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**NANYANG
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**HIGH TOUGHNESS MAGNESIUM ALLOY
THROUGH SEVERE PLASTIC DEFORMATION
AND SHORT ANNEALING**

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SCHOOL OF MECHANICAL AND AEROSPACE ENGINEERING

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Abstract

In this work, a thermomechanical treatment using severe plastic deformation (SPD) via a modified constrained groove pressing (CGP) technique and short duration post-annealing was introduced to improve the mechanical properties of AZ31 magnesium alloy plate. This method is effective for producing fine-grained microstructure in thin magnesium plates and also enhances the mechanical strength without sacrificing the fatigue and corrosion properties. In this process, the magnesium plate is subjected to repeated deformation at elevated temperature using a specified pressing sequence designed to accelerate the grain refinement process. This technique has unique advantages over other principal SPD techniques such as Equal Channel Angular Pressing (ECAP) and High-Pressure Torsion (HPT). Firstly, it circumvents the difficulties faced in ECAP and HPT such as buckling and size limitation, respectively. Secondly, it is possible to implement the pressing procedures into rolling process which will benefit continuous processing of long magnesium strip. Thirdly, CGP was demonstrated as an effective grain refinement process for improving the microstructure of squeeze-casted AZ31 alloy. This opens up to the possibility of producing fine-grained magnesium plate with improved properties by using lower cost magnesium preform prepared by casting.

Investigation of the deformation and temperature sequences in CGP process revealed interesting dependency of these conditions on strain, texture development and microstructure. Finite element (FE) simulation showed that the total strain imparted in the material was affected by the constraints imposed on the material by the die just before shear deformation and also by the compressive and stretching of the material during die filling. Experimental studies showed that decreasing processing temperature limit static recrystallization, recovery and grain growth and resulted in the development of micro and sub-micron grains. As such, effective choice of deformation and temperature sequences could positively influence the total strain, texture development and grain refinement efficiency.

Electron backscatter diffraction (EBSD) analysis of the microstructure evolution during modified CGP revealed that dislocation boundaries of initially low angle grain boundaries

(LAGB) were developed in the grain interiors and at the vicinity of the grain boundaries. This evidence suggests that mechanisms of both rotational dynamic recrystallization (rDRX) and continuous dynamic recrystallization (cDRX) were responsible for the efficient grain refinement and was unique to this process.

The microstructure stability in the strain-induced fine and ultrafine grain boundaries prepared by modified CGP was investigated by annealing and interpreted by grain growth kinetic equations. From this study, it was revealed that despite the lower microstructure stability, as indicated by the low activation energy, the average grain sizes can be maintained considerably smaller than the parent material at shorter annealing.

The hot tensile behaviour and deformation mechanism of the modified CGP processed alloy with short annealing was investigated at elevated temperatures and under various strain rates. From the room temperature tensile tests, the yield strength and elongation to failure were significantly improved by 34% and 11%, respectively. The results of the strain rate sensitivity and activation energy suggested that climb-controlled dislocation creep is the dominant deformation process associated with lattice diffusion. Enhanced ductility was measured at 523 K and $1 \times 10^{-3} \text{ s}^{-1}$ where a maximum elongation to failure of $100 \pm 2.5\%$ was obtained, and dynamic recovery was observed as the main restoration process.

From the biodegradation studies, it was established that the average corrosion rate was marginally higher after modified CGP. This reduction in corrosion resistance can be attributed to the non-uniformity of the microstructure; some grains contain high dislocation and some grains were almost without dislocation. This introduced strain energy difference and stress differences which worsen the corrosion properties despite having a higher area of grain boundaries. It was further established from the study of the fatigue crack growth rate that the CGP process does not significantly alter the fatigue performance. The above studies suggest that CGP enhances the yield strength of magnesium alloy without significantly affecting the fatigue and corrosion performance and that combining CGP treatment with coating technologies are viable approaches to improve the performances of magnesium material for biomedical implants.

New insights into the microstructure evolution and mechanical properties of severe

plastically deformed AZ31 magnesium alloy through modified CGP have been gained through this study. From an application point of view, this study has demonstrated very clearly the potential of the CGP process for preparing fine-grained AZ31 plate with enhanced mechanical strength and improved ductility by adopting the appropriate heat treatment strategy. The process can be made continuous through adaptation of its design into rolling process. It is reasonably believed that this thermomechanical processing route can be established for a wide range of commercial application in the foreseeable future, particularly for improving the mechanical properties of biodegradable magnesium alloy.

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List of Publications

- 1) K.S. Fong, D. Atsushi M-J Tan, B.W. Chua, “Effect of Deformation and Temperature Paths in Severe Plastic Deformation Using Groove Pressing on Microstructure, Texture, and Mechanical Properties of AZ31-O” *Journal of Manufacturing Science and Engineering*, Vol.137, (2015), pp. 051004-1-16
- 2) K.S. Fong, D. Atsushi M-J Tan, B.W. Chua, “Enabling wider use of Magnesium Alloys for lightweight applications by improving the formability by Groove Pressing”, *Procedia CIRP* 26 (2015), pp. 449 – 454
- 3) K.S. Fong, D. Atsushi, M.J Tan, B.W. Chua, M.K. Ho, “Effect of Severe Plastic Deformation on Microstructure of Squeeze-cast Magnesium Alloy AZ31 Plate”, *AIP Conference Proceedings* 1769, 200005 (2016)
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- 7) S.J. Bin, Y.T. Tan, K.S. Fong, M.J. Tan, Effect of severe plastic deformation and post-annealing on mechanical properties and bio-corrosion rate of AZ31 magnesium alloy. *International conference on the technology of plasticity, ICTP 2017*, 17-22 September 2017, Cambridge, United Kingdom
- 8) E. Salvati, H. Zhang, K.S. Fong, X. Song, R.J.H Paynter, A.M. Korsunsky, “Fatigue and Fracture behaviour of AZ31B Mg alloy plastically deformed by Constrained Groove Pressing in the Presence of Overloads”, *Procedia structural integrity*, Vol. 2, 2016, pp. 3772-3781
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Chapter 1 Introduction

1. Background and problem statement

Magnesium and its alloys are very attractive for replacement of structural steel for lightweight applications because of its low density ($2/3$ that of aluminium) and high specific strength ($57\text{-}218 \times 10^6 \text{ N.mm.kg}^{-1}$) [1]. They also possess many other useful properties such as good electromagnetic shielding, machinability, recyclability, high dent resistance, vibration damping and high dent resistance [2, 3]. Moreover, being the eight most abundant element on earth, comprising of about 2.7% in the earth's crust and 0.13% of the world's ocean [2-4], it is often regarded by many as virtually an inexhaustible source. As such, many researchers are encouraging greater utilization of magnesium and its alloys.

