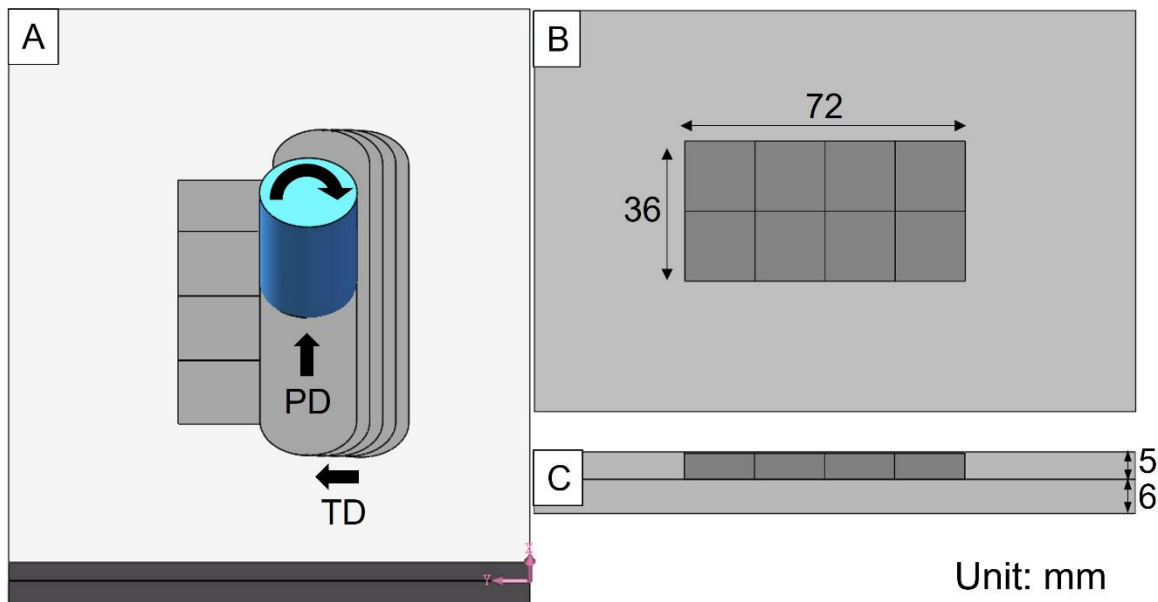


Figure 3.1 Schematic description of FSP trial; A) Multiple tracks of FSP, TD: transverse direction, PD: process direction. B) top view and C) side view of the start material (Unit: mm).

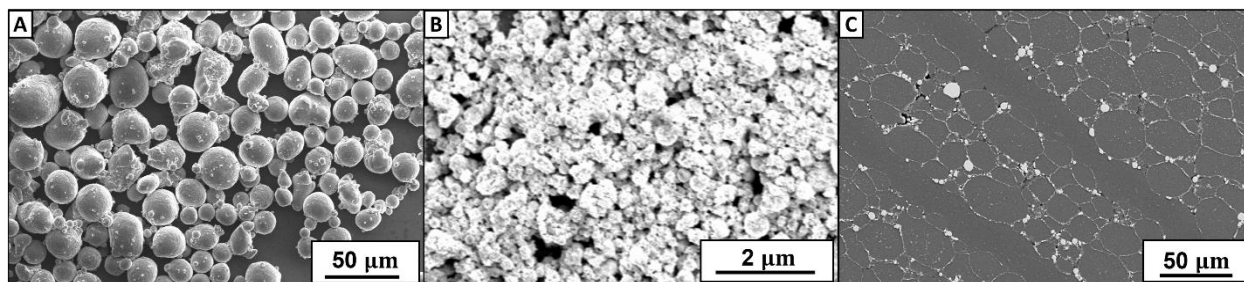


Figure 3.2 SEM micrographs of the A) as-received Al 7075 alloy powder, B) Ni nanopowder, and C) cross section of hot-compressed powder feedstock (HP) for ‘10Ni’ material.

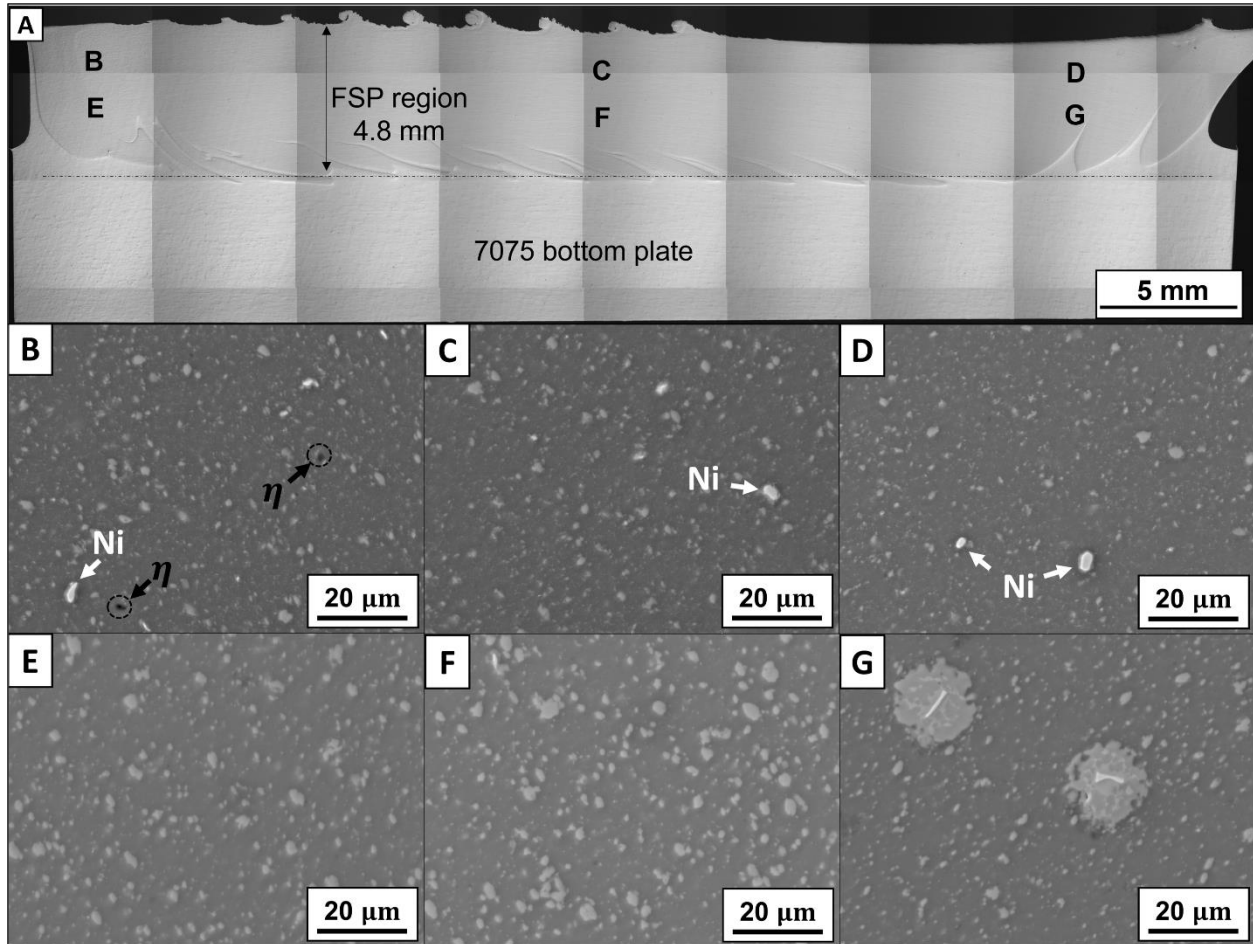


Figure 3.3 SEM micrographs of the material ‘10Ni’ that show A) overall cross section of the FSP region; B - D) show magnified sections in AP condition at locations ‘B’, ‘C’, and ‘D’ in Figure 3A. E - G) magnified micrographs in T6 aged condition at locations ‘E’, ‘F’, and ‘G’ in Figure 3.3A.

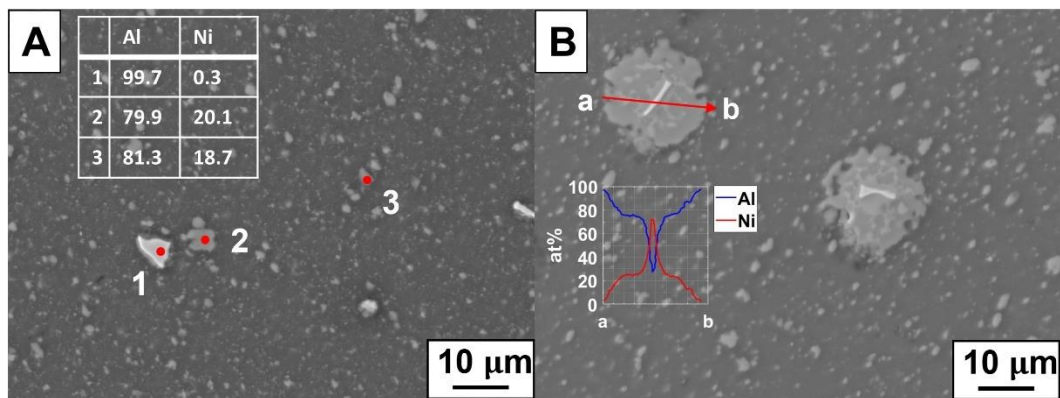


Figure 3.4 SEM/EDS analysis of Ni enriched particles in A) AP and B) T6 conditions.

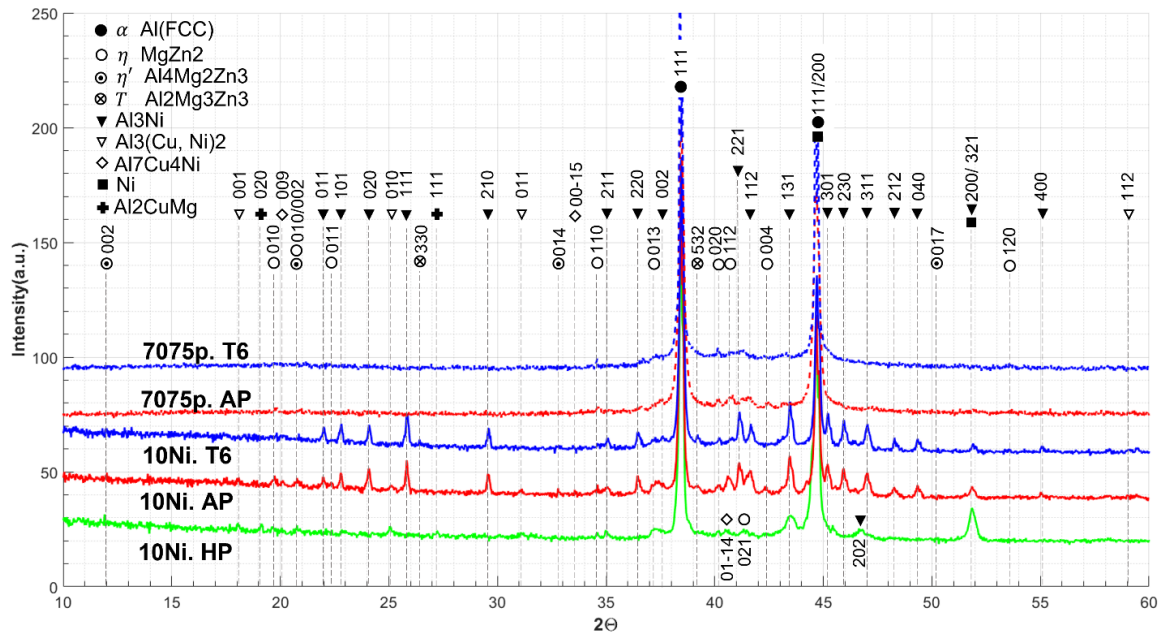


Figure 3.5 XRD diagrams of ‘10Ni’ and ‘7075p’ material at different heat treatment conditions.

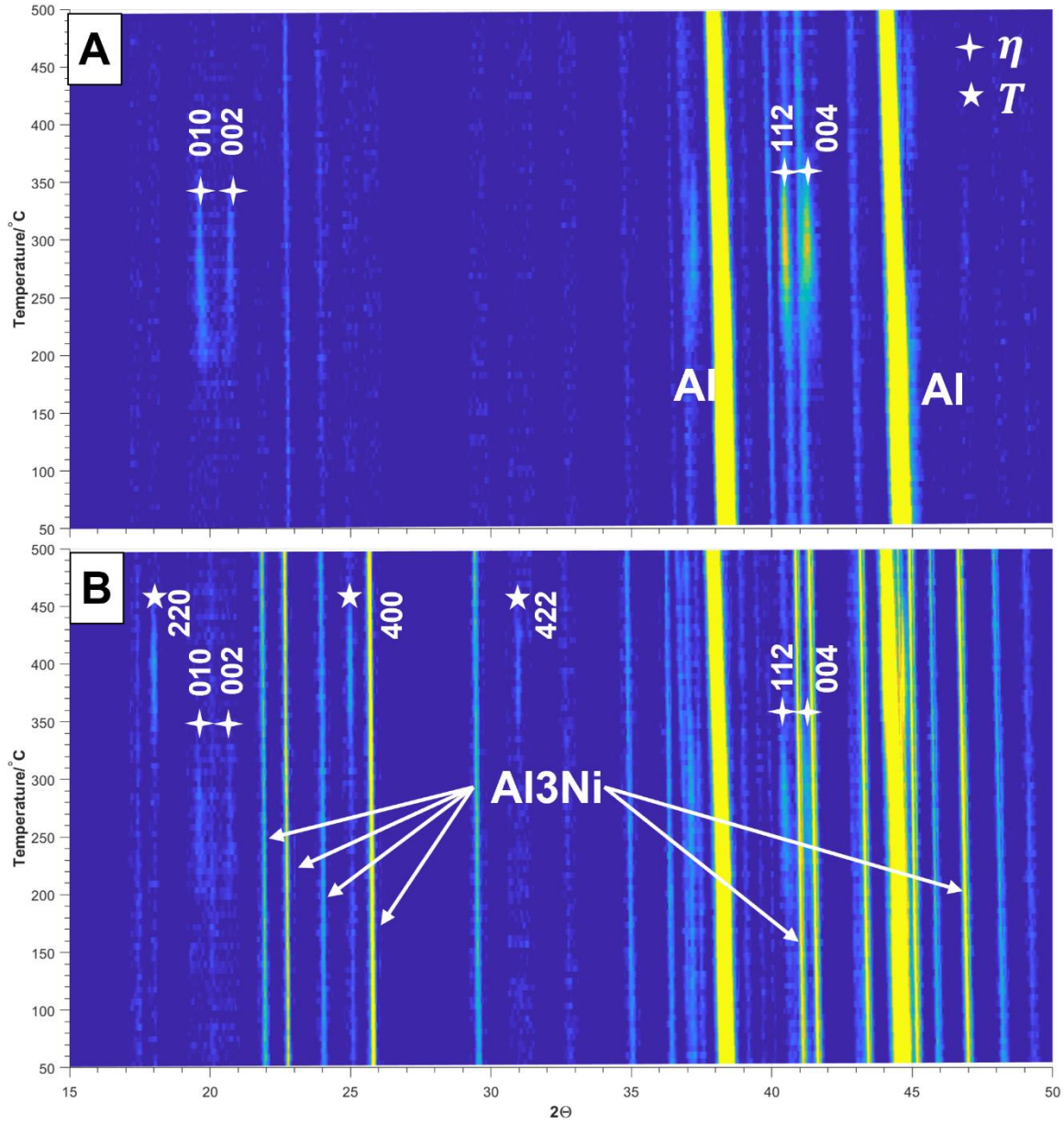


Figure 3.6 HTXRD pattern of A) '7075p' material and B) '10Ni' composite. The η precipitation peaks are marked by '+' and the T phase peaks are marked by '★'.