Since a long time, die casting technology has been the dominant manufacturing process for magnesium components [5] because of its relative ease in fabricating relatively complex product geometries as compared to press forming technology. However, the mechanical properties of cast components are widely known to be more inferior as compared to their wrought counterpart because of the cast microstructure and issues of porosities [1]. Even though wrought magnesium alloys have better mechanical properties, its usage in the industry is limited because of the different factors [6, 7]; 1) Poor room temperature formability which dictates the press forming operation to be carried out at elevated temperature. This, in turn, increases the manufacturing cost which limits its use for price-sensitive products. 2) The high cost of the material itself and 3) Poor corrosion resistance and serviceability challenges. In the recent years, increasing regulations to improve fuel efficiency and reduce carbon emission had led to a renewed interest in the greater use of

wrought magnesium in automotive components such as seat frame, covers, and body panels [4, 8]. This is promising if the challenges associated high cost and poor formability can be resolved.

Currently, wrought magnesium alloys sheet/bar are prepared by direct chill (DC) casting process followed by multiple stages of hot rolling/extrusion into the desired sizes. As such, the process is very costly because of the need to reheat the material several times during the procedures and also because of other factors such as stringent quality control, high equipment and energy cost [7]. More recently, twin-roll casting which combines casting and rolling into one process is emerging as an alternative process for the production of magnesium sheets up to 1.5 m in width [9]. However, this process remains challenging which requires delicate quality and process control to avoid defects such as hot cracking and centerline segregation.

Until now, not many have explored the use of squeeze casting process for the production of small to medium size wrought magnesium feedstock in the form of sheet or bar. In squeeze casting process, the magnesium melt is transferred to a die and pressed at high forging pressure by a punch in a hydraulic press setup. The melt solidified under the pressure resulting in parts without porosity, uniform microstructure, and better mechanical properties as compared to die casting parts. It is also reasonably believed that the feedstock produced by squeeze casting will be less costly for small volume production of small magnesium plate as compared to rolling mills for higher volume production of continuous sheet. The feedstock produced by this method can be subsequently used for machining or forming into final products. However, the challenge here is to produce magnesium sheet

with competitive properties as compared to wrought alloy produced by the conventional method

Based on the above background, the present research project is initiated with the objectives of addressing two research challenges. The first major research challenge is to address the issue of low room temperature formability of wrought AZ31 magnesium alloy sheet. Overcoming this limitation will encourage a greater use of wrought magnesium sheet in press forming operation. This objective was approached by the development of a suitable thermomechanical treatment by using severe plastic deformation (SPD) technology and heat treatment to improve the mechanical properties of magnesium sheet through grain refinement and texture modification. In this research, constrained groove pressing (CGP) was chosen as the primary SPD technique because of its suitability for processing of sheet geometry as compared to other techniques and ease of scaling up for continuous processing. The second research challenge is to address the issue of high cost of wrought magnesium alloy and expand the use of magnesium alloy beyond structural application. This was approached by the development of squeeze-casting process for manufacturing of thin magnesium plates and improving its mechanical properties by CGP. The biodegradation and fatigue performance of magnesium alloy was also investigated to assess the effect of SPD on these properties which are important for biomedical applications.

2. Objective and scope

Based on the gaps in previous studies, the objective of this research was defined as:

- i. To establish a comprehensive understanding of the influence of deformation paths

and temperature conditions on grain refinement efficiency and mechanical properties, and optimize the process into a sustainable production process for processing of difficult-to-work magnesium alloy.

ii. To establish a comprehensive understanding of the effect of the SPD process on material characteristics in terms of mechanical properties, thermal stability, elevated temperature deformation behaviour and its mechanism

ii. Furthermore, the effect of CGP process as a grain refinement technique for squeeze-casted magnesium will be investigated. The influences of CGP on biodegradation and fatigue performances of wrought AZ31 magnesium alloy were also examined to assess its potential for biomedical application.

To this end, the scope of this PhD study includes:

- a) Study the microstructural evolution during the process.
 - Fabrication of fine-grained AZ31 magnesium alloy plate to show the feasibility of the severe plastic deformation (SPD) process by constrained groove pressing (CGP).
 - Study of the effect of deformation paths on strain distribution and homogeneity in the material by Finite Element Simulation.
 - Comprehensive experimental studies to investigate the influences of temperatures and deformation paths on grain size, mechanical properties, and textures.

- Using EBSD techniques to elaborate the grain refinement mechanism in CGP.
- A preliminary study of the effect of CGP on grain refinement of AZ31 alloy plate prepared by squeeze casting to demonstrate its potential for production of low-cost magnesium plate.

b) Analyzing stability of microstructure of AZ31 after the large strain deformation by SPD. The issues that need to be addressed are the annealing processes of recovery, recrystallization and grain growth and their respective kinetics with respect to temperature and time which is not well researched into and currently lack experimental data for the SPD process by CGP.

- Recovery annealing of the CGP processed AZ31 alloy at different temperatures from 473 to 623 K at different time from 15 to 180 min.
- Grain growth study under respective annealing condition and analysis of its kinetics to establish the activation energy.

c) Investigation of the post-processed material behaviour.

- Tensile flow behaviour and deformation mechanism of the CGP processed and annealed alloy under moderately high temperatures.

- Investigation of the bio-degradation behaviour of the CGP processed alloy by potentiodynamic polarization test and immersion studies. The corrosion products were examined by X-ray diffraction and scanning electron microscopy
- Investigation of the fatigue crack propagation behaviour by using fatigue crack growth rate study using baseline amplitude cyclic loading with occurrences of both underload and overload.

3. Organization of thesis

The introduction chapter (chapter 1, as you have gone through), provides a rationale for the research and establishes the goals and scope that are directed towards developing a deeper understanding of the metallurgical aspects of the severe plastic deformation process by constrained groove pressing (CGP).

In Chapter 2, a literature survey of developed severe plastic deformation process is presented, with emphasis on different research in formability improvement of magnesium alloy by various thermomechanical and metallurgical processing. A brief introduction of squeeze casting process is also presented.

In Chapter 3, the experimental procedures and characterization methods are described. After a practical explanation of the processing methods, annealing methods and microstructural and mechanical characterization techniques are elaborated.

The effect of process parameters (deformation paths and temperature conditions) on the microstructure evolution, mechanical properties, and texture of AZ31 alloy is explained in Chapter 4 & 5. The material flow and strain homogeneity were elaborated using FE

simulation and correlated with the experimental finding help to highlight the importance of the role of deformation path on grain refinement efficiency, total strain and texture development. The yield strength and ductility are discussed with respect to the mechanisms that contribute to it and conclusive remarks on the mechanical properties after CGP are made at the end of the chapter.

Chapter 6 examines the microstructure evolution of CGP by EBSD techniques to clarify the grain refinement mechanism through a detailed investigation of the grain boundary characteristics and grain misorientation during dynamic recrystallization.

Chapter 7 reports the microstructural stability of the fine-grained AZ31 magnesium alloy processed by CGP. Conclusive remarks on the usage of a suitable thermo-mechanical route of CGP followed by annealing to design the required mechanical properties of AZ31 are made.

In Chapter 8, the effect of CGP and post-annealing on the mechanical properties of the AZ31 magnesium alloy at moderately high temperature is examined, with more focus on understanding the tensile flow behaviour and deformation mechanism. In Chapter 9, the potential of CGP for grain refining of squeeze-cast AZ31 magnesium alloy is briefly examined.

In Chapter 10, the influences of CGP on the corrosion resistance of AZ31 magnesium alloy are examined and discussed. Corrosion tests were performed by potentiodynamic polarization techniques and mass loss measurement by immersion tests which were both performed in Hank's balanced salt solution. Examination of the corrosion product and microstructure were performed by scanning electron microscopy (SEM), electron

diffraction spectroscopy (EDS), and x-ray diffraction (XRD), electron backscatter diffraction (EBSD) and transmission electron microscopy (TEM). The fatigue performance of the CGP-processed magnesium plate was jointly investigated with our collaborators from the University of Oxford. The results and discussion are included in the appendix.

Finally, conclusions and suggestions for future work are given in Chapter 11.

Chapter 2 Literature Review

This chapter provides a detailed literature review of the issues of magnesium alloy, state of art in the research to address these issues, from alloying to thermomechanical processing, and the scientific challenges associated with these research. Section 2.1 and 2.2 will provide a background on the issue of low formability in magnesium and common strategies to overcome this limitation. Section 2.3 and section 2.4 will provide a review of current research in alloying and thermomechanical processing that focus on addressing the low formability challenge. Section 2.5 provides an in-depth survey of Severe Plastic Deformation (SPD) which is the primary scope of this research. This section will provide a background of SPD, SPD using groove pressing and its brief history, mechanism of grain refinement in SPD, the recrystallization mechanism in magnesium alloy, current studies on the kinetics of grain growth, and effect of temperature-compensated strain rate parameter popularly known as the Zener-Hollomon parameter. Section 2.6 will briefly review the Squeeze Casting process which forms part of this research scopes where the effect of SPD on squeezed-cast Mg alloy sheet with or without alloying will be investigated.

Through the reviews from section 2.1 to 2.4, the motivation, relevance and potential to contribute towards knowledge of this research are presented. At the end of the chapter, the aim and scope of the thesis are defined.

2.1 Formability of Magnesium alloys

Magnesium has poor formability because of its hcp structure and a limited number of operating slip systems at room temperature. In order to satisfy Von Mises criterion for

homogenous shape change, at least five independent slip systems are necessary [10]. At room temperature, plastic deformation of magnesium is limited to the $\{0001\}$ $\langle 11\bar{2}0 \rangle$ basal $\langle a \rangle$ -slip while non-basal slip systems and twinning contribute to a small extent. The basal $\langle a \rangle$ -slip only have two independent slip systems which do not satisfy Von Mises criterion and hence magnesium have very low ductility at room temperature. In order to accommodate further plastic deformation, it is necessary to have additional non-basal slip systems such as $\{10\bar{1}0\}\langle 11\bar{2}0 \rangle$ prismatic $\langle a \rangle$ -slip, first-order $\{10\bar{1}1\}\langle 11\bar{2}0 \rangle$ pyramidal $\langle a \rangle$ -slip, and second order $\{11\bar{2}2\}\langle 11\bar{2}3 \rangle$ pyramidal $\langle c + a \rangle$ -slip. Unfortunately, these non-basal slip systems require larger critical resolved shear stress (CRSS) and are activated at higher processing temperatures ($>250^\circ\text{C}$).

The CRSS for the basal $\langle a \rangle$ -slip, prismatic $\langle a \rangle$ -slip, first order pyramidal $\langle a \rangle$ -slip, and second order pyramidal $\langle c + a \rangle$ -slip are approximate in the ratio of 1:38:50:100 [11]. Basically, the prismatic $\langle a \rangle$ -slip and first order pyramidal $\langle a \rangle$ -slip systems have the common $\langle a \rangle$ -slip direction and do not lead to deformation out of the basal plane. For greater formability, higher order pyramidal $\langle c + a \rangle$ -slip where the slip vectors are out of the basal plane is necessary. This slip mode has five independent slip systems that could satisfy von Mises criterion [12].

In addition to the basal and non-basal slip systems, there are two mechanical twinning modes for magnesium; the $\{10\bar{1}2\}\langle 10\bar{1}1 \rangle$ extension twinning which can accommodate tension straining along the c-axis and the $\{10\bar{1}1\}\langle 10\bar{1}2 \rangle$ contraction twinning which provides a favourable compression strain along the c-axis. However, contraction twin occur quite remotely because it has a much larger CRSS compare the extension twin. Figure 2-1

show the summary of various slip systems, and mechanical twinning in hcp magnesium.

Figure 2.1: Slip-systems of magnesium: (a) $\{0001\}$ $\langle 11\bar{2}0 \rangle$ basal $\langle a \rangle$ -slip, (b) $\{10\bar{1}0\}$ $\langle 11\bar{2}0 \rangle$ prismatic $\langle a \rangle$ -slip, (c) $\{10\bar{1}1\}$ $\langle 11\bar{2}0 \rangle$ pyramidal $\langle a \rangle$ -slip, (d) $\{11\bar{2}2\}$ $\langle 11\bar{2}3 \rangle$ pyramidal $\langle c + a \rangle$ -slip, (e) $\{10\bar{1}2\}$ $\langle 10\bar{1}1 \rangle$ Extension twin (f) $\{10\bar{1}1\}$ $\langle 10\bar{1}2 \rangle$ contraction twin

Unfavourable texture changes can occur in magnesium alloys during deformation which further limits the formability. In rolled magnesium sheets or extruded bars, a strong basal texture exists whereby the basal planes are primarily aligned parallel to the rolling and extrusion direction respectively. When compression loads are applied along the rolling or extrusion direction respectively, tensile strain will be imposed along the c -axis of the hcp crystals which massively activates the $\{10\bar{1}2\}$ extension twinning throughout the material. This causes the c -axis to rotate 86.3° from their original orientation and aligned close to the compression axis [12]. Subsequent deformation can only be accommodated along the c -axis but is difficult because

of the lack of deformation mechanism in the c-axis. Similarly, if tensile loads are applied along the rolling or extrusion direction, compression strains will be imposed along the c-axis which activates very little $\{10\bar{1}1\}$ contraction. As such very little thinning of the sheet or bar will occur and also there will not be any rotation of the hcp crystals. In this case, the grain orientation favours prismatic $\langle a \rangle$ -slip. However, prismatic $\langle a \rangle$ -slip is difficult to operate at ambient temperature because of the CRSS is much higher as compared to basal slip.