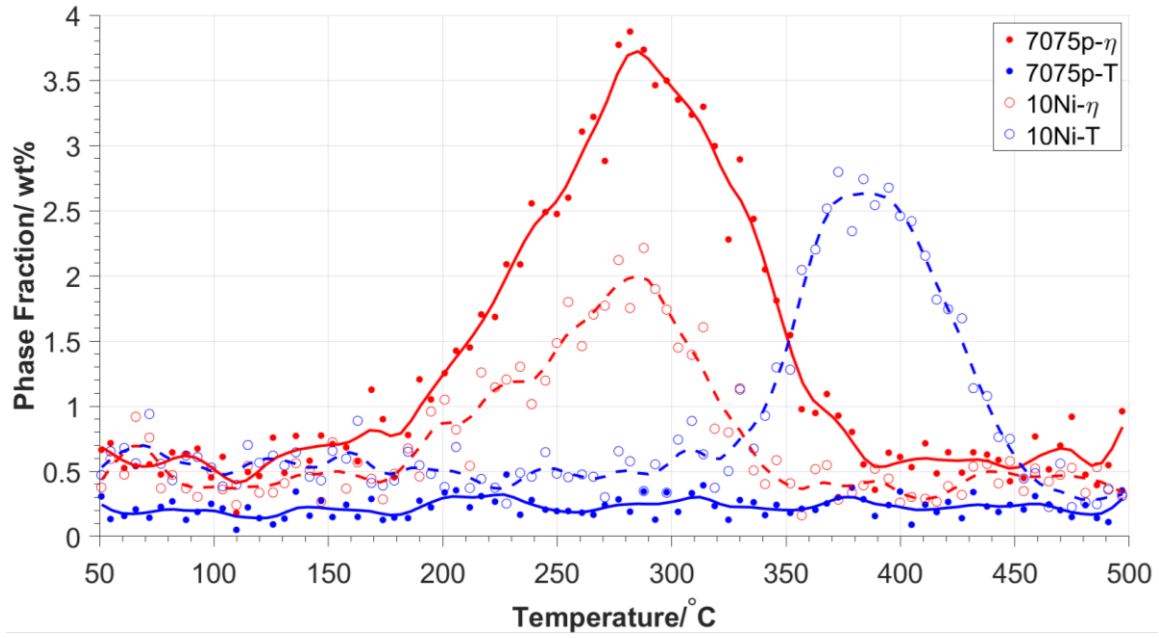


Figure 3.7 η and T phases weight fractions as functions of temperature from HTXRD pattern.

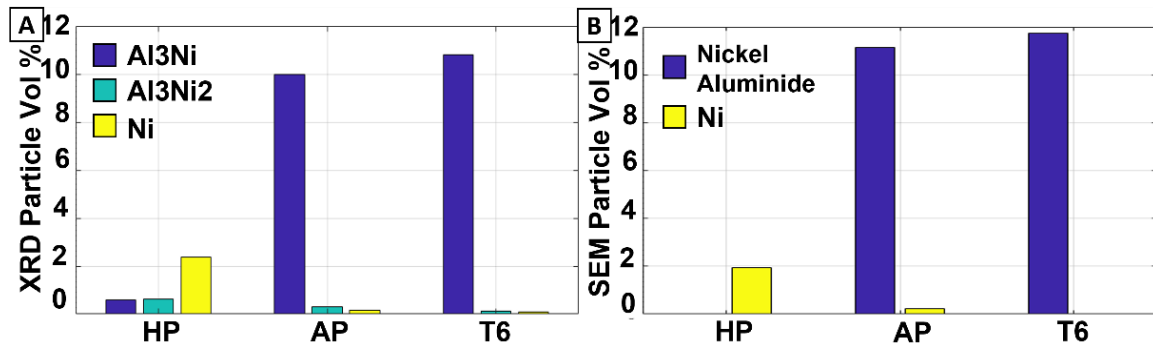


Figure 3.8 Volume fraction estimation from A) phase quantification of XRD and B) SEM micrographs.

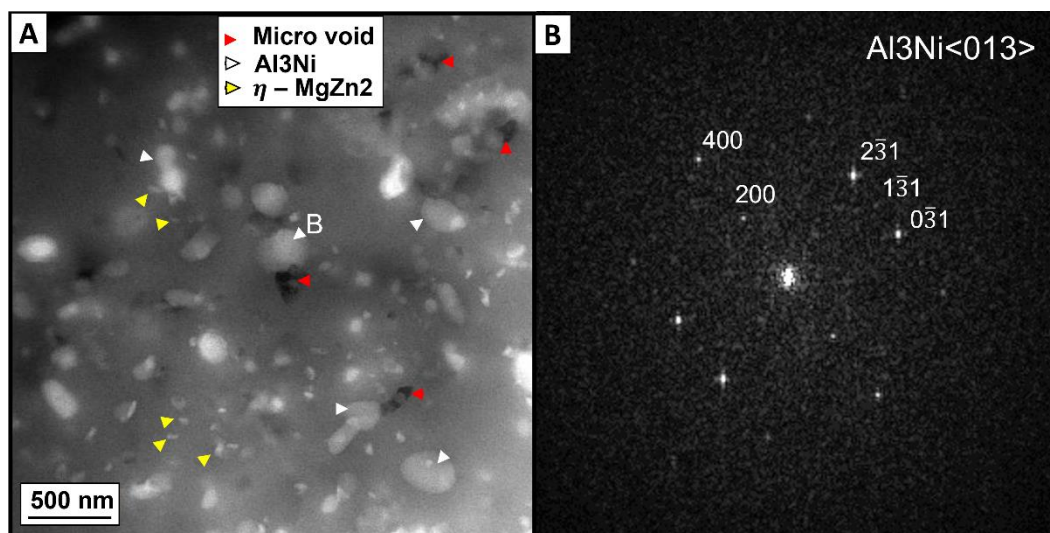


Figure 3.9 A) TEM dark field image (DFI) of 10Ni-AP material; B) SAED pattern of the particle B in Figure 9A.

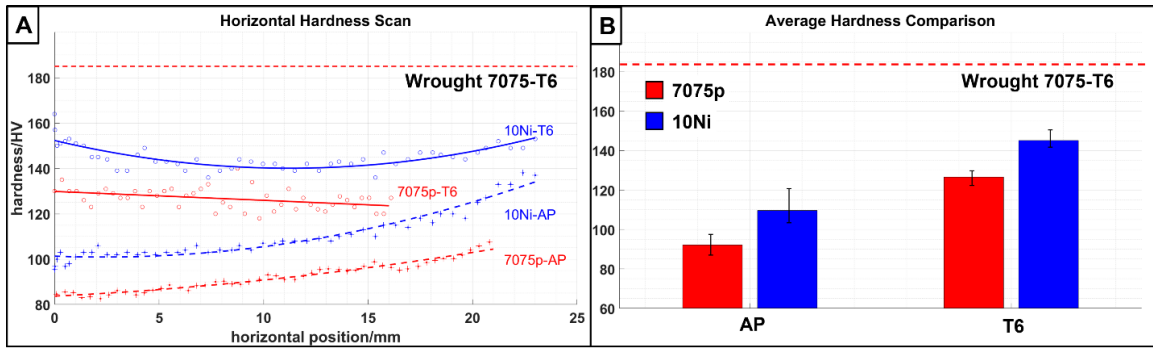


Figure 3.10 A) Vickers hardness measurement along horizontal direction in FSP region cross section; B) Average Vickers hardness of the FSP materials in AP and T6 conditions.

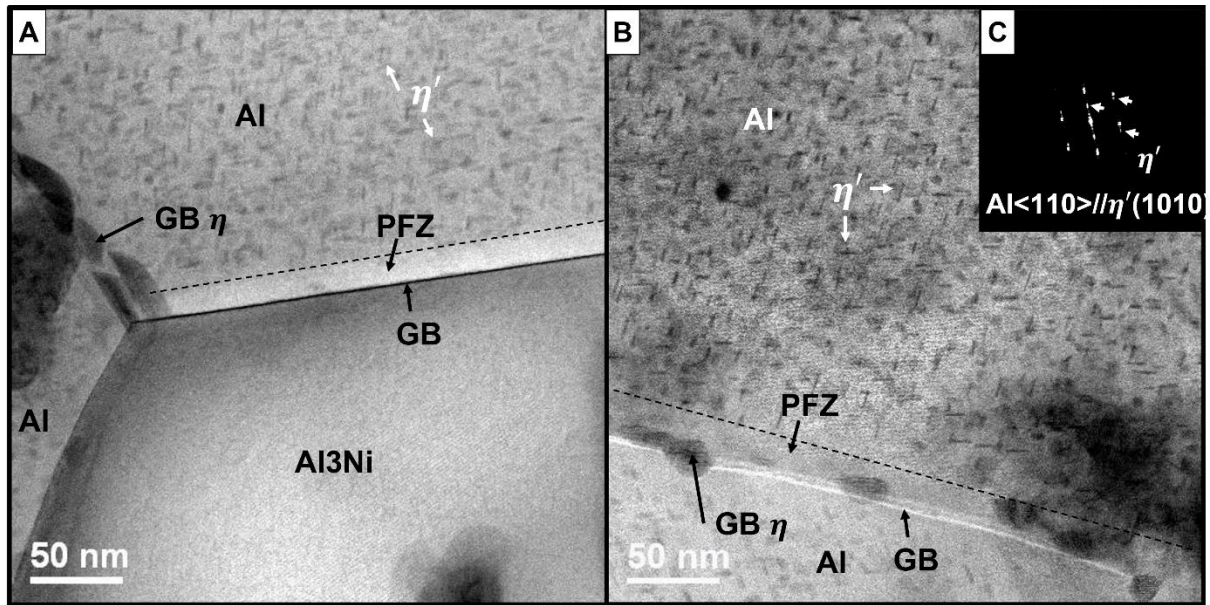


Figure 3.11 TEM micrographs of precipitation free zone (PFZ) at grain boundaries (GBs): A) grain boundary between Al_3Ni and Al in T6 aged '10Ni' material; B) grain boundary between Al grains in T6 aged '10Ni' material. White dashed circle marks out the GB η phase precipitate. C) SAED pattern shows $\text{Al}\langle 110 \rangle // \eta' \langle 1010 \rangle$ orientation in '10Ni'.

Chapter Four. Friction Stir Fabrication of 7075 Aluminum Alloy from Hot Compressed Powder

4.1. Abstract

The gas atomized Al 7075 alloy powder is used as a starting material for the fabrication of Al 7075 alloys involving hot compression and friction stir process (FSP). Hot compression on the powder creates bonded blocks that can withstand FSP. FSP further consolidates the powder blocks, eliminating pores and defects in the processed materials. The material fabricated from powder ('7075p') shows a higher hardness than wrought alloy ('7075s') at as-processed (AP) condition (92.1 HV for '7075p-AP' while 75.6 HV for '7075s-AP'). In contrast, '7075p' has a lower hardness (126.7 HV) than the '7075s' (187.3 HV) after solution heat treatment and T6 aging. X-ray diffraction (XRD) indicates the reduction of η -MgZn₂ and η' -Al₄Mg₂Zn₃ precipitation in the T6-aged '7075p' material compared to the T6-aged '7075s'. Scanning electron microscopy (SEM) and electron back scattered diffraction (EBSD) investigated the difference of grain size and dislocation density. The multi-track FSP produced identical fully-recrystallized grain structures from both powder and solid start materials. Hot compression in air introduced oxides into the powder metallurgy (PM) Al 7075 alloys which may impair the hardness.

4.2. Introduction

7xxx series Al alloys (Al-Zn-Mg-Cu) are widely used in automotive and aerospace structures due to the highest strength aluminum alloys in commercial use [2, 109, 110]. To improve the corrosion resistance and fracture toughness, microstructures need to be modified for the requires for refinement of grains and precipitation [164-166]. However, the conventional manufacturing techniques like rolling, extrusion and machining achieve a limited microstructural modification with considerable energy consumption and material wasting [82, 153, 167-169]. Alternative methods like powder metallurgy (PM) [170-172] and friction stir processing (FSP) [4, 7, 19, 20] have been proposed to address the issues by fabricating fine-structured Al alloys with a reduced energy and material usage.

PM produces solid materials by consolidating fine metallic powders into solid blocks. It is usually comprised of several steps that include powder compaction, press sintering, sizing, and post heat treatment [170, 171]. Materials with geometric complicity can be produced in near-net-shape fashion with the material utilization up to 98% [172]. The introduction of excessive particles

interfaces produces uniform and fine microstructures [173], enabling equivalent or superior properties compared to its wrought alloys for aerospace and automotive applications [174, 175]. As for Al 7075 PM alloy, the yield strength up to 440 MPa can be achieved [170, 172]. One of the few remaining drawbacks is the negative impact of the residual porosity on the ductility and fatigue resistance [176, 177]. The challenge can be overcome by combining FSP techniques into the PM route, in which a rotating tool introduces frictional heat and severe plastic flow to eliminate the porosity and other defects. The FSP techniques have been used for void mitigation of both PM Al alloys and cast Al alloys [8, 37, 39, 41, 61, 178]. FSP can enhance the ductility and sometimes even allow for the superplasticity by controlling microstructures via changing process conditions [4, 6, 20]. Therefore, it is anticipated that FSP can effectively fabricate defect-free fine-structured 7075 Al alloys from powder feedstock made by PM route. Multiple Al alloys (Al-Si) and Al-based composites are fabricated via the PM-FSP technique for the mechanical enhancement [24, 45, 48, 50, 62], while there is no report on making Al 7075 alloys solely from powder. It is of great importance to provide a fundamental understanding on the individual effect of powder on the final microstructures and mechanical properties of the FSP-fabricated 7075 Al alloy from powder.

In this research, a comparative study on using powder and solid Al 7075 alloy as start materials for multi-track FSP was conducted. The composition and morphology of secondary phases were investigated by XRD and SEM. The grain structure was characterized by EBSD. The microhardness was measured for mechanical assessment.

4.3. Experiment

4.3.1. Material Preparation

The feedstock material used in this work is Al 7076 alloy powder in 10-44 μm size (Valimet Inc). The powders were first cold-compressed into blocks under 210.6 MPa of pressure, achieving approximately 80% relative density of the solid Al 7075 alloy. The blocks were further consolidated by a hot compression at 400 °C and 40 MPa for 40 min, to achieve a final 93% green density (denoted as ‘HP’ condition). Solid blocks of Al 7075-T6 alloy (McMaster-Carr) were also used for support and facilitating FSP of powder materials. Figure 4.1 shows the material layout for friction stir processing trials. The hot-compressed blocks were cut into $(18 \times 18 \times 5) \text{ mm}^3$

rectangular blocks, and the eight rectangular blocks were placed into a pre-machined ($36 \times 72 \times 5$) mm³ opening in the 5 mm thick solid Al 7075 alloy plate (Figures 4.1B and 4.1C). Another 6 mm-thick Al 7075 alloy plate was placed beneath the powder blocks as the bottom support.

4.3.2. Friction Stir Processing

Friction stir processing (FSP) was applied to the feedstock described in Figure 4.1 to fabricate the Al 7075 alloy (denoted as ‘7075p’). MST-ISTIR friction stir welder was used for the FSP. The consolidated powder blocks and the plate were first welded into one piece by spot-wise FSP on the top surface using the pin-less $\phi 19$ mm H13 steel tool. The multi-track FSP swept through the powder block region using a $\phi 19$ mm H13 steel tool with a $\phi 6 \times 4.4$ mm threaded pin. The rotational speed of the tool was 550 RPM, and the linear travel speed is 25.4 mm/min. The tool tilt angle is 2° with 0.05 mm shoulder depth beneath the surface. The processed materials were naturally cooled down by air (denoted as as-processed or ‘AP’ condition). The friction stir processed materials were solution heat treated at 475°C for 1 hour and water quenched (denoted as condition ‘SS’). Some were further aged at 120°C for 24 hours to achieve the T6 condition (denoted as condition ‘T6’) [141]. Materials from the solid material (denoted as ‘7075s’) were prepared by applying the same process and post heat treatment on a piece of Al 7075-T6 solid plate. Comparative study between ‘7075p’ and ‘7075s’ was conducted to investigate the effect of FSP and the difference of starting feedstock.

4.3.3. Microstructural and Mechanical Characterization

The phases in the processed materials were identified by the X-ray diffraction (XRD) analysis using a Malvern Analytical Empyrean diffractometer with Cu K- α radiation (45 kV, 40 mA, 0.05°/sec). The precipitation kinetics was investigated by the high-temperature XRD tests (HTXRD) with continuous heating of the material, which was conducted by using the same machine. The X-ray diffraction signal of solution heat treated material was collected between 15° and 50° of 2 θ angle, increasing temperature from 50 °C to 500 °C at a heating rate of 1 °C/min. The Rietveld analysis for the quantification of the material using the XRD pattern was conducted using GSAS-II software [142].

The microstructures in processed materials were characterized by scanning electron microscope (SEM) on grinded and polished specimens. A MIRAS3 TESCAN SEM machine is equipped with energy dispersive X-ray spectroscopy (EDS) system and electron back-scattering diffraction (EBSD). The elemental distribution was identified by using EDS system installed on the SEM machine, and the grain structure and local misorientation in the materials were revealed by EBSD analysis.

The microhardness of the materials was measured, using microhardness tester (LECO LM100 AT) with a 25 g load and 10 sec dwelling time.

4.4. Results

4.4.1. Microstructure of Start Materials

Figure 4.2. shows the initial condition of the feedstock before FSP. The Al 7075 solid plates (Figure 4.2A) in T6 condition for making ‘7075s’ shows typical elongated grains along the plate rolling direction ‘TD’. The grain boundary spacing along the thickness direction ‘DD’ is measured as 27.9 μm in average with 9.1 μm standard deviation. The longitudinal grain size was not measured due to the imaging limits. Figure 4.2B shows the cross-section of the hot-compressed Al 7075 powder feedstock. Most of Al alloy particles remain near spherical morphology with deformation and joint at contact with others. The temperature and pressure (400 °C, 40 MPa) used in hot compression stage produced limited bonding and consolidation with remaining voids. The Al 7075 powder has an average particle diameter of $21.8 \pm 13.4 \mu\text{m}$ with micron sized sub-grain in each particle, which is common for the gas-atomized alloy powder. Solute-rich eutectic segregation at grain boundaries can be anticipated from the characterization in other studies [179, 180].