2.2 Formability improvement of Mg alloy

Formability of magnesium is strongly dependent on the orientation of basal texture. In the production of magnesium sheet, the rolling procedures will result in the development of a strong crystallographic grain orientation with the basal plane aligned parallel to the rolling direction. In the press forming magnesium sheet at room temperature, a majority of the stress axis tends to lie either perpendicular or parallel to the most favourable basal $\langle a \rangle$ -slip direction. As a result, the critical resolved shear stress will be zero and hence magnesium can only sustain little plastic deformation before fracture [13]. As shown in Figure 2.2, the material fails easily if stress direction is parallel to the basal plane as compared to 45° to the basal plane [14]. This result demonstrates that magnesium ductility can be improved if the stress direction is pointing out of the basal planes instead of parallel to the basal plane. Therefore, if a favourable grain orientation can be developed in the magnesium sheet, it would facilitate both basal $\langle a \rangle$ -slip and tensile twinning to accommodate both in-plane deformation and sheet thinning to achieve improved ductility. Furthermore, the relationship

between Erichsen values and textures ratio are shown in Figure 2.3 clearly indicate that a weaker basal texture would lead to improvement formability [15]. Hence, avoiding the strong basal texture from being developed during the sheet production process is one key strategy to improve the formability of magnesium alloy at room temperature.

Figure 2.2: Effect of texture orientation of tensile flow curve in AZ31 alloy. I: stress parallel to basal planes, II: stress at 45° with basal planes [14]

Figure 2.3: Relationship between Erichsen value and texture in AZ31[15]

Other than texture weakening, fine grain size also helps to improve the mechanical properties of the magnesium sheet and in turn improve the formability. It was reported that when the grain size is fine, twin is more likely to be suppressed and this leads to an improvement in the tensile-compressive anisotropy and also improvement in ductility [14,

16]. Studies have also shown that fine grain promotes non-basal dislocation activities and cross slip from basal to non-basal planes which greatly enhanced the ductility of the magnesium alloy [17]. Koike et al [17] observed in a higher percentage of non-basal a dislocation of around 40% of the total dislocation density that can be found even in the grain interior for fine-grained (7 μm) Mg alloy. This was in contrast to the coarse-grained (50 μm) alloy whereby the non-basal a dislocation was found near the grain boundaries while basal a-slip is dominant in the grain interior.

In recent year, many strategies for formability enhancement have been revolving around techniques to weaken or randomize the texture and to control the grain size of magnesium sheets. The research in thermomechanical processing by Severe Plastic Deformation has shown to be very promising for grain refinement in magnesium alloys with enhancement of both ductility and strength properties. More recently, there also has been a lot of research into the effect of rare earth alloying in magnesium and its effectiveness on grain size control and unusual texture change have been reported. While alloying with less expensive elements such as calcium and strontium remains as an attractive and cost-effective means to control grain size and texture. The detailed review of these various techniques will be presented in the following sections.

2.3 Formability improvement by alloying

2.3.1 Alloying using Rare Earth

In recent years, a lot of attention has been focused on the favourable effect of alloying using rare earth (RE) alloys for grain size refinement and for formability improvement by

modification the basal texture to have favourable orientation for plastic deformation and activation of non-basal slip systems. Alloying with RE elements is commonly done for pure magnesium or dilute magnesium-base alloys such as Mg-Mn, Mg-Zn or Mg-Zn-Zr. K. Hantzsche et al. [18] investigated the effect of each single RE elements – Ce, Nd, Y in pure magnesium after warm rolling. It was reported that only a small amount of element addition (~ 0.05 at.%) would sufficiently lead to near maximum grain size reduction (Figure 2.4). It was found that with increasing RE content, a larger fraction of compression (blue) and double twins (yellow) (Figure 2.5). The weakening of the texture was attributed to these twins which are located close proximity to newly formed grains after annealing.

Figure 2.4: Average grain size of all sheets after annealing vs. element content [18]

Figure 2.5: EBSD orientation maps in as-rolled condition highlighting twin boundaries (red: $\{10-12\}$ -tensile twins; blue: $\{10-11\}$ - and $\{10-13\}$ -compression twins; yellow: $\{10-11\}/\{10-12\}$ - and $\{10-13\}/\{10-12\}$ -double twins): (a) MgNd0.01; (b) MgNd0.04; and corresponding misorientation angles (c) MgNd0.01; (d) MgNd0.04. [18]

T. Al-Samman et al. [19] studied the effect of various RE (Gd, Nd, Ce, La, and Mischmetal) addition to ZEK100 magnesium alloy on texture modification and formability after warm rolling. Generally, alloy with RE addition exhibits remarkably higher elongation (18.84% to 30.34%), markedly lower yield strength and similar ultimate tensile strength as compared to that of the commercial AZ31 sheet. Highly soluble Gd element (0.73%) demonstrate the most pronounced rolling texture modification in the as-rolled material with a maximum basal pole intensity of 4 multiple of random distribution (MRD) tilted at 40° from the ND towards the TD. After annealing, an unusual texture changed was observed with the peak intensity of the basal poles tilted away from the ND by $\sim 42^\circ$ toward the circumference of the pole figure (Figure 2.6). This was due to the presence of high solute content of Gd in the grain boundaries which affects the grain boundary motion during

recrystallization and generating new grain orientation. Gd alloyed sheet also exhibited most isotropic and improved normal (1.025) and planar anisotropy (0.05). The improve formability was attributed to the lowering of the critical resolved shear stresses (CRSS) which affects the stacking fault energy of hard deformation mechanism which promotes a higher activity of prismatic $\langle a \rangle$ -slip and pyramidal $\langle c+a \rangle$ -slip or contraction twinning.

Figure 2.6: Effect of RE elements on texture evolution during warm rolling (a), annealing at 400°C for 1h (b), and tension to failure at RT (c) [19]

The effect of rare earth alloying in AZ31 alloy has been far less impressive. Pan, et al. [20], investigated the effect of Yttrium (Y) addition from wt% of 0.5 to 2.9% on as-extruded AZ31 microstructures and mechanical properties. The increased in ultimate tensile strength was mild while yield strength increased was found to be highest at 209 MPa at 0.5wt% of Y (Figure 2.7). However, the elongation decreased with Y content in the alloy due to the

formation of the block formation of blocky Al₂-Y and Al₃Y₅Mn₇ observed in the microstructures.

Figure 2.7 Relationship between mechanical properties and Y content [20]

2.3.2 Alloying using Lithium

Lithium addition to magnesium reduces the c/a ratio and enhances dislocation glides on the prismatic planes which lead to improvement in room temperature formability [21]. Increase activity of the prismatic planes can lead to an increased in the spread of basal poles in the transverse direction [22]. It was also reported that in an Mg-Li alloy that lithium addition eases the glide of $\langle c + a \rangle$ dislocations on $\{11\bar{2}2\}$ pyramidal planes and resulted in rotation of the basal poles [23]. In a recent study by R. Li et al. [24], the effect of Li addition on the mechanical behaviour and texture of as-extruded AZ31 magnesium alloy was examined. It was found that with 5% Li content, the alloy exhibited lowest planar anisotropy, improved tensile elongation (Table 2.1) and increased in rotation of the basal poles in the TD (Figure 2.8). The rotation of basal poles was attributed to the combined

effect of finer grain size and decreased in c/a ratio.