4.4.2. Phase Determination by XRD

XRD results displayed in Figure 4.3 depicted the phase evolution in FSP and post heat treatment. The red patterns are for 7075p material as hot compressed feedstock (‘PHP’), as-processed FSP block (‘PAP’) and T6 aged block (‘PT6’). The blue patterns are for 7075s material in AP and T6 conditions after FSP (‘SAP’ and ‘ST6’). Multiple common secondary phases present

including η -MgZn₂, η' -Al₄Mg₂Zn₃, T-Mg₃Al₃(Cu, Zn)₃, S-Al₂MgCu and Fe-rich Al₇Cu₂Fe, Al₂₃Fe₄Cu [181-183]. S and η phases in 7075p precipitate out in the 400 °C hot compression ('PHP'). The S phase reduction in AP condition ('PAP') indicate that the FSP reached temperature above 450 °C for S phase to dissolve [183]. The increase of η and η' precipitates is anticipated in T6 aging ('PT6'). Same trends are shown in the 7075s from AP to T6 condition. The Fe-rich intermetallics, Al₇Cu₂Fe and Al₂₃Fe₄Cu, became distinguished in 'PAP' and 'PT6' material, which may indicate introduction of Fe into 7075p material by FSP.

The Rietveld quantification of the XRD results (Figure 4.4) also indicated changes of the oxidation and Fe-rich Al₂₃Fe₄Cu intermetallic in different materials. 7075p material in both 'HP' and 'AP' conditions has more oxides (AlMg₂O₄ and Al₂O₃) than 7075s material. The introduction of oxides in powder happened during hot compression in air, which may change the available alloy compound for reinforcing precipitate formation and resultant mechanical properties. It is difficult to observe the presence of oxides in relative low weight fraction by SEM and EDS tests [184, 185]. The analysis of oxide and the related microstructural difference needs detailed investigation from TEM in the future.

4.4.3. SEM/EDS of the FSP Material

Figure 4.5 shows microstructural difference of the FSP material. No visible porosity is seen in 7075p and 7075s in AP condition (Figure 4.5A and 4.5C). The porosity in powder feedstock (Figure 4.2B) was eliminated by FSP. While several voids with smooth curvature re-emerged in 7075p-T6 material (Figure 4.5B). 7075s material, on the contrary, shows no porosity. Two types of intermetallics can be distinguished from morphology and EDS results. Plate-like precipitates (marked by yellow arrows) enriched in Mg and Zn from point EDS analysis are identified as η -MgZn₂ phase. The coarser irregular shaped particles (marked by red arrows) indicate a higher Fe and Cu content with a Fe:Cu ratio close to 3:1. The particles are identified as Al₂₃Fe₄Cu. The 7075p material (Figures 4.5A and 4.5B) has more Al₂₃Fe₄Cu particles than 7075s (Figure 4.5C and 4.5D) in both AP and T6 conditions which is a confirmation of XRD results. A significant reduction of η -MgZn₂ is found in 7075s-T6 material (Figure 4.5D) from AP condition (Figure 4.5), while such trend is not evident in 7075p from the AP to T6 condition.

4.4.4. Electron Back Scattering Diffraction (EBSD)

EBSD is employed to analyze the change of Al grain structures in the materials. Figure 4.6 shows the grain structure with Al grain orientation for color contrast. High-angle grain boundaries (HAGBs) with misorientation larger than 15° are plotted as solid black lines. Low-angle grain boundaries (LAGBs) with misorientation above 1.5° are plotted as grey lines. Most Al grains were presented as equiaxed structures, but they were partially elongated to 'DD' direction due to the material flow in FSP. Al grains in 7075p were refined after T6 aging (from Figure 4.6A to 4.6B). The Al grains in 7075s became coarse and less oriented to 'DD' direction instead (from Figure 4.6C to 4.6D).

Figure 4.7 is a summary of grain size measurement from the EBSD analysis. The results are from the measurement over 600 grains in each material. Both 7075p and 7075s in AP condition demonstrated similar average grain sizes (1.78 and $1.88\ \mu\text{m}$). After the T6 aging, the average grain size of 7075p was reduced to $1.52\ \mu\text{m}$, whereas the average grain size of 7075s-T6 slightly increases to $1.94\ \mu\text{m}$. Meanwhile, the grain size of all materials shows a bi-modal distribution with one size peak at less than $1\ \mu\text{m}$ and the other at $\sim 2\ \mu\text{m}$, which is in a good agreement with the observation of the coexistence of sub-micron grains and coarser $2\text{-}5\ \mu\text{m}$ grains.

4.4.5. Microhardness Measurement

Figure 4.8 shows the microhardness measurement along the direction 'TD' at the $1.5\ \text{mm}$ depth beneath the top surface of the FSP region. Blue data and trend curves are from 7075s material, and the red ones are from 7075p material. The average hardness of 7075p-AP and 7075s-AP are $92.1 (\pm 5.4\ \text{HV})$ and $126.7\ \text{HV} (\pm 3.9\ \text{HV})$, respectively, while the average hardness of 7075p-T6 and 7075s-T6 are $75.6 (\pm 4.7\ \text{HV})$ and $187.3\ \text{HV} (\pm 3.1\ \text{HV})$, respectively. The hardness of 7075s in AP and T6 conditions are comparable to the annealed and T6 aged wrought 7075 alloy (black dashed line '7075-T6 Ref'). The average hardness of 7075-T6 plate for making 7075s in this study is $185.6\ \text{HV}$. The hardness of 7075p was increased by $17.5\ \text{HV}$ in AP condition but significantly reduced by $60.6\ \text{HV}$ in T6 condition. Such changes are discussed in the discussion part (Section 4.5).

4.5. Discussions

4.5.1. Grain Structure Evolution

During FSP, the intense plastic deformation with high temperature was applied to the material, causing the consolidation and thermal restoration of the feedstock. In the high stacking-fault-energy materials like Al alloys, refined grains are formed due to dynamic recrystallization (DRX) and recovery (DRV) [186, 187]. Continuous dynamic recrystallization (CDRX) is considered as the main mechanism for FSP, where LAGBs are formed first and progressively evolved into HAGBs by the rearrangement and accumulation of the dislocations [87, 188]. Geometric dynamic recrystallization (GDRX) can happen concurrently, where the original grains are elongated and serrated to form refined grains surrounded by HAGBs [188]. The internal deformation and dislocation density are significant low in the recrystallized grains. The grain size produced by FSP strongly depends on the process parameters. In general, the grain are refined with increasing plastic straining and reducing thermal input [4, 40, 189, 190]. Identical process conditions of FSP on 7075p and 7075s produced average grain size with little difference. The higher number fraction (20% vs 12%) of submicron grain in 7075p-AP than 7075s-AP material may originate from the initial fine grain structure of Al 7075 powder.

The fraction of recrystallization is quantified by measuring inter-grain misorientation using the Grain orientation spread (GOS) as the metric. The GOS is defined as the average of the misorientation angles to the grain mean orientation [191, 192]. Figure 4.9 shows the GOS map of the same regions in Figure 4.6. In the present study, the grain with the GOS below 1° and above 3° are considered as fully-recrystallized ('blue' in Figure 4.8) and deformed grains ('red' in Figure 4.8) [193]. The grain with GOS in between is categorized as partially recrystallized grains ('green' in Figure 4.8). Most grains have been fully recrystallized in both 'AP' and 'T6' conditions. The deformed and partially recrystallized grains are either elongated or partitioned by sub-boundaries ('white' lines $< 1.5^\circ$ misorientation), which supports that the RDX and RDV are the main restoration mechanisms in FSP of Al 7075 alloys.

Figure 4.9 summarizes the grain boundary fraction, recrystallized fraction, and grain size. In AP condition, 7075p and 7075s (Figures 4.9A and 4.9B) show similarly high values of HAGB

fraction and recrystallized fraction (~80%), demonstrating that the current FSP conditions produced complete recrystallized grain structures [4, 87, 191, 194]. The recrystallized fraction is increased to 86.2 % and 90.4 % in T6 condition due to the recrystallization and recovery in the solution heat treatment and T6 aging (Figure 4.9B). The reduction of HAGB fraction and grain size of 7075p-T6 to 71.3% and 1.52 μm represents an additional recrystallization in the post heat treatment of 7075p material. This may be attributed to the Fe rich $\text{Al}_{23}\text{Fe}_4\text{Cu}$ particles in 7075p material, depicted by XRD and SEM/EDS results. $\text{Al}_7\text{Cu}_2\text{Fe}$ and $\text{Al}_{23}\text{Fe}_4\text{Cu}$ inhibit the grain growth by pinning the grain boundary and dislocations in the thermal restoration in the post heat treatment [195-197]. The particles can also serve as heterogeneous nucleation sites for Al grains recrystallization [198, 199]. Fe-rich intermetallics not likely comes from the original powder because of the similar chemical composition with 7075-T6 plate shown in Table 4.1. The Fe addition may come from tool's wear in the FSP. It is common that small amount of Fe and other alloy elements from the steel tool can be mixed into the Al alloy in form of the wear particles [200]. Uniform distribution of the fine size Fe-rich intermetallics in Figure 4.5B can be formed by the rigorous material flow in FSP. This phenomenon can be aggravated in the repetitive strain and thermal cycle created by multiple-track process in the present study [200, 201]. The reason of the absence of such Fe addition in the FSP of 7075s awaits further analysis and confirmation in the future FSP trials.

In the post heat treatment, the material was solution treated at 475 °C and water quenched to obtain supersaturated solid solution prior to T6 aging process. The high cooling rate creates residue stress and sometimes distortion in non-uniform structure. On the other hand, the hot-compressed powder has a residue porosity. The hot compression was conducted in air. The surface oxidation of the Al alloy particles is inevitable. FSP removes porosity, creating metallurgical bonding by overcoming the oxidation layer of Al particle surfaces. Neither visible porosity nor residue oxide was found in SEM or XRD results of 7075p-AP. Still, some weak bonding between Al alloy particles may remain. Voids would form to accommodate the quench induced residue stress and form new voids originating from the weak points, intermetallics and oxide inclusion. The distortion also generates extra dislocation, which facilitates fine grain formation and reduces the grain size of 7075p-T6 material.

4.5.2. Microhardness

The hardness of Al 7075 alloy can be contributed by multiple strengthening factor including grain boundaries, dislocation density, and strengthening precipitates. Precipitation strengthening from Mg and Zn rich η' and η phase provides the largest contribution among them [202, 203]. The 7075s after FSP and T6 aging (7075s-T6) displays similar hardness as the starting 7075-T6 solid plate (187.3 vs 185.6 HV) despite their completely different grain structure. It is fair to assume that their fractions of η' and η precipitation are close. The precipitation sequence is well known as [189, 202-204]

Supersaturated solid solution (SSSS) $\rightarrow$ Guinier-Preston (GP) zone $\rightarrow \eta'$ precipitate $\rightarrow \eta$ precipitate

The needle and plate-like η' precipitation in size of 0.1 μm contribute much more to the hardness than other intermetallic due to its semi-coherent interface to Al and high number density. Main content of Mg and Zn precipitate as inter-grain metastable η' precipitation via T6 aging at 120 °C for 24 hours. Part of Mg, Zn and Cu tend to form micron scale grain-boundary η phase at the grain boundaries. Boundary η phase has limited strengthening effect. However, it can affect other properties like ductility, corrosion and cracking resistance [197, 205]. Higher thermal input results in the formation of non-coherent micron-scale η and the loss of strengthening effect.

Both 7075s and 7075p in AP condition have hardness close to the annealed alloys due to the air cooling from high temperature in FSP [19, 187]. The hardness difference between 7075s-AP and 7075p-AP can be attributed to the difference of η'/η precipitate. From the Rietveld quantification of XRD results (Figure 4.3), as-compressed feedstocks for 7075p (7075p-HP) are closer to solid solution than T6 aged starting plate for making 7075s (1.3 vs 2.9 wt% η -MgZn₂). After FSP, 7075p-AP has 1.6 wt% η -MgZn₂ and 0.6 wt% η' -Al₄Mg₂Zn₃, while 7075s-AP contains 4.1 wt% η -MgZn₂ and 0.9 wt% η' -Al₄Mg₂Zn₃. Multiple previous studies demonstrated that the different initial aging conditions with the same FSP would be subject to varied phase transformation., producing different hardness profiles [206, 207]. In FSP of 7075s material, initial η' precipitation and fine size η dissolves quickly under the temperature above 450 °C. However, the short time of heating (~ 1 min) and cooling cycles triggered incomplete η'/η dissolving as well

as a $\eta' \rightarrow \eta$ transformation and growth. Coarse η formation is expected in the air-cooling stage in the material starting from T6 than solution treated material [206]. Therefore, 7075p-AP is more strengthened by the Mg and Zn solute remaining in Al matrix with less formation of coarse η .

7075p-T6 failed to achieve the same hardness after T6 aging, which may be due to the additional Fe-rich intermetallics. As discussed above, $\text{Al}_{23}\text{Fe}_4\text{Cu}$ acted as grain refiner in the post process heat treatment. The grain size was reduced to 1.52 μm from 1.78 μm . Newly generated grain boundaries induce more boundary η formation in T6 aging [208, 209]. The total amount for nano-scale η' precipitate was reduced. The η' contents in 7075p-T6 and 7075s-T6 were estimated as 0.3 wt% and 2.5 wt%, respectively. The SEM micrograph confirmed the existence of micron-scale η - MgZn_2 in 7075p-T6 (Figure 4.5B). The lack of micron-scale precipitation in 7075s-T6 (Figure 4.5D) indicates a distribution of fine size η'/η precipitates, which are hard to observe under current SEM magnification. Such distribution provides more effective strengthening to 7075s material.

4.6. Conclusion

Solid Al 7075 alloys were fabricated by multi-track FSP on hot-compressed 7075 powder feedstock. Post process heat treatment including solution treatment and T6 aging was conducted on the materials for microstructural and mechanical assessment. A comparative analysis between the material from powder (7075p) and solid (7075s) on microstructure and hardness was conducted.

1) Micron-scale intermetallics, such as η - MgZn_2 and S- Al_2MgCu , were found in SEM micrographs and XRD results in both 7075p and 7075s. Additional inclusion of Fe-rich $\text{Al}_7\text{Cu}_2\text{Fe}$ or $\text{Al}_{23}\text{Fe}_4\text{Cu}$ was detected in 7075p after FSP. The Fe inclusion may be introduced from tool's wearing during the FSP of 7075p, which is not significant in 7075s. No evident porosity was found in 7075p and 7075s materials in AP condition. However, several voids were generated after T6 aging, which can be attributed to quench-induced straining interaction with non-uniformity in 7075p materials (e.g., intermetallics, possible oxidation, and residual weak bonding between particles).

2) FSP produced complete recrystallized grain structures in both 7075p and 7075s materials. The average grain sizes of 7075p and 7075s under the as-processed (AP) condition were 1.78 and

1.88 μm , respectively. After solution heat treatment and T6 aging, the 7075p grains experienced further refinement to 1.52 μm , while 7075s's grain structure remained stable at 1.94 μm . Dynamic recrystallization (RDX) took place in the FSP from the analysis of grain orientation spread (GOS) map and fraction of high-angle grain boundary (HAGB). The grain refinement of 7075p-T6 is attributed to the Fe rich intermetallics that restrict grain growth and provide heterogeneous nucleation sites for Al recrystallization in the post heat treatment.

3) Microhardness was measured for understanding the mechanical properties. 7075p has an average microhardness of 92.1 and 126.7 HV in AP and T6 conditions. The 7075s has an average microhardness of 75.6 and 187.3 HV in AP and T6 conditions. The higher hardness of 7075p-AP than 7075s-AP results from less formation of coarse η -MgZn₂ from an initial heat treatment condition of powder feedstock. The lower hardness of 7075p-T6 is due to the lack of fine η'/η precipitates with grain refinement in the post heat treatment.