Table 2.1: Tensile properties of the as-extruded alloys with different tensile directions [24]

Alloy	UTS (MPa)			YS (MPa)			E (%)			n value		
	ED	45°	TD	ED	45°	TD	ED	45°	TD	ED	45°	TD
Li0	250	228	227	177	91	70	15	23	16	0.203	0.411	0.486
Li1	246	227	243	168	116	109	14	26	21	0.215	0.342	0.369
Li3	232	213	233	157	101	91	18	30	27	0.209	0.380	0.433
Li5	229	210	242	161	112	113	18	31	25	0.187	0.340	0.377

Figure 2.8: (0002) pole figures of the as-extruded alloys (1) Li0 alloy, (b) Li1 alloy, (c) Li3 alloy, and (d) Li5 alloy [24]

2.3.3 Alloying using Calcium

Calcium (Ca) is an attractive element for alloying because of its low cost and low density and is widely known to be effective for improving the ignition and oxidation resistance of Mg melt [25]. Ca also improves high-temperature strength and creep resistance of AZ31 alloy [26], and helps refine the grain size in magnesium casting due to the formation of thermally stable second phase such as $(\text{Mg,Al})_2\text{Ca}$, Mg_2Ca or Al_2Ca [27]. However, high content ($>1\%$ wt.) of Ca would reduce the corrosion resistance and generally reduce the ductility at a lower temperature of AZ31 [28, 29].

Kim et al. [30] examined the mechanical properties of AZ31 alloy with Ca addition

(AZ31+0.7%Ca and AZ31+2.0%Ca) after casting and hot extrusion. It was reported that Ca addition clearly resulted in more homogeneous and finer grain size as compared to the AZ31 based alloy. At low temperature (150°C) and high strain rate (10^{-1}s^{-1}), AZ31+2.0Ca showed poor ductility while at high temperature (400°C) and low strain rate (10^{-3}s^{-1}) showed a remarkable increase in tensile elongation ($\sim 550\%$) (Figure 2.9). The improvement of elongation was attributed to change from creep deformation to grain boundary sliding (GBS) deformation due to the large volume fraction of fine $(\text{Mg,Al})_2\text{Ca}$ particles that suppress grain growth during high temperature deformation.

Figure 2.9: Tensile flow stress versus strain curves (a,b) 150°C , and (c,d) 400°C parallel to the extrusion axis [30]

2.3.4 Alloying using Strontium (Sr)

Sadeghi et al. [31] examined the texture evolution after hot extrusion (250°C to 450°C) at various composition of Sr (0.05, 0.4, and 0.8wt.%) in AZ31 alloy (Figure 2.10). It was found that the basal texture was weakened at high level of Sr (0.8%wt.) and high

deformation temperature (350°C) as a result of particle simulated nucleation (PSN) from the higher amount of Al-Sr precipitates that acted as nucleation sites for formation of new grains with a change in orientation from the basal texture. However, at lower extrusion temperature (250°C), any amount of Sr addition would result in a strengthening of the basal textures due to bulging at grain boundaries and twinning which acted as nucleation sites for dynamic recrystallization mechanism.

Figure 2.10: Inverse pole figures at extrusion direction of at different temperature and level of Sr [31]

2.3.5 Alloying with a combination of Calcium, Strontium and other Rare Earths

The combined effect of calcium addition with other elements such as Strontium (Sr) and Rare Earth elements such as Cerium (Ce) and Yttrium (Y) have been studied in recent years. Shang et al [32] investigated the hot formability of a commercial AZ31 alloy (hot extruded) microalloyed with Ca, Sr, and Ce (AZ31+0.2%Ca+0.2%Sr+0.2%Ce) which were cast and hot rolled at 400°C. It was reported that the tensile elongation significantly

increased from 347% (based alloy) to 552% at 450°C and 0.0003 s⁻¹ strain rate. Microalloying was found to affect the shape of the flow curve at high temperature. Microalloying increased the pre-UTS region at low Z (Zener-Hollomon parameter) and increased the post-UTS region at high Z when compared to base AZ31. It was suggested the deformation mode change from dislocation creep at high Z to grain boundary sliding (GBS) at low Z. At the low Z parameter (450°C and 0.0003s⁻¹), the m-value increased from 0.5 to 0.69 while n-value decreased from 2 to 1.5. The presence of thermally stable secondary phase particles can resist grain coarsening, promote grain boundary sliding, retard strain localization or necking and postpone cavitation to higher strain values.

Laser et al. [33] studied the influences of Ca and Ce mischmetal on the microstructure and mechanical properties of AZ31 after hot extrusion. It was found that Ca containing alloy have smaller mean grain size than conventional AZ31 alloy, whereas Alloy with Ce mischmetal did not show a systematic difference in grain size. Alloy with AZ31 +0.4% Ce mischmetal + 0.8% Ca alloy exhibited the smallest mean grain size. Alloying containing Ca showed a decrease in the ratio of yield stress in tension to yield stress in compression only at the highest extrusion temperature of 350°C. Alloy with AZ31 +0.4% Ce mischmetal + 0.8% Ca alloy exhibited largest decreased from 1.9 to 1.6 at 350°C. The results suggest that Ce mischmetal alone had little impact on the properties and microstructure as compared to Ca containing alloy while the best result was obtained in Ca and Ce mischmetal containing alloy.

2.4 Formability improvement by thermomechanical processing

2.4.1 Formability improvement of magnesium alloy by severe plastic deformation

Yang and Ghosh [34] investigated the effect of using a process of alternate biaxial reverse corrugation (ABRC), a derivative method similar to groove pressing, on the room temperature properties of AZ31B alloy. It was shown that a homogeneous average grain size of 1.4 μm could be achieved at a cumulative strain of 5.0. The as-processed tensile yield strength increased from 160 to 280 MPa and tensile elongation increased from 13.0% to 22.6%. The difference in tensile-compressive yield strength was also decreased due to the grain refinement (Figure 2.11). The improvement in the tensile-compressive anisotropy was attributed to the reduction of twinning activities in the in-plane compression of the fine grain alloy. However, the normal anisotropy of the as-processed alloy increased to 6.0 from 3.8. This high anisotropy is generally detrimental to press formability. This remarkably high anisotropy was attributed to the stronger basal texture and high amount of non-basal $\langle a \rangle$ slip. The stronger basal texture was due to the thickness reduction during the straightening compression passes. Huo, et al. [35] performed a similar test using a sin-wave die on AZ31 alloy but with a 45° rotation between each passes and only flattening after the last pass. After 4-passes of bending at 400°C, the average grain size was reduced from 40 μm to 8 μm . Texture randomization was observed after 4-bending passes (Figure 2.12) and the room temperature fracture elongation was improved from ~12% to ~25%. The Erichsen value (IE) was increased from 1.3 to 2.6 showing an improved formability of the as-processed alloy. The normal and planar anisotropy of the sheet as well as the tensile-compressive anisotropy was not reported.

Figure 2.11: Stress–strain curves in tension and compression for (a) as-received alloy and (b) as-processed alloy. (c) Stress vs. strain relationship for normal-to plane compression of the as-received and the as-processed materials [36]

Figure 2.12: {0001} pole figures of AZ31B Mg alloy sheet during cross-wavy bending at 673 K, corresponding to (a) 0 pass, (b) 1 pass, (c) 2 passes, (d) 3 passes and (e) 4 passes [35]

Miura, et al. [37] studied multidirectional forging (MDF) of AZ31B Mg alloy with a

decreasing temperature from 350 to 150°C. Using this approach a final average grain size of 0.36 μm is developed at $\Sigma\epsilon = 4.8$ with a final basal texture was approximately 90° to the final compression axis. Tension test was conducted using different orientation (0, 45, 90°) with respect to the final compression axis at 150°C. It was found that the anisotropy in yield strength in the different orientation was lower at a low strain rate of $5 \times 10^{-5} \text{ s}^{-1}$ as compared to higher strain rate $5 \times 10^{-3} \text{ s}^{-1}$ (Figure 2.13).

Figure 2.13: Effect of MDF on anisotropy at 423K at different strain rates [37]

In most of these SPD studies, the starting materials were mainly wrought Mg alloy and there are limited studies that examine the effect on cast material. There are also very few studies that investigate the combined effect of alloying and SPD on formability improvement. In one of such studies, Janeček, et al. [38] investigated the effect of equal-channel angular pressing (ECAP) on an initial squeezed-cast AZ31 alloy. It was reported that the room temperature compressive yield strength increased by 2.2 times. However, at a temperature above 200°C the compressive yield strength became worse than the initial squeezed cast material. The effect on anisotropy and texture was not been reported.

Masoudpanah and Mahmudi [39] investigated the effect of alloying using lanthanum-rich mischmetal (RE) and calcium addition followed by ECAP on AZ31 alloy. RE and Ca addition caused a marginal reduction in grain size and a decreased in tensile elongation (Figure 2.14).

Figure 2.14: Engineering stress-strain curves after 4 ECAP passes for AZ31, AZ31-0.6%RE, AZ31-0.6%Ca and AZ31-0.3%RE-0.3%Ca alloys, and as-extruded AZ31 alloy [38]

2.4.2 Formability improvement by other thermomechanical processes

Huang et al. [40] showed an improvement in formability of AZ31B alloy processed by differential speed rolling (DSR) with a roll speed ratio of 1.167. At room temperature, the Erichsen values significantly increased from 2.6 to 4.0 (53.8%) as compared to normal rolled sheet. At 423 K, the value increased from 4.1 to 7.6 (85.4%). The deep drawing temperature limited for a draw ratio of 1.5 was reduced from 443 K to 423 K. DSR processed sheet also exhibited a slight decrease in 0.2% proof stress (12.6%) in the RD. The normal anisotropy decreased from 3.15 to 2.52 (20%) and planar anisotropy decreased from 0.11 to 0.09 (18%). Average n-values increased slightly from 0.257 to 0.280 (9%). It was shown

that the average grain size was reduced from 54 μm to 16 μm and the basal texture exhibits an inclination of about 7° from the normal towards the rolling direction. The increase in formability at low temperatures was attributed to the texture modification. Watanabe, et al. [41] studied the effect of rolling temperature on room temperature mechanical properties and textures in AZ31 magnesium alloy. It was shown that the decreased in rolling temperature from 573 K to 473 K had little impact on the yield strength while the elongation-to-failure increased from 13.6 to 18.5%. The DSR processed material exhibited approximately 1.5 times larger ductility as compared to symmetrically rolled material.

2.5 Severe Plastic Deformation

Severe plastic deformation (SPD) process is widely known to be an effective method for producing ultrafine grain structures (UFG) in a wide range of bulk polycrystalline materials [42-44]. Depending of the type of materials, SPD processes, and processing conditions, the achievable grain size can be in the order of 1 μm down to about <100 nm [42, 45]. This level of grain size reduction has significant implication as grain refinement has been long known to improve the strength and toughness of the material. For many materials, the yield strength, σ_Y , varies with grain size, d , according to the Hall-Petch equation [13]:

$$\sigma_Y = \sigma_0 + A d^{-1/2} \quad (2.1)$$

Where σ_0 and A are constants for a particular material. From this equation, a decrease in grain size will result in an increase in the yield strength of the material. This is because fine grain materials have larger total grain boundary areas which could impede dislocation motions and increases the strength of the material.

Generally, SPD process can be defined as any metal processing technique that could impart extreme hydrostatic pressure and shear strain in the bulk material without intentionally changing the initial geometry of the material [42]. The method generally needs to be repeated in order to accumulate high amount of strain (typically $\sim 5-8$) in the material in order to achieve the ultrafine grain size. The most widely accepted mechanism of grain refinement can be explained by dislocation density based model which described the formation of fine grains from the formation of a dislocation cell wall which gradually transforms into high-angle grain boundaries [42]. While more recently, the model of grain fragmentation due to induced lattice curvature resulting in the formation of geometrically necessary grain boundaries (GND) and subsequent formation of subgrains have been introduced [46]. The detail of the mechanism will be reviewed in greater detail in the later section. The major advantage of SPD process is in its unique ability to produce nearly uniformly distributed equiaxed ultrafine grain structures in bulk material without an intentional change in the geometry of the processed material. A typical characteristic of the microstructure produced by SPD process consists of high-angle grain boundaries which is an indication non-equilibrium boundaries due to high internal stresses induced by the intensive deformation process [45, 47]. The resulting consequence is often an increase in strength and decrease in ductility. Annealing is generally required to recover the ductility but often resulted in increased grain size and some decrease in strength properties [42, 43].