Appendix. Figures and Tables

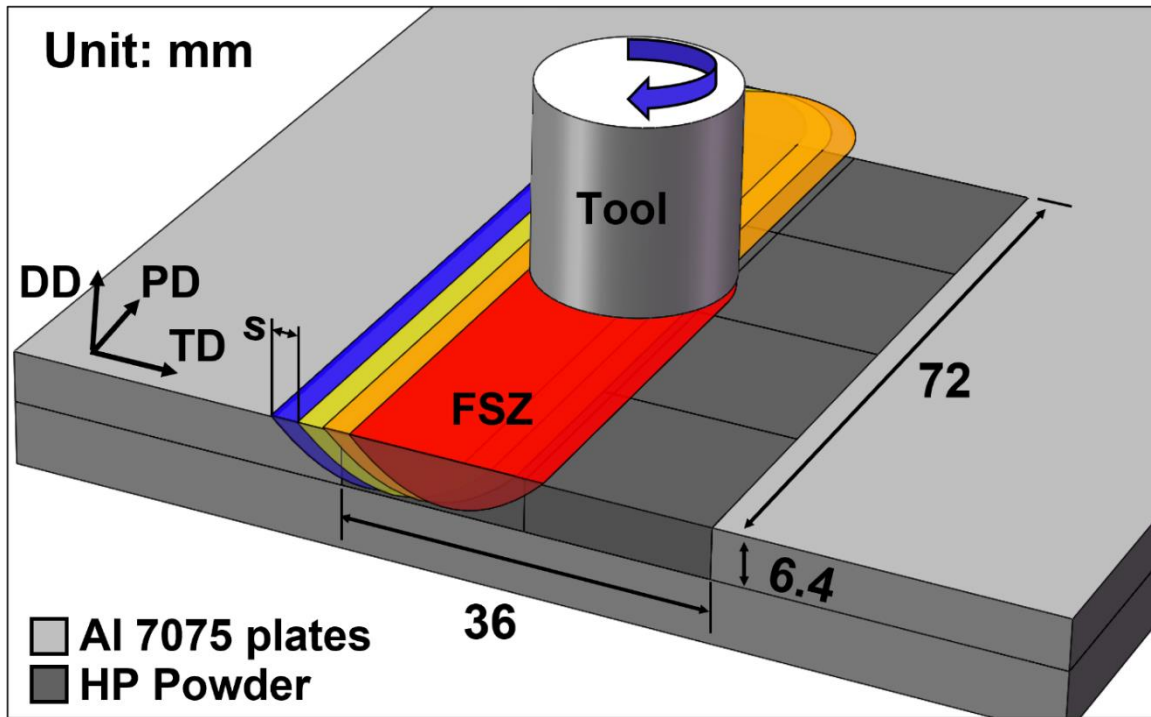


Figure 4.1 Schematic description of multi-track FSP from powder (DD: depth direction; TD: transverse direction; PD: process direction; and S: transverse spacing between individual FSP passes). (Unit: mm).

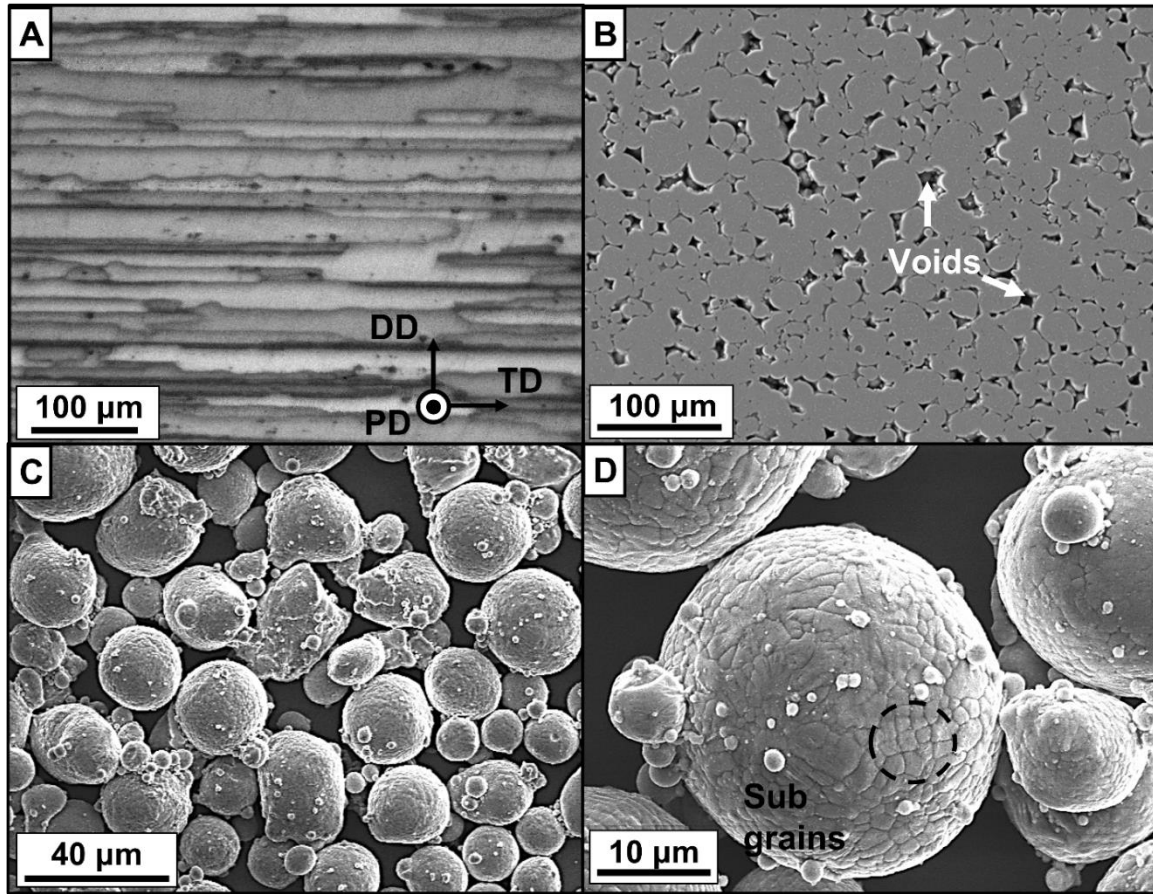


Figure 4.2 SEM micrographs of the feedstocks before FSP: A) Al 7075-T6 alloy solid plates; B) cross section of hot-compressed Al 7075 powder blocks; C) as-received Al 7075 powder; and D) magnified image showing multi-grain structure of an Al 7075 particle.

Table 4.1 Chemical composition (wt%) of the starting material

Material	Al	Cu	Mg	Zn	Ni	Cr	Fe	O
Original 7075 powder	90.13	1.57	2.22	5.68	0.01	0.19	0.1	0.1
Original 7075 plate	90.18	1.44	2.11	5.95	0.01	0.21	0.1	<0.01

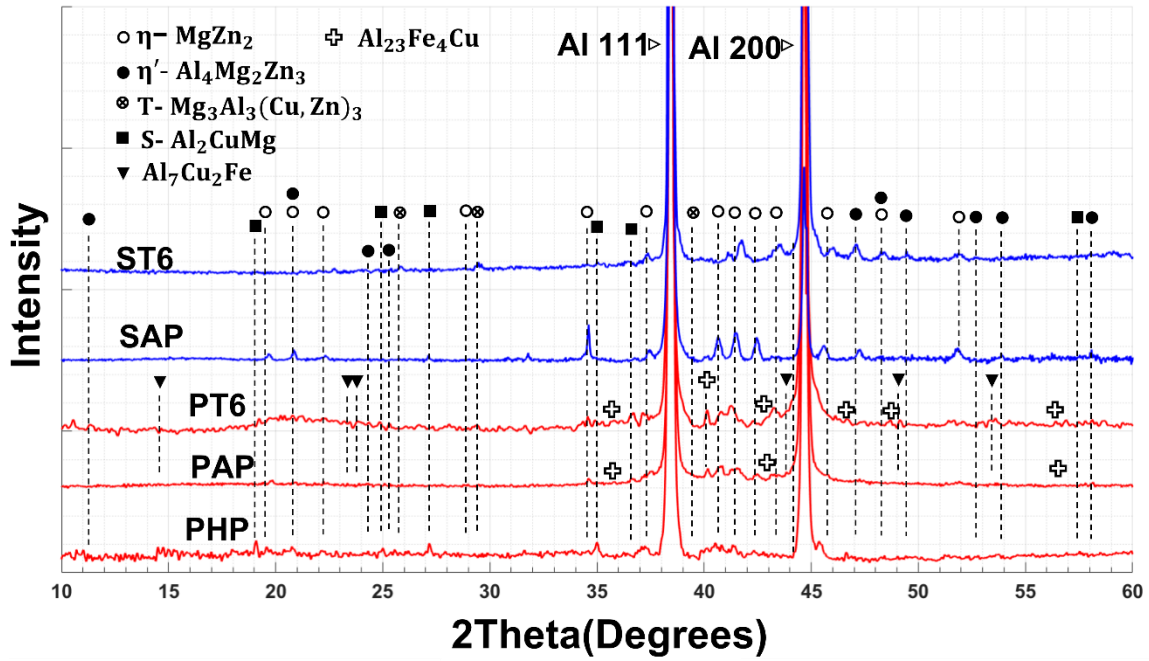


Figure 4.3 XRD results with red lines for 7075p material in hot-compressed ('PHP'), as-processed ('PAP'), and T6 aged ('PT6') conditions. Blue lines are for 7075s material in as-processed ('SAP') and T6 aged ('ST6') conditions.

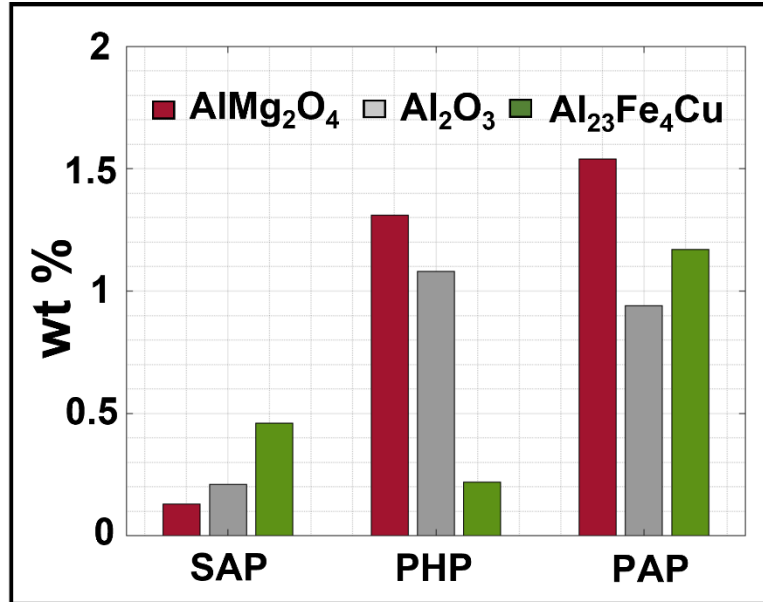


Figure 4.4 Weight fraction of oxidation and Fe-rich intermetallics from XRD results in the materials. SAP: 7075s material in as-processed condition. PHP and PAP: 7075p material in hot-compressed and as-processed conditions, respectively.

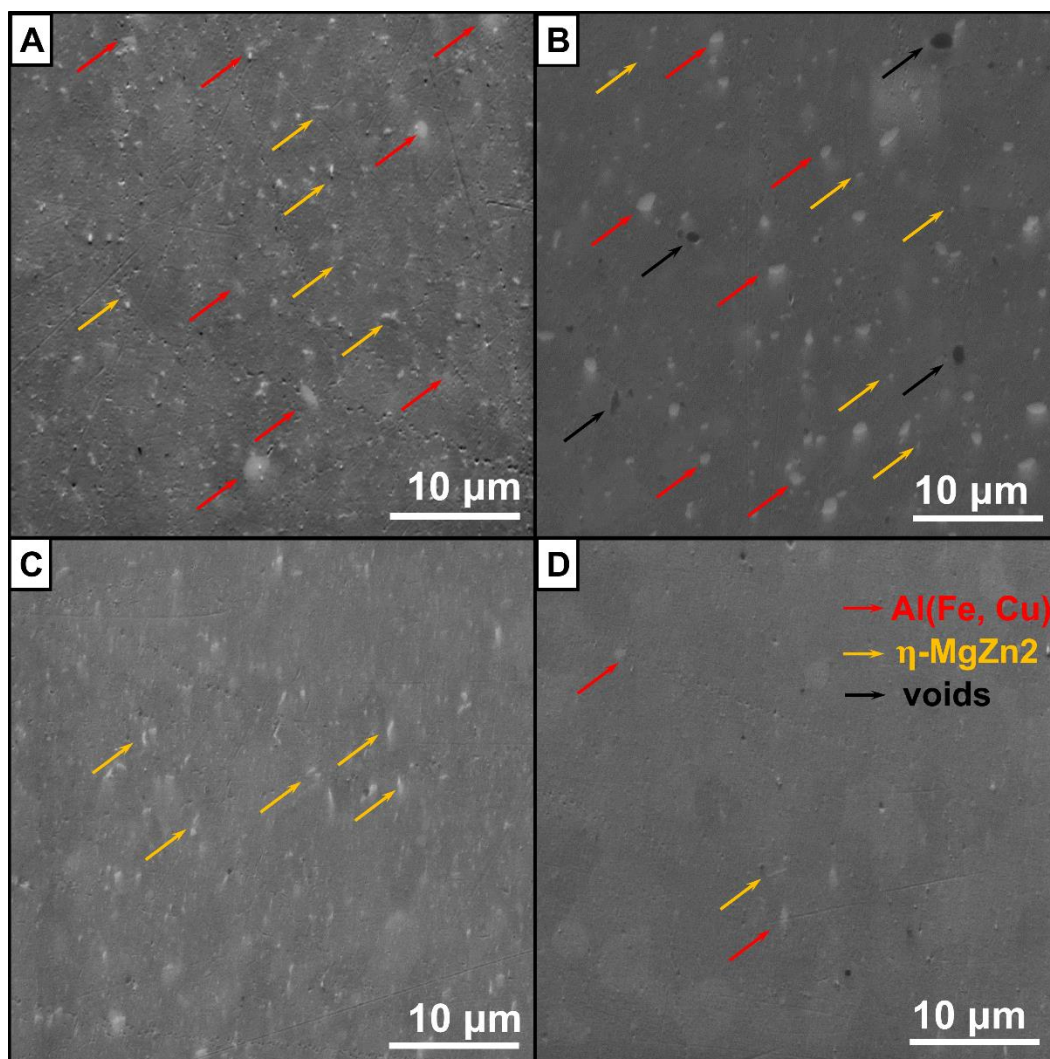


Figure 4.5 SEM micrographs of the FSP material with different conditions: A) 7075p-AP, B) 7075p-T6, C) 7075s-AP and D) 7075s-T6.

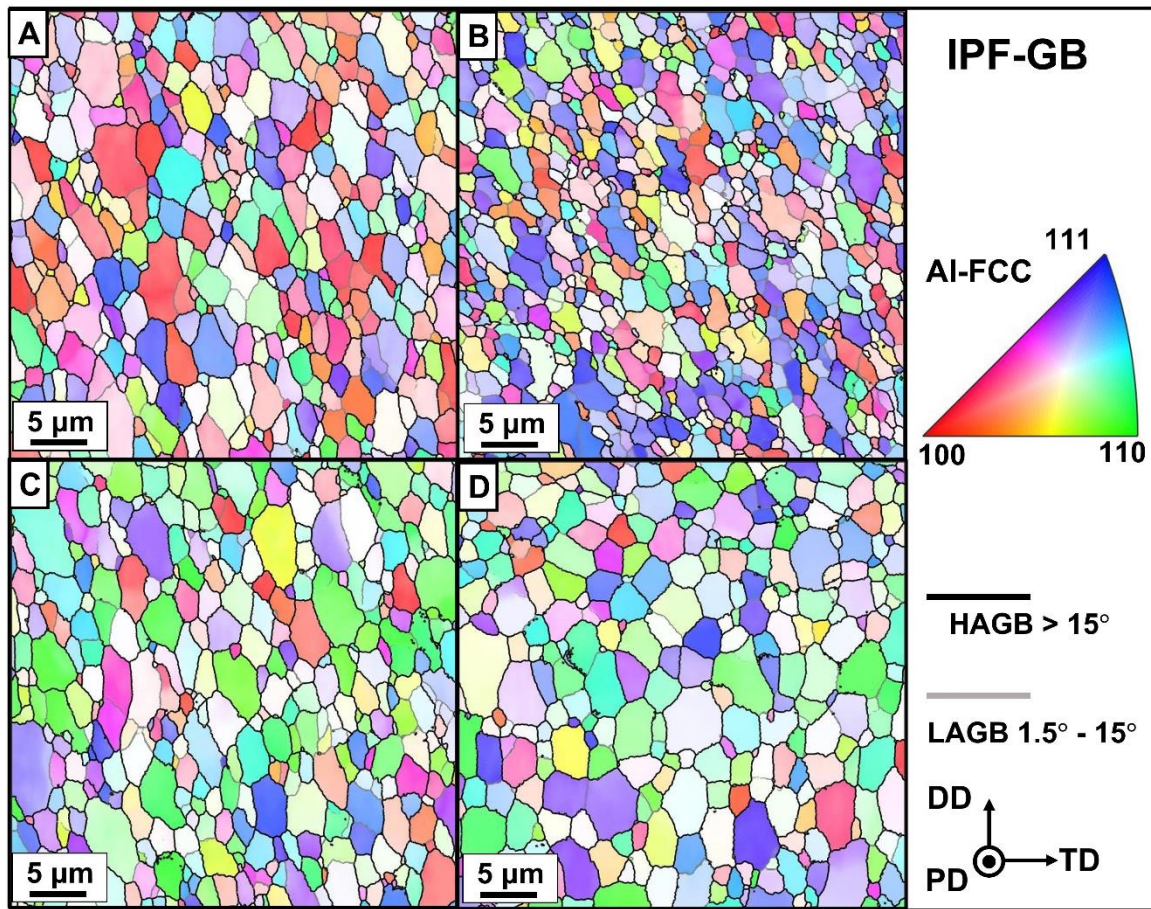


Figure 4.6 Inverse pole figures (IPF) superimposed with grain boundaries (GB) plot for A) 7075p-AP, B) 7075p-T6, C) 7075s-AP, and D) 7075s-T6.