2.5.1 Overview of Severe Plastic Deformation

The principals underlying severe plastic deformation techniques (SPD) first came from

Bridgman in the 1930s on his work concerning the effects on materials from the combination of high hydrostatic pressures with shear deformation [48]. Another major development came from Segal in the 1970s which led to the development of equal-channel angular pressing (ECAP) which became one of the most popular principal techniques [49, 50] till date. Since then, the research in SPD has been growly steading with a great number of research activities coming from the group of work of R.Z. Valiev et al. (ECAP), G. Langdon et al. (high-pressure torsion, HPT), T. Sakai (Multi-directional forging, MDF) [47], and Y. Saito (accumulative roll bonding, ARB) which investigate the mechanical properties and characteristic of grain refinement on a wide variety of material. Over the years, many techniques have been developed with significant attention focus on continuous and hybrid processing in order improve processing efficiency. Examples of such processes include, but are not limited to, ECAP-conform, Continuous Repetitive corrugating and straightening (RCS). Majority of these techniques are more suitable for processing of bulk material with the exception of ARB. However, ARB process is quite laborious as it involves repetitive cutting, cleaning and stacking of rolled sheets. Another more relatively recent technique known as constraint groove pressing (CGP) developed by Shin et al. (2002) [51] is particularly attractive for processing of thin sheet material. This technique is capable of delivering intensive shear strain in thin sheet using relatively simple tooling design with little change in initial sheet thickness. With suitable processing routes, this process is capable of producing uniformly distributed fine-grain structures with minimal material wastage as compare to ECAP. The method can also be scaled up relatively easily because of the low tooling pressure. The processing principal will be explained in greater detail in

the next section. A comparison of the different SPD processes is shown in Table 2.2.

Table 2.2: Comparison of different SPD processes

	ECAP	HPT	ARB	MDF	GP/RCS
Shear strain	high	high	high	high	high
Hydrostatic pressure	very high	very high	Average to high	Average to high	Average
Grain Size reduction	excellent	excellent	good	good	good
Uniformity	excellent	average	average	good	good
Geometry	Bulk	thin disc (lab-scale)	plate	bulk	thin sheet/Plate
Productivity (cycle time)	good ^	good	poor	average	average - good
Productivity (Yield)	average	High	High	High	High
Ease of scale up	average	poor	good	average	good

Legend:

ECAP – Equal channel angular pressing, HPT – High pressure torsion, ARB – Accumulative roll bonding, MDF- Multi-directional forging, GP/RCS – Groove pressing/Repetitive corrugation and straightening

^ - Continuous ECAP is of higher productivity but limited to material, shape and size

2.5.2 History of constrained groove pressing (CGP)

The first ideal of inducing severe plastic deformation between patterned die features was probably first introduced in what is known as repetitive corrugation and straightening (RCS) by Huang et al. [52] in 2001 which demonstrated the effectiveness of the process for producing nanostructure grains in high purity Cu plates by using a process of repetitive pressing between corrugated and flat platen die set. A continuous approach was also

discussed whereby the process can be performed by passing the plate between a set of corrugated sine wave roller and flat rollers arrangement. A variant of the concept was introduced in what is known as constraint groove pressing process by Shin et al. [51] in 2004. The key difference from that of RCS is that the severe straining in the material was introduced by pressing between a more defined patterned groove features and the material is semi-constrained along the longitudinal direction of the die. Uniform straining of the material is achieved by rotating the workpiece by 180° during the pressing procedure. Huang et al. [53] in 2004, again introduced a variant of the RCS technique which had a very similar groove features as that of GP. The main difference in RCS is that the material was not constrained and uniform straining was achieved by rotating the die instead of the workpiece. Huang et al. [53] discussed the main issue of this design concerning the low cycle fatigue failure and insufficient grain refinement if the die was only rotated by 180° and subsequently proposed a 90° rotation instead to overcome the issues. This deformation route was further discussed in the simulation work by Alkorta et al. [54] whereby it was concluded that the optimal ratio of $r = 0.25$ to 0 (r is sample thickness to groove period) and a groove angle of 30 to 45° was recommended. A variant of the process was further introduced by Yang and Ghosh [34] in 2006 whereby the AZ31 Mg alloy plate was biaxially deformed between sine wave dies and its thickness gradually reduced during the intermediate flattening steps. Most recently, Huo et al. [35] demonstrated the process also on AZ31 Mg alloy using a similar sine wave die design but with a rather large peak to peak spacing in relation to the sheet thickness and a 45° rotation of the sheet in between pressing.

2.5.3 Principal of constrained groove pressing process

The conventional constrained groove pressing (CGP) using a semi-constrained die was designed by Shin, et al. [51] is illustrated schematically in Figure 2.15

Figure 2.15: Schematic diagram of Constraint groove pressing process

In this process, a well lubricated plate is pressed between the upper and lower groove dies (a-b) and forced to deform into the shape of the dies. The final closing gap between the dies should be of the same distance to the plate thickness and the inclined surface should be at an angle of 45° . The material in the inclined region of the dies will ideally undergo a simple shear deformation while the flat region of the material remains un-deformed (1st pass). A flattening step (2nd pass) is subsequently carried out (c) to return the deformed plate back to the original geometry using two flat platen dies. In order to induce uniform straining throughout the material, the plate has to be rotated by 180° about its normal direction (ND) so that the un-deformed region of the material can undergo the same shear deformation using the same groove dies (d-e) (3rd pass). A final flattening pressing (f) (4th pass) is then carried

out to return the deformed material to its original geometry. Therefore, a complete cycle would consist of a total of 4 presses or passes in order to produce a uniform shear straining in the material. It is often necessary often to repeat the above steps to achieve a higher number of pressing cycles in order to accumulate high enough strain for grain refinement.

2.5.4 Estimation of strain in constrained groove pressing

The effective strain can be readily determined from the flow law governed by Mises yield criterion. This section will briefly cover the theoretical derivation of the effective strain for estimating the cumulative strain from the simple shear deformation during the groove pressing process [55].

According to R.Von Mises, the second invariant of stress deviator tensor is given by

$$J_2 = \frac{1}{2} S_{ij} S_{ij} = K_M^2 \quad (2.2)$$

Where S is the deviator tensor for stress which signifies that yielding is independent of hydrostatic pressure and is given by

$$S_{ij} = \tau_{ij} - \frac{1}{3} \tau_{kk} \delta_{ij} \quad (2.3)$$

K_M is the yield stress in pure shear k if K_M is determined from a simple shear test. The yield function accordingly to above condition is given by

$$f(J_2) = J_2 - K_M^2 \quad (2.4)$$

The Mises flow law is determined by setting $f=0$ which can be shown to equal to the Prandtl-Reuss equation

$$\varepsilon_{ij}^p = \lambda S_{ij} \quad (2.5)$$

Taking the inner product of above equation above gives

$$\dot{\epsilon}_{ij}^p \dot{\epsilon}_{ij}^p = \dot{\Lambda}^2 S_i S_i \quad (2.6)$$