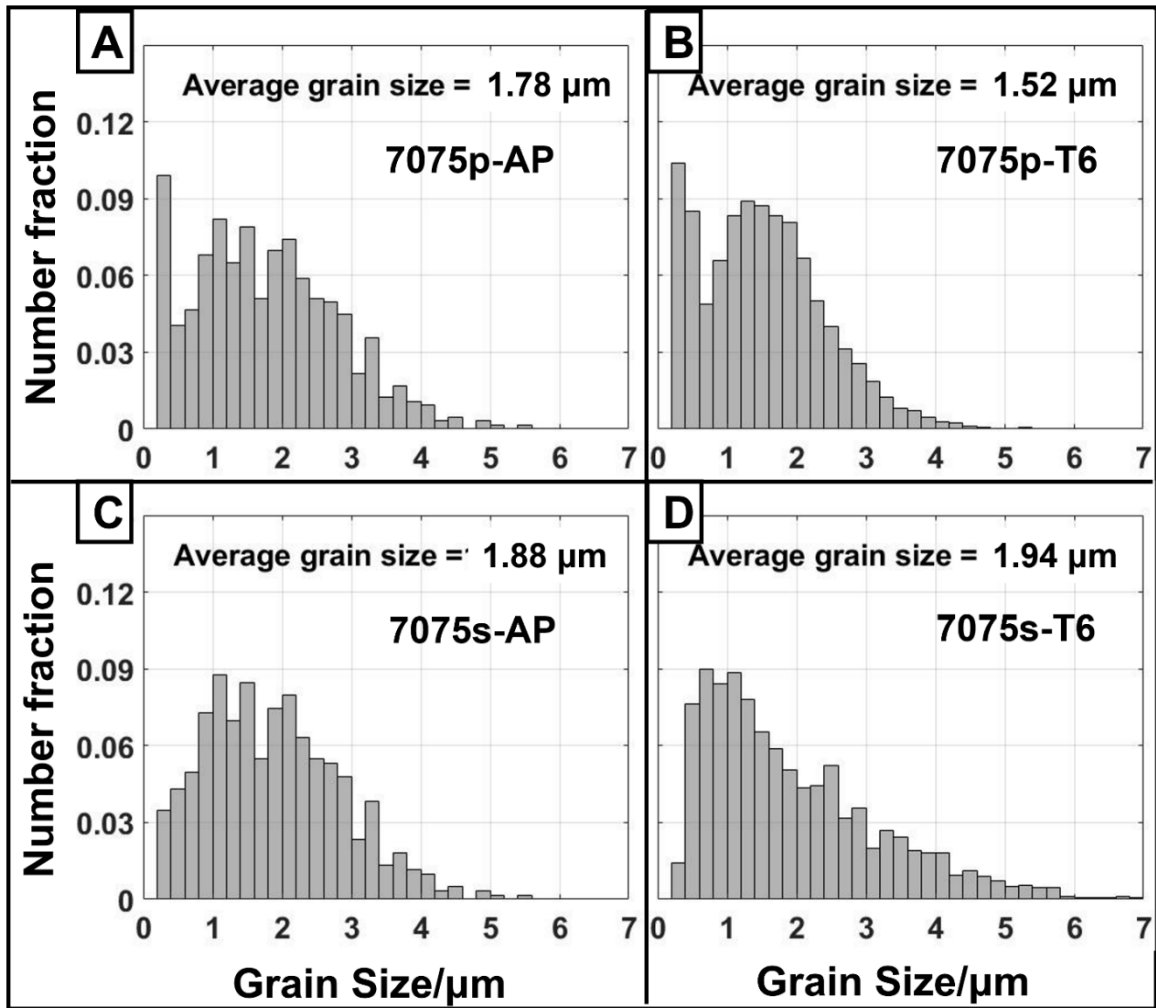


Figure 4.7 Grain size histograms for A) 7075p-AP, B) 7075p-T6, C) 7075s-AP, and D) 7075s-T6.

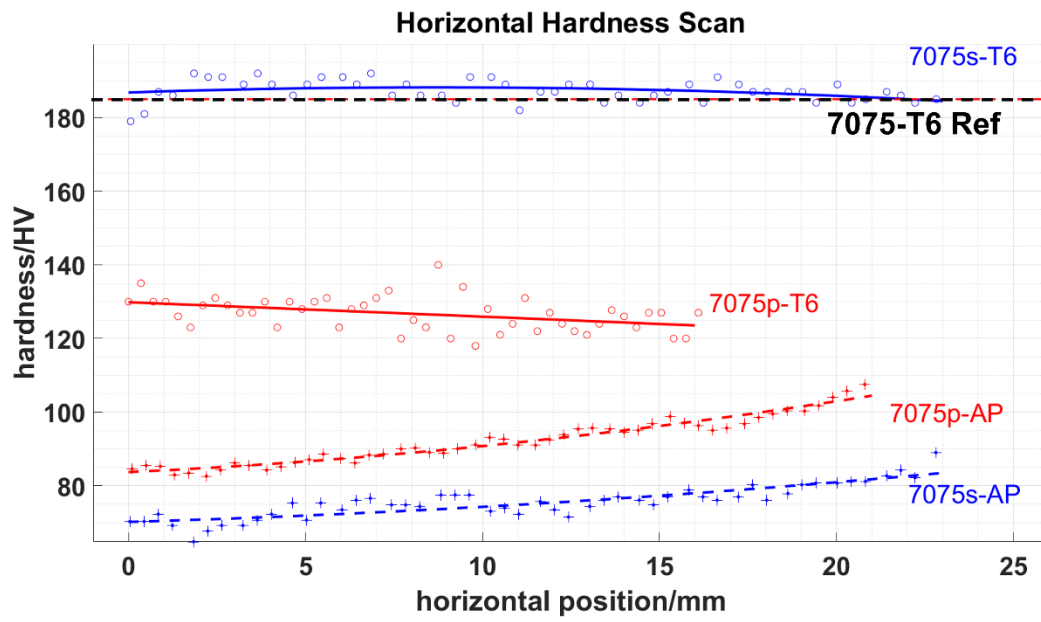


Figure 4.8 Microhardness scanning along the direction ‘TD’ of the FSP material.

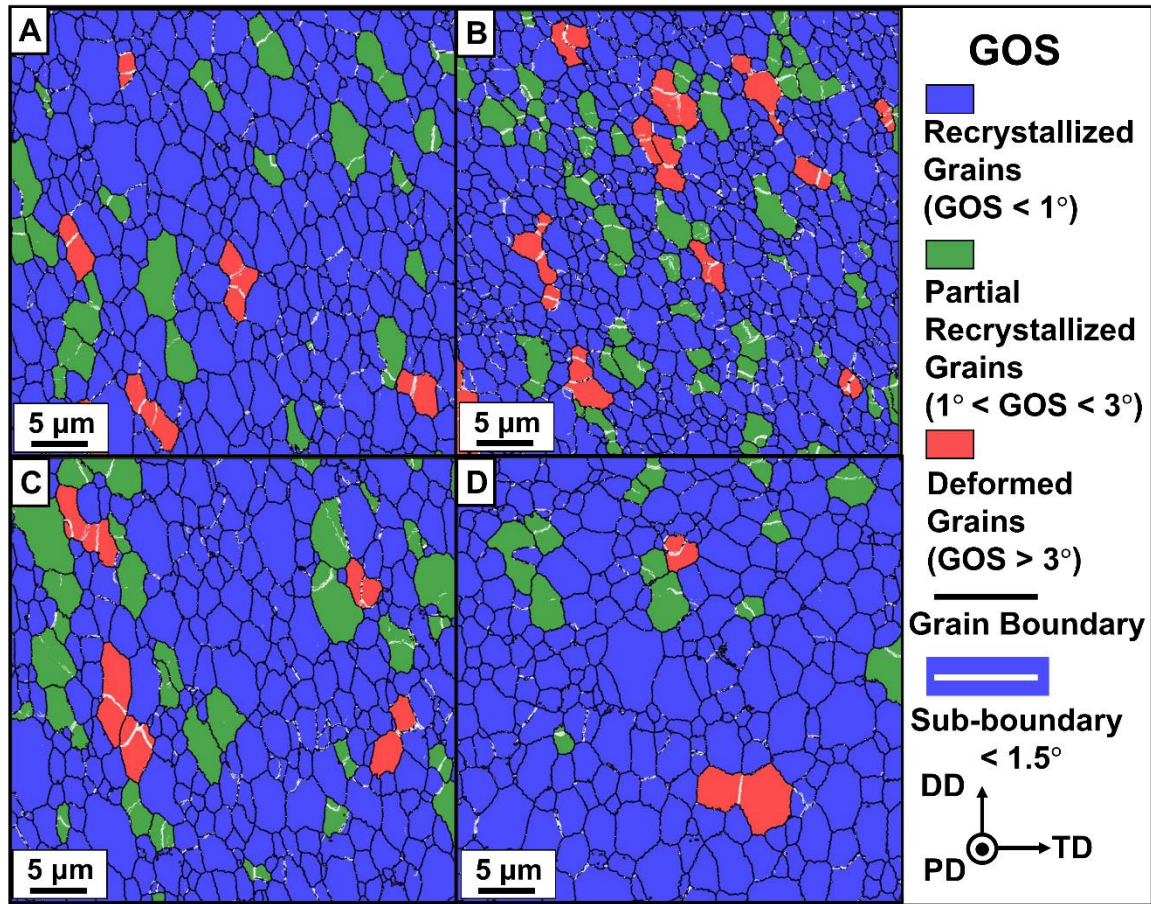


Figure 4.9 Grain orientation spread (GOS) plots with grain boundaries (GB) plot for A) 7075p-AP, B) 7075p-T6, C) 7075s-AP, and D) 7075s-T6.

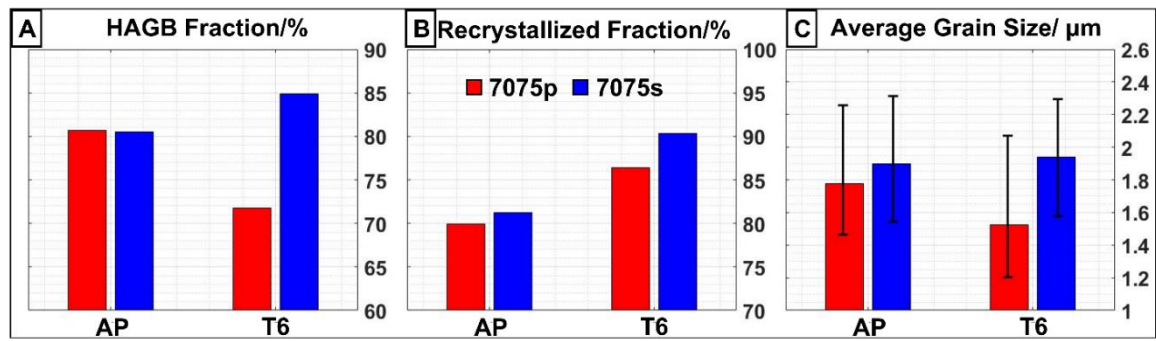


Figure 4.10 Summary of A) HAGB fraction, B) recrystallized fraction, and C) average grain size of all FSP materials.

Chapter Five. Summary and Conclusions

The main goal of this dissertation was developing novel friction stir process (FSP) for age hardenable Al alloys and providing more understanding of microstructural evolution in the process. The relationship between the microstructure and mechanical properties has been studied. Two types of FSP techniques were assessed: 1) Friction stir backward extrusion (FSBE) for tube extrusion and 2) friction stir processing (FSP) on hot compressed powder.

This chapter presents conclusions of the research results and recommendations for further understanding the relationship between microstructures and the mechanical properties.

5.1. Conclusions of the Present Studies

5.1.1. *Friction Stir Backward Extrusion (FSBE) for Tube Structures*

1) 6063 alloy tubes were successfully extruded out from a FSBE tool set-up with an extrusion ratio of 1.15. The thread tool with rotational speed of 500 RPM and 63-76 mm/min plunge rate generated adequate thermal input that caused material solutioning for over 20 sec followed by the air-cooling. Shear and compressing plastic flow was concentrated at the tubes' inner wall with 1200 N extruding force and 110 N-m spindle torque.

2) The unique load and thermal cycle produced globular recrystallized grain structure which can be attributed to dynamic recovery (DRV) and dynamic recrystallization (DRX) mechanism. The grain size increased with reducing shearing strain along the wall thickness to the outer diameter. The starting material has an average grain size of 58.2 μm . The grains at inner diameter were refined to 20.2 μm . While the grains at outer diameter were coarsened to 89.1 μm .

3) The lamellar distribution of β -AlFeSi and Mg_2Si precipitates indicated the existence of the shear-concentrated band along the tube's wall circumference. The relative high density of inter-grain dislocation provided nucleation sites for the precipitation.

4) Microhardness of the extruded tube was 60-75 HV because of its close-to-annealing condition. Extruded tubes presents less asymmetry on hardness with respect to the starting material

(made by conventional hot extrusion). It indicated that FSBE has the potential producing extrudate with better homogeneity with respect to the conventional hot extrusion.

5.1.2. Al 7075-Al₃Ni Composite Fabrication by FSP from Premixed Powder

1) A novel FSP technique was developed by using hot compressed powder as feedstock. The setup enables continuous material fabrication in large scale.

2) Al 7075 alloy powder with 10 wt % nano-sized Ni powder is used for composite making. FSP produced complete in-situ transformation of Al₃Ni in Al 7075 alloy in no need of post heat treatment.

3) Agglomeration of Ni powder existed with the current powder mixing approach. Such Ni agglomeration results in micron-scale Al₃Ni formation in the composite.

4) Al₃Ni in Al 7075 alloy introduced a tendency of promoting T-Mg₂Al₃Zn₃ while inhibiting η -MgZn₂ precipitation.

5) The Al 7075-Al₃Ni composite presents Vickers hardness of 109.6 HV and 145.2 HV in as-processed (AP) and T6 aged conditions, which achieves 19.0% and 14.6% hardness increment than the material with no Ni addition. The fine sized Al₃Ni provided more effective strengthening effect than relative coarse Al₃Ni reinforcement in the previous studies.

5.1.3. Comparative Study of Al 7075 made by FSP from Powder and from Solid

1) Al 7075 alloy is fabricated by FSP using hot compressed Al 7075 powder. The material fabricated from powder shows higher hardness than wrought alloy at as-processed (AP) condition (92.1 HV vs 75.6 HV) because of less formation of coarse η -MgZn₂ from the different initial heat treatment conditions. However, the hardness is lower than that from solid in T6 aged condition (126.7 HV vs 187.3 HV) which due to increased formation of grain boundary η -MgZn₂ at the recrystallized structure in the post heat treatment.

2) FSP produced similar grain structure in both materials. The ~1.8 μ m grains with high recrystallized fraction were produced by the RDX and RDV mechanism governed by thermal and straining of FSP.

3) XRD and SEM micrograph indicated increased Fe-rich phase in the material from powder, which may be due to the unexpected tool's wear in FSP. The intermetallics $\text{Al}_{23}\text{Fe}_4\text{Cu}$ acted as grain refiner and caused grain refinement to $1.5\text{ }\mu\text{m}$ in the post heat treatment.

4) Porosity was produced in the T6 aging of the material from powder, which may imply a heat treatment induced distortion of in-homogeneities in the material.

5.2 Future Work

The following are recommended for the process development and achieving better understanding of microstructural and mechanical features of the studied FSP techniques:

5.2.1. FSBE for Tube and Wire Extrusion

1) FSBE process with higher extrusion ratio needs to be designed for practical use of the technique.

2) Parametric study is required to optimize the process conditions (rotation speed, extrusion rate, and cooling condition).

3) Tests for other properties like strength, ductility, corrosion resistance are required. The post heat treatment to more commonly used T6 aged condition need to be conducted so that the relevant effect caused by FSBE can be studied.

5.2.2. Al 7075- Al_3Ni Composite Fabrication by FSP

1) The powder preparation process needs to be modified to reduce the agglomeration of nano Ni powder in the premixed powder feedstock. Uniformly distributed nano-scale reinforcements should provide more strengthening to the material.

2) To determine the Ni content for optimum properties of the composite material, a comprehensive study needs to be performed on the phase diagram Al-Mg-Zn-Cu-Ni with a wide range of compositional change of Ni.

3) More detailed TEM analysis is needed on the Al7075 - Al₃Ni composite to investigate any effect on the η' precipitate distribution caused by Al₃Ni. Since the η' precipitate still makes the main role of strengthening the alloy.

5) More mechanical properties tests are necessary to assess properties other than hardness. High temperature performances including strength, toughness and creep properties are especially of interest for the Al-Al₃Ni composite material in the relevant commercial applications.

5.2.3. Al 7075 Alloy Fabrication by FSP from Hot-compressed Powder

1) The hot compression with inert gas protection needs to be applied for the feedstock preparation. The possible difference between the powder with and without gas protection will help to determine the suitable process in consideration of both properties and cost.

2) To fabricate material from powder with comparable properties to the solid, the process from powder preparation to FSP needs modification, which can mitigate unwanted material pollution like Fe and other possible elements. Higher process load of FSP is needed to further eliminate the weak bonding in powder feedstock.

3) TEM analysis on the current Al 7075 material made by powder-FSP route is required to investigate the change of microstructure and phase morphology with respect to the wrought Al 7075 alloy.

List of References

- [1] G.E. Totten, D.S. MacKenzie, *Handbook of Aluminum: vol. 1: Physical Metallurgy and Processes*, CRC press, 2003.
- [2] K. Anderson, J.G. Kaufman, J. Weritz, *ASM Handbook: vol. 2B: Properties and Selection of Aluminum Alloys*, ASM International Materials Park, OH, USA, 2019.
- [3] W.M. Thomas, E.D. Nicholas, J.C. Needham, M.G. Murch, P. Templesmith, C.J. Dawes, “Friction Stir Butt Welding”, GB Patent Application No. 9125978.8, International Patent Application No. PCT/GB92/02203, 1991.
- [4] R.S. Mishra, M. Mahoney, S. McFaden, N. Mara, A. Mukherjee, High strain rate superplasticity in a friction stir processed 7075 Al alloy, *Scripta Materialia* 42(2) (1999) 163-168.
- [5] R.S. Mishra, M.W. Mahoney, Friction stir processing: a new grain refinement technique to achieve high strain rate superplasticity in commercial alloys, *Materials Science Forum*, Trans Tech Publ, 2001, pp. 507-514.
- [6] P.B. Berbon, W.H. Bingel, R.S. Mishra, C.C. Bampton, M.W. Mahoney, Friction stir processing: a tool to homogenize nanocomposite aluminum alloys, *Scripta Materialia* 44(1) (2001) 61-66.
- [7] R.S. Mishra, Z.Y. Ma, Friction stir welding and processing, *Materials Science and Engineering: R: reports* 50(1-2) (2005) 1-78.
- [8] Z. Ma, S.R. Sharma, R.S. Mishra, Effect of multiple-pass friction stir processing on microstructure and tensile properties of a cast aluminum–silicon alloy, *Scripta Materialia* 54(9) (2006) 1623-1626.
- [9] Y.S. Sato, S.H.C. Park, H. Kokawa, Microstructural factors governing hardness in friction-stir welds of solid-solution-hardened Al alloys, *Metallurgical and Materials Transactions A* 32(12) (2001) 3033-3042.
- [10] Y.S. Sato, H. Kokawa, M. Enomoto, S. Jogan, Microstructural evolution of 6063 aluminum during friction-stir welding, *Metallurgical and Materials Transactions A* 30(9) (1999) 2429-2437.
- [11] C. Rhodes, M. Mahoney, W. Bingel, M. Calabrese, Fine-grain evolution in friction-stir processed 7050 aluminum, *Scripta Materialia* 48(10) (2003) 1451-1455.
- [12] J.-Q. Su, T.W. Nelson, C.J. Sterling, A new route to bulk nanocrystalline materials, *Journal of Materials Research* 18(8) (2003) 1757-1760.
- [13] Y.S. Sato, M. Urata, H. Kokawa, K. Ikeda, Hall–Petch relationship in friction stir welds of equal channel angular-pressed aluminium alloys, *Materials Science and Engineering: A* 354(1-2) (2003) 298-305.
- [14] K. Ma, H. Wen, T. Hu, T.D. Topping, D. Isheim, D.N. Seidman, E.J. Lavernia, J.M. Schoenung, Mechanical behavior and strengthening mechanisms in ultrafine grain precipitation-strengthened aluminum alloy, *Acta Materialia* 62 (2014) 141-155.
- [15] K.A.A. Hassan, A.F. Norman, P.B. Prangnell, The stability of the nugget zone grain structure in AA7010 alloy friction stir welds during solution treatment, *Materials Science Forum*, Trans Tech Publ, 2002, pp. 1549-1554.
- [16] R. Fonda, J. Bingert, K. Colligan, Development of grain structure during friction stir welding, *Scripta Materialia* 51(3) (2004) 243-248.
- [17] Y. Kwon, I. Shigematsu, N. Saito, Mechanical properties of fine-grained aluminum alloy produced by friction stir process, *Scripta Materialia* 49(8) (2003) 785-789.

- [18] V.V. Patel, V. Badheka, A. Kumar, Friction stir processing as a novel technique to achieve superplasticity in aluminum alloys: process variables, variants, and applications, *Metallography, Microstructure, and Analysis* 5(4) (2016) 278-293.
- [19] L. Johannes, R. Mishra, Multiple passes of friction stir processing for the creation of superplastic 7075 aluminum, *Materials Science and Engineering: A* 464(1-2) (2007) 255-260.
- [20] Z. Ma, R.S. Mishra, M.W. Mahoney, R. Grimes, Effect of friction stir processing on the kinetics of superplastic deformation in an Al-Mg-Zr alloy, *Metallurgical and Materials Transactions A* 36(6) (2005) 1447-1458.
- [21] T. Nishihara, Development of friction stir forming, *Materials Science Forum*, Trans Tech Publ, 2003, pp. 2971-2978.
- [22] T. Nishihara, A. Ito, Measurement of die temperature during friction stir forming, *Welding in the World* 49(3) (2005) 22-26.
- [23] S. Lazarevic, K.A. Ogata, S.F. Miller, G.H. Kruger, B.E. Carlson, Formation and structure of work material in the friction stir forming process, *Journal of Manufacturing Science and Engineering* 137(5) (2015).
- [24] W. Cheng, C. Liu, Z. Ge, Optimizing the mechanical properties of Al-Si alloys through friction stir processing and rolling, *Materials Science and Engineering: A* 804 (2021) 140786.
- [25] Z. Feng, K. Manchiraju, Direct Solid-State Conversion of Recyclable Metals and Alloys, No. NFE-11-03251. Oak Ridge National Lab.(ORNL), Oak Ridge, TN (United States); Mound Plant (MOUND), Miamisburg, OH (United States), 2012.
- [26] F. Abu-Farha, A preliminary study on the feasibility of friction stir back extrusion, *Scripta Materialia* 66(9) (2012) 615-618.
- [27] M.S. Khorrami, M. Movahedi, Microstructure evolutions and mechanical properties of tubular aluminum produced by friction stir back extrusion, *Materials & Design* (1980-2015) 65 (2015) 74-79.
- [28] I. Dinaharan, R. Sathiskumar, S.J. Vijay, N. Murugan, Microstructural characterization of pure copper tubes produced by a novel method friction stir back extrusion, *Procedia Materials Science* 5 (2014) 1502-1508.
- [29] S. Whalen, V. Joshi, N. Overman, D. Caldwell, C. Lavender, T. Skrzek, Scaled-up fabrication of thin-walled ZK60 tubing using shear assisted processing and extrusion (ShAPE), *Magnesium Technology 2017*, Springer, 2017, pp. 315-321.
- [30] H. Zhang, X. Zhao, X. Deng, M.A. Sutton, A.P. Reynolds, S.R. McNeill, X. Ke, Investigation of material flow during friction extrusion process, *International Journal of Mechanical Sciences* 85 (2014) 130-141.
- [31] H. Zhang, X. Li, W. Tang, X. Deng, A.P. Reynolds, M.A. Sutton, Heat transfer modeling of the friction extrusion process, *Journal of Materials Processing Technology* 221 (2015) 21-30.
- [32] Z.Y. Hang, M.E. Jones, G.W. Brady, R.J. Griffiths, D. Garcia, H.A. Rauch, C.D. Cox, N. Hardwick, Non-beam-based metal additive manufacturing enabled by additive friction stir deposition, *Scripta Materialia* 153 (2018) 122-130.
- [33] B. Phillips, D. Avery, T. Liu, O. Rodriguez, C. Mason, J. Jordon, L. Brewer, P. Allison, Microstructure-deformation relationship of additive friction stir-deposition Al-Mg-Si, *Materialia* 7 (2019) 100387.
- [34] H.Z. Yu, R.S. Mishra, Additive friction stir deposition: a deformation processing route to metal additive manufacturing, *Materials Research Letters* 9(2) (2021) 71-83.

- [35] S. Whalen, N. Overman, V. Joshi, T. Varga, D. Graff, C. Lavender, Magnesium alloy ZK60 tubing made by shear assisted processing and extrusion (ShAPE), *Materials Science and Engineering: A* 755 (2019) 278-288.
- [36] S.A. Nazari Tiji, A. Asgharzadeh, T. Park, S.A. Whalen, M. Eller, F. Pourboghrat, Microstructure and mechanical properties of the AA7075 tube fabricated using shear assisted processing and extrusion (ShAPE), *Archives of Civil and Mechanical Engineering* 21(2) (2021) 1-10.
- [37] W. Tang, A.P. Reynolds, Production of wire via friction extrusion of aluminum alloy machining chips, *Journal of Materials Processing Technology* 210(15) (2010) 2231-2237.
- [38] K. Tahmasbi, M. Mahmoodi, Evaluation of microstructure and mechanical properties of aluminum AA7022 produced by friction stir extrusion, *Journal of Manufacturing Processes* 32 (2018) 151-159.
- [39] M. Santella, T. Engstrom, D. Storjohann, T.-Y. Pan, Effects of friction stir processing on mechanical properties of the cast aluminum alloys A319 and A356, *Scripta Materialia* 53(2) (2005) 201-206.
- [40] Z. Ma, S. Sharma, R. Mishra, Microstructural modification of as-cast Al-Si-Mg alloy by friction stir processing, *Metallurgical and Materials Transactions A* 37(11) (2006) 3323-3336.
- [41] H. Izadi, A. Nolting, C. Munro, D. Bishop, K. Plucknett, A. Gerlich, Friction stir processing of Al/SiC composites fabricated by powder metallurgy, *Journal of Materials Processing Technology* 213(11) (2013) 1900-1907.
- [42] Q. Zhang, B.L. Xiao, D. Wang, Z.Y. Ma, Formation mechanism of in situ Al_3Ti in Al matrix during hot pressing and subsequent friction stir processing, *Materials Chemistry and Physics* 130(3) (2011) 1109-1117.
- [43] L. Ke, C. Huang, L. Xing, K. Huang, Al-Ni intermetallic composites produced in situ by friction stir processing, *Journal of Alloys and Compounds* 503(2) (2010) 494-499.
- [44] J. Qian, J. Li, J. Xiong, F. Zhang, X. Lin, In situ synthesizing Al_3Ni for fabrication of intermetallic-reinforced aluminum alloy composites by friction stir processing, *Materials Science and Engineering: A* 550 (2012) 279-285.
- [45] C. Hsu, P. Kao, N. Ho, Ultrafine-grained Al- Al_2Cu composite produced in situ by friction stir processing, *Scripta Materialia* 53(3) (2005) 341-345.
- [46] A. Shahi, M.H. Sohi, D. Ahmadvani, M. Ghambari, In situ formation of Al- Al_3Ni composites on commercially pure aluminium by friction stir processing, *The International Journal of Advanced Manufacturing Technology* 75(9) (2014) 1331-1337.
- [47] Q. Zhang, B. Xiao, W. Wang, Z. Ma, Reactive mechanism and mechanical properties of in situ composites fabricated from an Al- TiO_2 system by friction stir processing, *Acta Materialia* 60(20) (2012) 7090-7103.
- [48] Q. Zhang, B. Xiao, Q. Wang, Z. Ma, Effects of processing parameters on the microstructures and mechanical properties of in situ ($\text{Al}_3\text{Ti} + \text{Al}_2\text{O}_3$)/Al composites fabricated by hot pressing and subsequent friction-stir processing, *Metallurgical and Materials Transactions A* 45(6) (2014) 2776-2791.
- [49] F. Khodabakhshi, A. Simchi, A. Kokabi, M. Nosko, F. Švec, Microstructure and texture development during friction stir processing of Al-Mg alloy sheets with TiO_2 nanoparticles, *Materials Science and Engineering: A* 605 (2014) 108-118.
- [50] P.S. Zangabad, F. Khodabakhshi, A. Simchi, A. Kokabi, Fatigue fracture of friction-stir processed Al- Al_3Ti -MgO hybrid nanocomposites, *International Journal of Fatigue* 87 (2016) 266-278.

- [51] G. You, N. Ho, P. Kao, In-situ formation of Al_2O_3 nanoparticles during friction stir processing of AlSiO_2 composite, *Materials Characterization* 80 (2013) 1-8.
- [52] H. Izadi, A.P. Gerlich, Distribution and stability of carbon nanotubes during multi-pass friction stir processing of carbon nanotube/aluminum composites, *Carbon* 50(12) (2012) 4744-4749.
- [53] X. Cao, Q. Shi, D. Liu, Z. Feng, Q. Liu, G. Chen, Fabrication of in situ carbon fiber/aluminum composites via friction stir processing: Evaluation of microstructural, mechanical and tribological behaviors, *Composites Part B: Engineering* 139 (2018) 97-105.
- [54] S. Zhang, G. Chen, J. Wei, Y. Liu, R. Xie, Q. Liu, S. Zeng, G. Zhang, Q. Shi, Effects of energy input during friction stir processing on microstructures and mechanical properties of aluminum/carbon nanotubes nanocomposites, *Journal of Alloys and Compounds* 798 (2019) 523-530.
- [55] C.-H. Jeon, Y.-H. Jeong, J.-J. Seo, H.N. Tien, S.-T. Hong, Y.-J. Yum, S.-H. Hur, K.-J. Lee, Material properties of graphene/aluminum metal matrix composites fabricated by friction stir processing, *International Journal of Precision Engineering and Manufacturing* 15(6) (2014) 1235-1239.
- [56] S. Basavarajappa, G. Chandramohan, K. Mukund, M. Ashwin, M. Prabu, Dry sliding wear behavior of Al 2219/SiCp-Gr hybrid metal matrix composites, *Journal of Materials Engineering and Performance* 15(6) (2006) 668-674.
- [57] V.A. Chianeh, H.M. Hosseini, M. Nofar, Micro structural features and mechanical properties of Al- Al_3Ti composite fabricated by in-situ powder metallurgy route, *Journal of Alloys and Compounds* 473(1-2) (2009) 127-132.
- [58] R. Varin, Intermetallic-reinforced light-metal matrix in-situ composites, *Metallurgical and Materials Transactions A* 33(1) (2002) 193-201.
- [59] H. Peng, D. Wang, L. Geng, C. Yao, J. Mao, Evaluation of the microstructure of in-situ reaction processed Al_3Ti - Al_2O_3 -Al composite, *Scripta Materialia* 37(2) (1997) 199-204.
- [60] Z. Ma, S. Tjong, In situ ceramic particle-reinforced aluminum matrix composites fabricated by reaction pressing in the TiO_2 (Ti)-Al-B (B_2O_3) systems, *Metallurgical and Materials Transactions A* 28(9) (1997) 1931-1942.
- [61] I. Lee, C. Hsu, C. Chen, N. Ho, P. Kao, Particle-reinforced aluminum matrix composites produced from powder mixtures via friction stir processing, *Composites Science and Technology* 71(5) (2011) 693-698.
- [62] C. Hsu, C. Chang, P. Kao, N. Ho, C. Chang, Al- Al_3Ti nanocomposites produced in situ by friction stir processing, *Acta Materialia* 54(19) (2006) 5241-5249.
- [63] H.G. Rana, V.J. Badheka, A. Kumar, Fabrication of Al7075/ B_4C surface composite by novel friction stir processing (FSP) and investigation on wear properties, *Procedia Technology* 23 (2016) 519-528.
- [64] I. Dinaharan, N. Murugan, A. Thangarasu, Development of empirical relationships for prediction of mechanical and wear properties of AA6082 aluminum matrix composites produced using friction stir processing, *Engineering Science and Technology, an International Journal* 19(3) (2016) 1132-1144.
- [65] Z. Gxowa-Penxa, P. Daswa, R. Modiba, M.N. Mathabathe, A.S. Bolokang, Development and characterization of Al- Al_3Ni -Sn metal matrix composite, *Materials Chemistry and Physics* (2020) 124027.

- [66] T. Marcelo, M.H. Carvalho, E. Lopes, J.-D. Bartout, Y. Bienvenu, Fabrication of Al/Al₃Ni matrix composites with a low coefficient of thermal expansion, *Key Engineering Materials*, Trans Tech Publ, 2002, pp. 189-192.
- [67] T.P.D. Rajan, R.M. Pillai, B.C. Pai, Functionally graded Al-Al₃Ni in situ intermetallic composites: fabrication and microstructural characterization, *Journal of Alloys and Compounds* 453(1-2) (2008) L4-L7.
- [68] M. Krasnowski, S. Gierlotka, T. Kulik, Nanocrystalline matrix Al₃Ni₂-Al-Al₃Ni composites produced by reactive hot-pressing of milled powders, *Intermetallics* 54 (2014) 193-198.
- [69] J.T. Kim, V. Soprunyuk, N. Chawake, Y.H. Zheng, F. Spieckermann, S.H. Hong, K.B. Kim, J. Eckert, Outstanding strengthening behavior and dynamic mechanical properties of in-situ Al-Al₃Ni composites by Cu addition, *Composites Part B: Engineering* (2020) 107891.
- [70] B. Stojanović, L. Ivanović, Application of aluminium hybrid composites in automotive industry, *Tehnički vjesnik* 22(1) (2015) 247-251.
- [71] I. Festus, P. Gohil, V. Nampoothiri, S. Joshi, Design and Development of Small Scale Solar Powered Remote Controlled Aircraft, *ICWSTCSC-2017*, BVM College, Vallabh Vidyanagar.
- [72] TWI, Friction Stir Welding, online database, <https://www.twi-global.com/technical-knowledge/job-knowledge/friction-stir-welding-147>, TWI. Ltd, 2022.
- [73] S. Zhang, A. Frederick, Y. Wang, M. Eller, P. McGinn, A. Hu, Z. Feng, Microstructure Evolution and Mechanical Property Characterization of 6063 Aluminum Alloy Tubes Processed with Friction Stir Back Extrusion, *JOM* 71(12) (2019) 4436-4444.
- [74] M. Bauser, G. Sauer, K. Siegert, *Extrusion*, ASM International, Materials Park, Ohio, Estados Unidos, 2006, pp. 13-37.
- [75] W. Thomas, E. Nicholas, J. Needham, M. Murch, P. Templesmith, C. Daws, GB Patent application no. 9125978.8, December 1991, TWI Bull 124 (1995).
- [76] D. Baffari, G. Buffa, D. Campanella, L. Fratini, A.P. Reynolds, Process mechanics in Friction Stir Extrusion of magnesium alloys chips through experiments and numerical simulation, *Journal of Manufacturing Processes* 29 (2017) 41-49.
- [77] Aluminum Association, *Aluminum: properties and physical metallurgy*, ASM international, 1984, pp. 381-396.
- [78] American Society for Testing and Materials (Filadelfia, Pennsylvania), *ASTM E112-96 (2004) e2: Standard Test Methods for Determining Average Grain Size*, 2004.
- [79] Y.S. Sato, H. Kokawa, M. Enomoto, S. Jogan, T. Hashimoto, Precipitation sequence in friction stir weld of 6063 aluminum during aging, *Metallurgical and Materials Transactions A* 30(12) (1999) 3125-3130.
- [80] S.K. Panigrahi, R. Jayaganthan, Effect of annealing on precipitation, microstructural stability, and mechanical properties of cryorolled Al 6063 alloy, *Journal of Materials Science* 45(20) (2010) 5624-5636.
- [81] J. Wu, P.J. Wray, C.I. Garcia, M. Hua, A.J. DeArdo, Image quality analysis: A new method of characterizing microstructures, *ISIJ international* 45(2) (2005) 254-262.
- [82] M. Rokni, A. Zarei-Hanzaki, H. Abedi, Microstructure evolution and mechanical properties of back extruded 7075 aluminum alloy at elevated temperatures, *Materials Science and Engineering: A* 532 (2012) 593-600.
- [83] H. McQueen, Development of dynamic recrystallization theory, *Materials Science and Engineering: A* 387 (2004) 203-208.

- [84] H. Hu, L. Zhen, B. Zhang, L. Yang, J. Chen, Microstructure characterization of 7050 aluminum alloy during dynamic recrystallization and dynamic recovery, *Materials Characterization* 59(9) (2008) 1185-1189.
- [85] S. Gourdet, F. Montheillet, A model of continuous dynamic recrystallization, *Acta Materialia* 51(9) (2003) 2685-2699.
- [86] W. Blum, Q. Zhu, R. Merkel, H. McQueen, Geometric dynamic recrystallization in hot torsion of Al-5Mg-0.6Mn (AA5083), *Materials Science and Engineering: A* 205(1-2) (1996) 23-30.
- [87] K. Huang, R. Logé, A review of dynamic recrystallization phenomena in metallic materials, *Materials & Design* 111 (2016) 548-574.
- [88] S. Karabay, M. Zeren, M. Yilmaz, Investigation extrusion ratio effect on mechanical behaviour of extruded alloy AA-6063, *Journal of Materials Processing Technology* 135(1) (2003) 101-108.
- [89] F. Liu, F. Yu, D. Zhao, L. Zuo, Microstructure and mechanical properties of an Al-12.7Si-0.7Mg alloy processed by extrusion and heat treatment, *Materials Science and Engineering: A* 528(10-11) (2011) 3786-3790.
- [90] L. Saraf, Kernel average misorientation confidence index correlation from FIB sliced Ni-Fe-Cr alloy surface, *Microscopy and Microanalysis* 17(S2) (2011) 424-425.
- [91] S.I. Wright, M.M. Nowell, D.P. Field, A review of strain analysis using electron backscatter diffraction, *Microscopy and Microanalysis* 17(3) (2011) 316-329.
- [92] M. Guerra, C. Schmidt, J.C. McClure, L. Murr, A. Nunes, Flow patterns during friction stir welding, *Materials Characterization* 49(2) (2002) 95-101.
- [93] O. Lorrain, V. Favier, H. Zahrouni, D. Lawrjaniec, Understanding the material flow path of friction stir welding process using unthreaded tools, *Journal of Materials Processing Technology* 210(4) (2010) 603-609.
- [94] F. Liu, T. Nelson, In-situ material flow pattern around probe during friction stir welding of austenitic stainless steel, *Materials & Design* 110 (2016) 354-364.
- [95] A. Tongne, C. Desrayaud, M. Jahazi, E. Feulvarch, On material flow in friction stir welded Al alloys, *Journal of Materials Processing Technology* 239 (2017) 284-296.
- [96] S. Panigrahi, R. Jayaganthan, V. Pancholi, M. Gupta, A DSC study on the precipitation kinetics of cryorolled Al 6063 alloy, *Materials Chemistry and Physics* 122(1) (2010) 188-193.
- [97] R. Joseph, V. Kliman, J. Jelemenska, *Aluminum and aluminum alloys*. ASM Specialty Handbook, ASM International, London, 1993, pp. 377.
- [98] G. Al-Marableh, Effect of heat treatment on the distribution and volume fraction of Mg₂Si in structural aluminum alloy 6063, *Metal Science and Heat Treatment* 48(5) (2006) 205-209.
- [99] A. Gerlich, M. Yamamoto, T. North, Strain rates and grain growth in Al 5754 and Al 6061 friction stir spot welds, *Metallurgical and materials transactions A* 38(6) (2007) 1291-1302.
- [100] H.-Y. Li, C.-T. Zeng, M.-S. Han, J.-J. Liu, X.-C. Lu, Time-temperature-property curves for quench sensitivity of 6063 aluminum alloy, *Transactions of Nonferrous Metals Society of China* 23(1) (2013) 38-45.
- [101] Y.S. Sato, M. Urata, H. Kokawa, Parameters controlling microstructure and hardness during friction-stir welding of precipitation-hardenable aluminum alloy 6063, *Metallurgical and Materials Transactions A* 33(3) (2002) 625-635.
- [102] S. Adeosun, S. Balogun, O. Sekunowo, M. Usman, Effects of heat treatment on strength and ductility of rolled and forged aluminum 6063 alloy, *Journal of Minerals & Materials Characterization & Engineering*, 9(8) (2010) 763-773.

- [103] I. Ansara, A. Dinsdale, and M. Rand, CALPHAD Database, *Al-Mg COST 507 Thermochemical database for light metal alloys*, 1998, URI: <http://hdl.handle.net/11256/618>.
- [104] S.H.C. Park, Y.S. Sato, H. Kokawa, Basal plane texture and flow pattern in friction stir weld of a magnesium alloy, *Metallurgical and Materials Transactions A* 34(4) (2003) 987-994.
- [105] J.L. Cavazos, R. Colás, Quench sensitivity of a heat treatable aluminum alloy, *Materials Science and Engineering: A* 363(1-2) (2003) 171-178.
- [106] R.A. Siddiqui, H.A. Abdullah, K.R. Al-Belushi, Influence of aging parameters on the mechanical properties of 6063 aluminium alloy, *Journal of Materials Processing Technology* 102(1-3) (2000) 234-240.
- [107] Y. Ohmori, L.C. Doan, Y. Matsuura, S. Kobayashi, K. Nakai, Morphology and crystallography of β -Mg₂Si precipitation in Al-Mg-Si alloys, *Materials Transactions* 42(12) (2001) 2576-2583.
- [108] D. Chakrabarti, D.E. Laughlin, Phase relations and precipitation in Al-Mg-Si alloys with Cu additions, *Progress in Materials Science* 49(3-4) (2004) 389-410.
- [109] M.E. Fine, Precipitation hardening of aluminum alloys, *Metallurgical Transactions A* 6(4) (1975) 625-630.
- [110] T. Gladman, Precipitation hardening in metals, *Materials Science and Technology* 15(1) (1999) 30-36.
- [111] A.R. Farkoosh, X.G. Chen, M. Pekguleryuz, Dispersoid strengthening of a high temperature Al-Si-Cu-Mg alloy via Mo addition, *Materials Science and Engineering: A* 620 (2015) 181-189.
- [112] S. Kumar, R.S. Panwar, O.P. Pandey, Wear behavior at high temperature of dual-particle size zircon-sand-reinforced aluminum alloy composite, *Metallurgical and Materials Transactions A* 44(3) (2013) 1548-1565.
- [113] A.B. Pandey, B.S. Majumdar, D.B. Miracle, Deformation and fracture of a particle-reinforced aluminum alloy composite: Part I. Experiments, *Metallurgical and Materials Transactions A* 31(3) (2000) 921-936.
- [114] R.A. Prado, L.E. Murr, K.F. Soto, J.C. McClure, Self-optimization in tool wear for friction-stir welding of Al 6061+ 20% Al₂O₃ MMC, *Materials Science and Engineering: A* 349(1-2) (2003) 156-165.
- [115] A.A. Premnath, T. Alwarsamy, T. Rajmohan, R. Prabhu, The influence of alumina on mechanical and tribological characteristics of graphite particle reinforced hybrid Al-MMC, *Journal of Mechanical Science and Technology* 28(11) (2014) 4737-4744.
- [116] M. Ferry, P. Munroe, Recrystallization kinetics and final grain size in a cold rolled particulate reinforced Al-based MMC, *Composites Part A: Applied Science and Manufacturing* 35(9) (2004) 1017-1025.
- [117] Y. Fan, M.M. Makhlof, The Al-Al₃Ni Eutectic Reaction: Crystallography and Mechanism of Formation, *Metallurgical and Materials Transactions A* 46(9) (2015) 3808-3812.
- [118] N. Belov, D. Eskin, N. Avxentieva, Constituent phase diagrams of the Al-Cu-Fe-Mg-Ni-Si system and their application to the analysis of aluminium piston alloys, *Acta materialia* 53(17) (2005) 4709-4722.
- [119] Y. Du, S. Liu, L. Zhang, H. Xu, D. Zhao, A. Wang, L. Zhou, An overview on phase equilibria and thermodynamic modeling in multicomponent Al alloys: Focusing on the Al-Cu-Fe-Mg-Mn-Ni-Si-Zn system, *Calphad* 35(3) (2011) 427-445.
- [120] ASM Handbook, vol. 3: *Alloy phase diagram*, ASM International, Materials Park, 1992, pp. 556 and 1107.

- [121] I. Dinaharan, Liquid metallurgy processing of intermetallic matrix composites, *Intermetallic Matrix Composites*, Elsevier, 2018, pp. 167-202.
- [122] K. Wada, J. Yamabe, H. Matsunaga, Mechanism of hydrogen-induced hardening in pure nickel and in a copper-nickel alloy analyzed by micro Vickers hardness testing, *Materials Science and Engineering: A* 805 (2021) 140580.
- [123] C.S. Tiwary, S. Kashyap, D.H. Kim, K. Chattopadhyay, Al based ultra-fine eutectic with high room temperature plasticity and elevated temperature strength, *Materials Science and Engineering: A* 639 (2015) 359-369.
- [124] K. Morsi, reaction synthesis processing of Ni-Al intermetallic materials, *Materials Science and Engineering: A* 299(1-2) (2001) 1-15.
- [125] C. Suwanpreecha, P. Pandee, U. Patakham, C. Limmaneevichitr, New generation of eutectic Al-Ni casting alloys for elevated temperature services, *Materials Science and Engineering: A* 709 (2018) 46-54.
- [126] Y. Yang, K. Yu, Y. Li, D. Zhao, X. Liu, Evolution of nickel-rich phases in Al-Si-Cu-Ni-Mg piston alloys with different Cu additions, *Materials & Design* 33 (2012) 220-225.
- [127] W.R. Osório, L.C. Peixoto, M.V. Canté, A. Garcia, Microstructure features affecting mechanical properties and corrosion behavior of a hypoeutectic Al-Ni alloy, *Materials & Design* 31(9) (2010) 4485-4489.
- [128] F. Czerwinski, Critical Assessment 40: A search for the eutectic system of high-temperature cast aluminium alloys, *Materials Science and Technology* 37(7) (2021) 683-692.
- [129] M. Lieblich, J.L. González-Carrasco, G. Caruana, Thermal stability of an Al-Ni₃Al composite processed by powder metallurgy, *Intermetallics* 5(7) (1997) 515-524.
- [130] R.S. Mishra, Z.Y. Ma, I. Charit, Friction stir processing: a novel technique for fabrication of surface composite, *Materials Science and Engineering: A* 341(1-2) (2003) 307-310.
- [131] A. Zykova, A. Chumaevskii, A. Gusarova, T. Kalashnikova, S. Fortuna, N. Savchenko, E. Kolubaev, S. Tarasov, Microstructure of In-Situ Friction Stir Processed Al-Cu Transition Zone, *Metals* 10(6) (2020) 818.
- [132] K. Nakata, S. Inoki, Y. Nagano, M. Ushio, Friction stir welding of Al₂O₃ particulate 6061 Al alloy composite, *Mater Sci Forum*, 2003, pp. 2873-2878.
- [133] J. Qu, H. Xu, Z. Feng, K. An, R. Battiste, L. An, H. Heinrich, Forming Al-Al₂O₃ Nanocomposite Surfaces Using Friction Stir Processing, *Transactions of NAMRI/SME* 37 (2009).
- [134] M. Golmohammadi, M. Atapour, A. Ashrafi, Fabrication and wear characterization of an A413/Ni surface metal matrix composite fabricated via friction stir processing, *Materials & Design* 85 (2015) 471-482.
- [135] I. Lee, P. Kao, C. Chang, N. Ho, Formation of Al-Mo intermetallic particle-strengthened aluminum alloys by friction stir processing, *Intermetallics* 35 (2013) 9-14.
- [136] V. Kishan, A. Devaraju, K.P. Lakshmi, Tribological properties of nano TiB₂ particle reinforced 6061-T6 aluminum alloy surface composites via friction stir processing, *Materials Today: Proceedings* 5(1) (2018) 1615-1619.
- [137] J. Geng, G. Liu, T. Hong, M. Wang, D. Chen, N. Ma, H. Wang, Tuning the microstructure features of in-situ nano TiB₂/Al-Cu-Mg composites to enhance mechanical properties, *Journal of Alloys and Compounds* 775 (2019) 193-201.
- [138] L.H. Dai, Z. Ling, Y.L. Bai, Size-dependent inelastic behavior of particle-reinforced metal-matrix composites, *Composites Science and Technology* 61(8) (2001) 1057-1063.
- [139] D.C. Dunand, A. Mortensen, On plastic relaxation of thermal stresses in reinforced metals, *Acta Metallurgica et Materialia* 39.2 (1991) 127-139.

- [140] N. Belov, V. Belov, A. Alabin, S. Mishurov, New generation of economically alloyed aluminum alloys, *Metallurgist* 54(5) (2010) 311-316.
- [141] ASM Handbook, vol. 2: *Properties and Selection: Nonferrous Alloys and Special-Purpose Materials*. ASM International, 1990, pp. 610-614.
- [142] B.H. Toby, R.B. Von Dreele, GSAS-II: the genesis of a modern open-source all purpose crystallography software package, *Journal of Applied Crystallography* 46(2) (2013) 544-549.
- [143] T. Ando, E. Lavernia, N. Grant, A TEM study of the microstructures of A modified 7075 and X2020 aluminum alloys produced by liquid dynamic compaction, *Materials Letters* 5(1-2) (1986) 17-28.
- [144] E. Colgan, A review of thin-film aluminide formation, *Materials Science Reports* 5(1) (1990) 1-44.
- [145] H. Alimadadi, C. Kjartansdóttir, A. Burrows, T. Kasama, P. Møller, Nickel-aluminum diffusion: A study of evolution of microstructure and phase, *Materials Characterization* 130 (2017) 105-112.
- [146] F. Cardellini, G. Mazzone, A. Montone, M.V. Antisari, Solid state reactions between Ni and Al powders induced by plastic deformation, *Acta Metallurgica et Materialia* 42(7) (1994) 2445-2451.
- [147] J.M. Pauls, C.E. Shuck, A. Genç, S. Rouvimov, A.S. Mukasyan, In-situ transmission electron microscopy determination of solid-state diffusion in the aluminum-nickel system, *Journal of Solid State Chemistry* 276 (2019) 114-121.
- [148] S. Carbonin, F. Martignago, G. Menegazzo, A. Dal Negro, X-ray single-crystal study of spinels: in situ heating, *Physics and Chemistry of Minerals* 29(8) (2002) 503-514.
- [149] K. Hilpert, D. Kobertz, V. Venugopal, M. Miller, H. Gerads, F. Bremer, H. Nickel, Phase diagram studies on the Al-Ni system, *Zeitschrift für Naturforschung A* 42(11) (1987) 1327-1332.
- [150] L. Mondolfo, S. Ausgabe, *Aluminium alloys: Structure and Properties*, Butter Worths, London-Boston, vol. 1, 1976, pp. 72.
- [151] Y. Fukui, K. Takashima, C. Ponton, Measurement of Young's modulus and internal friction of an in situ Al-Al₃Ni functionally gradient material, *Journal of Materials Science* 29(9) (1994) 2281-2288.
- [152] P. Mohanty, K. Pant, J. Parikh, D. Sharma, Liquid fuel production from syngas using bifunctional CuO-CoO-Cr₂O₃ catalyst mixed with MFI zeolite, *Fuel Processing Technology* 92(3) (2011) 600-608.
- [153] N. Yazdian, F. Karimzadeh, M. Tavoosi, Microstructural evolution of nanostructure 7075 aluminum alloy during isothermal annealing, *Journal of Alloys and Compounds* 493(1-2) (2010) 137-141.
- [154] A.D. Isadare, B. Aremo, M.O. Adeoye, O.J. Olawale, M.D. Shittu, Effect of heat treatment on some mechanical properties of 7075 aluminium alloy, *Materials Research* 16(1) (2013) 190-194.
- [155] J.V. Grabel, J.R. Cost, Ultrasonic velocity measurement of elastic constants of Al-Al₃Ni unidirectionally solidified eutectic, *Metallurgical and Materials Transactions B* 3(7) (1972) 1973-1978.
- [156] F.J. Garcia-Garcia, Ph.D dissertation, *Effect of Magnesium, Nickel and Titanium on the Electrochemical Behaviour of AA1050 Aluminium Alloys in Nitric Acid*, The University of Manchester (United Kingdom), 2009, pp. 140-156.
- [157] T.H. Courtney, *Mechanical Behavior of Materials*, Waveland Press, 2005, pp.309-325.

- [158] J.F. Nie, B.C. Muddle, I.J. Polmear, The effect of precipitate shape and orientation on dispersion strengthening in high strength aluminium alloys, *Materials science forum*, Trans Tech Publ, 1996, pp. 1257-1262.
- [159] H. Wen, T.D. Topping, D. Isheim, D.N. Seidman, E.J. Lavernia, Strengthening mechanisms in a high-strength bulk nanostructured Cu-Zn-Al alloy processed via cryomilling and spark plasma sintering, *Acta Materialia* 61(8) (2013) 2769-2782.
- [160] E. Arbtin Jr, and G. Murphy, *Correlation of Vickers hardness number, modulus of elasticity, and the yield strength for ductile metals*, US Atomic Energy Commision, 1953. URI: <https://dr.lib.iastate.edu/handle/20.500.12876/6854>
- [161] C.N.S. Kumar, D. Yadav, R. Bauri, G.D.J. Ram, Effects of ball milling and particle size on microstructure and properties 5083 Al-Ni composites fabricated by friction stir processing, *Materials Science and Engineering: A* 645 (2015) 205-212.
- [162] F. Adel Mehraban, F. Karimzadeh, M. Abbasi, Development of Al-Al₃Ni Nanocomposite by Duplex Processing of Flame Spray and Friction Stir Processing, and Evaluation of Its Properties, *Metallurgical and Materials Transactions A* 48(10) (2017) 4693-4700.
- [163] T.-F. Chung, Y.-L. Yang, B.-M. Huang, Z. Shi, J. Lin, T. Ohmura, J.-R. Yang, Transmission electron microscopy investigation of separated nucleation and in-situ nucleation in AA7050 aluminium alloy, *Acta Materialia* 149 (2018) 377-387.
- [164] C. Peel, P. Poole, The Effect of Grain Structure on the Stress Corrosion Resistance Al-Zn-Mg-Cu Alloys, Royal Aircraft Establishment Farnborough (England), 1978.
- [165] M.O. Speidel, M.V. Hyatt, *Stress-corrosion cracking of high-strength aluminum alloys*, *Advances in corrosion science and technology*, Springer, 1972, pp. 115-335.
- [166] R. Wanhill, M. Windisch, *Corrosion and stress corrosion testing of aerospace vehicle structural alloys*, *Corrosion and Stress Corrosion Testing of Aerospace Vehicle Structural Alloys*, Springer, 2018, pp. 1-63.
- [167] H. McQueen, O. Celliers, Application of hot workability studies to extrusion processing. Part III: physical and mechanical metallurgy of Al-Mg-Si and Al-Zn-Mg alloys, *Canadian Metallurgical Quarterly* 36(2) (1997) 73-86.
- [168] U. Curle, G. Govender, Semi-solid rheocasting of grain refined aluminum alloy 7075, *Transactions of Nonferrous Metals Society of China* 20 (2010) s832-s836.
- [169] S.K. Panigrahi, R. Jayaganthan, Development of ultrafine grained high strength age hardenable Al 7075 alloy by cryorolling, *Materials & Design* 32(6) (2011) 3150-3160.
- [170] I. MacAskill, A. LaDepha, J. Milligan, J. Fulton, D. Bishop, Effects of cold and hot densification on the mechanical properties of a 7XXX series powder metallurgy alloy, *Powder metallurgy* 52(4) (2009) 304-310.
- [171] J. Martin, T. Gomez-Acebo, F. Castro, Sintering behaviour and mechanical properties of PM Al-Zn-Mg-Cu alloy containing elemental Mg additions, *Powder Metallurgy* 45(2) (2002) 173-180.
- [172] D. Bishop, W. Caley, G. Kipouros, R. Hexemer, I. Donaldson, Powder metallurgy processing of 2xxx and 7xxx series aluminium alloys, *Canadian Metallurgical Quarterly* 50(3) (2011) 246-252.
- [173] J. Pickens, Aluminium powder metallurgy technology for high-strength applications, *Journal of Materials Science* 16(6) (1981) 1437-1457.
- [174] Z.-q. Tan, Q. Zhang, X.-y. Guo, W.-j. Zhao, C.-s. Zhou, Y. Liu, New development of powder metallurgy in automotive industry, *Journal of Central South University* 27(6) (2020) 1611-1623.

- [175] W.E. Quist, R.E. Lewis, The need for rapidly solidified powder metallurgy aluminum alloys for aerospace applications, *Rapidly Solidified Powder Aluminum Alloys*, *ASTM STP* 890 (1986) 7-38.
- [176] W. Reschetnik, J.-P. Brüggemann, M. Aydinöz, O. Grydin, K.-P. Hoyer, G. Kullmer, H. Richard, Fatigue crack growth behavior and mechanical properties of additively processed EN AW-7075 aluminium alloy, *Procedia Structural Integrity* 2 (2016) 3040-3048.
- [177] T. Hu, L. Jiang, H. Yang, K. Ma, T.D. Topping, J. Yee, M. Li, A.K. Mukherjee, J.M. Schoenung, E.J. Lavernia, Stabilized plasticity in ultrahigh strength, submicron Al crystals, *Acta Materialia* 94 (2015) 46-58.
- [178] S.R. Sharma, Z.Y. Ma, R.S. Mishra, Effect of friction stir processing on fatigue behavior of A356 alloy, *Scripta Materialia* 51(3) (2004) 237-241.
- [179] M.J. Taleghani, E.R. Navas, J. Torralba, Microstructural and mechanical characterisation of 7075 aluminium alloy consolidated from a premixed powder by cold compaction and hot extrusion, *Materials & Design* 55 (2014) 674-682.
- [180] M. Rokni, C. Widener, V. Champagne, G. Crawford, S. Nutt, The effects of heat treatment on 7075 Al cold spray deposits, *Surface and Coatings Technology* 310 (2017) 278-285.
- [181] S.S. Singh, E. Guo, H. Xie, N. Chawla, Mechanical properties of intermetallic inclusions in Al 7075 alloys by micropillar compression, *Intermetallics* 62 (2015) 69-75.
- [182] A. Mukhopadhyay, On the nature of the Fe-bearing particles influencing hard anodizing behavior of AA 7075 extrusion products, *Metallurgical and Materials Transactions A* 29(13) (1998) 979-987.
- [183] C. Mondal, A. Mukhopadhyay, On the nature of T ($\text{Al}_2\text{Mg}_3\text{Zn}_3$) and S (Al_2CuMg) phases present in as-cast and annealed 7055 aluminum alloy, *Materials Science and Engineering: A* 391(1-2) (2005) 367-376.
- [184] B. Prabhu, C. Suryanarayana, L. An, R. Vaidyanathan, Synthesis and characterization of high volume fraction Al- Al_2O_3 nanocomposite powders by high-energy milling, *Materials Science and Engineering: A* 425(1-2) (2006) 192-200.
- [185] S.A. Sajjadi, H.R. Ezatpour, H. Beygi, Microstructure and mechanical properties of Al- Al_2O_3 micro and nano composites fabricated by stir casting, *Materials Science and Engineering: A* 528(29-30) (2011) 8765-8771.
- [186] J.-Q. Su, T.W. Nelson, C.J. Sterling, Microstructure evolution during FSW/FSP of high strength aluminum alloys, *Materials Science and Engineering: A* 405(1-2) (2005) 277-286.
- [187] A. Goloborodko, T. Ito, X. Yun, Y. Motohashi, G. Itoh, Friction stir welding of a commercial 7075-T6 aluminum alloy: Grain refinement, thermal stability and tensile properties, *Materials Transactions* 45(8) (2004) 2503-2508.
- [188] T. Sakai, A. Belyakov, R. Kaibyshev, H. Miura, J.J. Jonas, Dynamic and post-dynamic recrystallization under hot, cold and severe plastic deformation conditions, *Progress in Materials Science* 60 (2014) 130-207.
- [189] T. Morishige, T. Hirata, M. Tsujikawa, K. Higashi, Comprehensive analysis of minimum grain size in pure aluminum using friction stir processing, *Materials Letters* 64(17) (2010) 1905-1908.
- [190] Z.Y. Ma, R.S. Mishra, M.W. Mahoney, Superplastic deformation behaviour of friction stir processed 7075 Al alloy, *Acta Materialia* 50(17) (2002) 4419-4430.
- [191] W. Tao, D. Shuwei, K. Matsuda, Z. Yong, Dynamic Recrystallization and Dynamic Precipitation in AA6061 Aluminum Alloy During Friction Stir Welding, *Transactions of the Indian Institute of Metals* (2022) 1-11.

- [192] G. Padhy, C. Wu, S. Gao, L. Shi, Local microstructure evolution in Al 6061-T6 friction stir weld nugget enhanced by ultrasonic vibration, *Materials & Design* 92 (2016) 710-723.
- [193] A. Malakar, V. Pancholi, V.V. Dabhade, Recrystallization and strengthening mechanism in friction-stir-processed Al powder compacts, *Journal of Materials Engineering and Performance* 29(5) (2020) 3243-3252.
- [194] A. Orozco-Caballero, O.A. Ruano, E.F. Rauch, F. Carreño, Severe friction stir processing of an Al-Zn-Mg-Cu alloy: Misorientation and its influence on superplasticity, *Materials & Design* 137 (2018) 128-139.
- [195] A. Abolhasani, A. Zarei-Hanzaki, H. Abedi, M. Rokni, The room temperature mechanical properties of hot rolled 7075 aluminum alloy, *Materials & Design* 34 (2012) 631-636.
- [196] S.Y. Tarasov, V.Y. Rubtsov, E. Kolubaev, A. Ivanov, S. Fortuna, A. Eliseev, Ultrasonic-assisted friction stir welding on V95AT1 (7075) aluminum alloy, *AIP Conference Proceedings*, AIP Publishing LLC, 2015, p. 020231.
- [197] S.S. Singh, C. Schwartzstein, J.J. Williams, X. Xiao, F. De Carlo, N. Chawla, 3D microstructural characterization and mechanical properties of constituent particles in Al 7075 alloys using X-ray synchrotron tomography and nanoindentation, *Journal of Alloys and Compounds* 602 (2014) 163-174.
- [198] Z. Que, Y. Zhou, Y. Wang, C.L. Mendis, Z. Fan, Effects of Mg addition on the Al₆ (Fe, Mn) intermetallic compounds and the grain refinement of α -Al in Al-Fe-Mn alloys, *Materials Characterization* 171 (2021) 110758.
- [199] B. Murty, S. Kori, M. Chakraborty, Grain refinement of aluminium and its alloys by heterogeneous nucleation and alloying, *International Materials Reviews* 47(1) (2002) 3-29.
- [200] S.Y. Tarasov, V. Rubtsov, E. Kolubaev, A proposed diffusion-controlled wear mechanism of alloy steel friction stir welding (FSW) tools used on an aluminum alloy, *Wear* 318(1-2) (2014) 130-134.
- [201] P. Sahlot, K. Jha, G. Dey, A. Arora, Wear-induced changes in FSW tool pin profile: effect of process parameters, *Metallurgical and Materials Transactions A* 49(6) (2018) 2139-2150.
- [202] H. Kolkman, W. t'Hart, L. Schra, *Quench Sensitivity of Airframe Aluminium Alloys*, *Strength of Metals and Alloys (ICSMA 8)*, Elsevier, 1989, pp. 597-602.
- [203] S. Liu, Q. Zhong, Y. Zhang, W. Liu, X. Zhang, Y. Deng, Investigation of quench sensitivity of high strength Al-Zn-Mg-Cu alloys by time-temperature-properties diagrams, *Materials & Design* 31(6) (2010) 3116-3120.
- [204] Y. Lin, Y.-Q. Jiang, X.-M. Chen, D.-X. Wen, H.-M. Zhou, Effect of creep-aging on precipitates of 7075 aluminum alloy, *Materials Science and Engineering: A* 588 (2013) 347-356.
- [205] D. Dumont, A. Deschamps, Y. Brechet, On the relationship between microstructure, strength and toughness in AA7050 aluminum alloy, *Materials Science and Engineering: A* 356(1-2) (2003) 326-336.
- [206] Z. Zhou, S. Chen, Q. Liu, Microhardness Profile and Microstructure Characterization in Friction Stir Processing Zone of the Aged and Solid Solution Treated 7075 Aluminum Alloys, *ICAA13*, Pittsburgh, Springer, 2012, pp. 637-642.
- [207] K. Dehghani, R. Ghorbani, A. Soltanipoor, Microstructural evolution and mechanical properties during the friction stir welding of 7075-O aluminum alloy, *The International Journal of Advanced Manufacturing Technology* 77(9) (2015) 1671-1679.
- [208] R. Goswami, S. Lynch, N. Holroyd, S.P. Knight, R.L. Holtz, Evolution of grain boundary precipitates in Al 7075 upon aging and correlation with stress corrosion cracking behavior, *Metallurgical and Materials Transactions A* 44(3) (2013) 1268-1278.

[209] K. Rajan, W. Wallace, J. Beddoes, Microstructural study of a high-strength stress-corrosion resistant 7075 aluminium alloy, *Journal of Materials Science* 17(10) (1982) 2817-2824.

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