From analogy with J2

$$K_2 = \frac{1}{2} e_{ij} e_{ij} \quad (2.7)$$

From the formulation of the universal plastic stress-strain curve for valid for isotropic hardening, the effective stress and effective plastic strain rate are as follows

$$\tilde{\tau} = \sqrt{3J_2} = \frac{\sqrt{2}}{2} [(\tau_{11} - \tau_{22})^2 + (\tau_{22} - \tau_{33})^2 + (\tau_{33} - \tau_{11})^2 + 6(\tau_{12}^2 + \tau_{23}^2 + \tau_{31}^2)]^{1/2} \quad (2.8)$$

$$\tilde{\epsilon} = \frac{2}{3} \sqrt{3K_2} = \frac{\sqrt{2}}{3} \{(\dot{\epsilon}_{11} - \dot{\epsilon}_{22})^2 + (\dot{\epsilon}_{22} - \dot{\epsilon}_{33})^2 + (\dot{\epsilon}_{33} - \dot{\epsilon}_{11})^2 + 6[(\dot{\epsilon}_{12})^2 + (\dot{\epsilon}_{23})^2 + (\dot{\epsilon}_{31})^2]\}^{1/2} \quad (2.9)$$

For incompressible deformation and by analogy with above equation, the effective plastic strain can be given by

$$\tilde{\epsilon} = \frac{\sqrt{2}}{3} \{(\epsilon_{11} - \epsilon_{22})^2 + (\epsilon_{22} - \epsilon_{33})^2 + (\epsilon_{33} - \epsilon_{11})^2 + 6[(\epsilon_{12})^2 + (\epsilon_{23})^2 + (\epsilon_{31})^2]\}^{1/2} \quad (2.10)$$

In the first groove pressing pass, the inclined region of the material ideally undergoes a simple shear deformation as illustrated in Figure 2.16. The shear strain $\gamma_{12} = 2\epsilon_{12}$ is given by

$$\gamma_{12} = \tan \theta \approx \frac{dy}{x} \approx 1.0 \quad (2.11)$$

For simple shear deformation and plane strain condition, $\epsilon_{11} = \epsilon_{22} = \epsilon_{33} = \epsilon_{23} = \epsilon_{31} =$

0. Therefore, from the equation above, the effective strain in the 1st pass is equal to

$$\tilde{\epsilon} = \frac{\sqrt{2}}{3} \left\{ 6 \left[\left(\frac{1}{2} \right)^2 \right] \right\}^{1/2} \approx 0.58 \quad (2.12)$$

The flattening step will undergo the same shearing deformation in the reverse direction and the total cumulative strain equals to 1.16.

Figure 2.16: Shear strain induced in constrained groove pressing process

2.5.5 Review of the mechanism of grain refinement in SPD

The production of ultrafine grains in severe plastic deformation (SPD) process which can occur at relatively low temperatures is different from that of the developed thermomechanical processing method of grain refinement by plastic cold working followed by annealing or hot working. In SPD process, grain refinement is considered to occur in a single step through the process of continuous dynamic recrystallization (cDRX) [47]. While production of fine grains by plastic cold working follows by annealing or hot working is considered to be a two-step process with a distinct nucleation and growth stages occur through the process of conventional discontinuous dynamic recrystallization (dDRX). In SPD process, at low strains, fine grains are found to be heterogeneously distributed throughout the grain structure while at higher cumulative strains, ultrafine grains will eventually develop uniformly over the entire grain structure. The development of nanocrystalline structures during SPD is accompanied by a reduction in dislocation density at large strains. The presence of large internal distortion in the submicrocrystalline structures

implies a non-equilibrium state of the strain-induced boundaries [47].

Formation of new grains by grain subdivision during deformation is fundamental to the understanding of SPD. At the initial stage of deformation and at low strains, dislocation densities reorganized into cellular substructures with dense dislocation walls of large misorientations. At medium straining, various deformation bands appear in the grains which are of even larger misorientations. This process eventually leads to the subdivision of the original grains into ultrafine grains with high misorientations between the neighbouring grains. These dislocations walls and deformation bands are essentially a type dislocation boundary called geometrically necessary boundaries (GNBs) which are high angle boundaries with misorientation greater than $15\text{-}20^\circ$ [56]. This is in contrast to cell boundaries classified as incidental dislocation boundaries (IDB) which have low misorientation angles.

This section will briefly review the established grain refinement mechanism of dislocation density model, and the recent proposed mechanisms by Toth et al. [57] on grain fragmentation through lattice curvature and Sakai et al. [47] strain induced formation of ultrafine grains through development of microshear bands (MSBs) or kinks bands (in hcp materials).

2.5.5.1 Dislocation density model

There are a few grain refinement models in severe plastic deformation as reviewed and proposed by various authors [42, 45, 47, 57, 58]. The most popular grain refinement model that described the grain refinement mechanism is the dislocation density based model which is reviewed in details by Estrin and Vinogradov [42]. In this model, the grain refinement

occurs through the formation of dislocation cell and dislocation boundaries in the original grains during plastic straining. The misorientation across the cell boundaries increases with the accumulation of plastic deformation until a large portion of the cell boundaries transform into high angle grain boundaries and resulting in the formation of new fine grains. The brief history of the dislocation density model date back to the work of Kocks and Mecking [59] which effectively account for stages II and III of strain hardening. Later work by Mughrabi [60] which treat the cell walls and cell interiors as a ‘composite’ helps to take into account for stage IV and stage V hardening which dominates at large strains. Estrin et al. [58] and Zehetbauer et al. [61] further extend the concept of Mughrabi’s composite principals and proposed dislocation density models that detail the evolution of dislocation densities in the cell walls and cell interiors as well as their interactions with each other. These models based on the assumption that dislocation density increases with cold working and the dislocation cell size, D_{dc} , decreases with increasing dislocation density according to the following:

$$D_{dc} = \frac{K}{\sqrt{\rho}} \quad (2.13)$$

Where K is proportionality constant. The dislocation will tend to saturate leading to a steady state of the volume fraction of the dislocation cells and cell walls. Dislocation cell size, D_{dc} , can also be related to the applied shear stress, τ , according to [62]:

$$D_{dc} = \frac{K'Gb}{\tau - \tau_0} \cong \frac{K'Gb}{\tau} \quad (2.14)$$

Where K’ is a constant of value close to ten, G is the shear modulus, b is the burger vector and τ_0 is the friction stress. As the applied shear stress increases, D_{dc} and eventually the grain size become smaller. There exist a critical grain size achievable from this dislocation-based model according to [63]:

$$d_c = \left(\frac{D_{GB} b}{\dot{\gamma}} \right)^{1/3} \quad (2.15)$$

Where D_{GB} is grain boundary diffusivity, $\dot{\gamma}$ is shear strain. Below this critical grain size, the accumulation of dislocation is negligible because the diffusivity relaxation is predominant.

2.5.5.2 Grain subdivision through lattice curvature

Recently, Toth et al. [45, 57] proposed the concept of grain fragmentation by lattice curvature. The hypothesis is that the crystal rotation does not occur uniformly within the grains during plastic deformation and that this rotation is slow down near the grain boundary because of the constraint exerted by the neighbouring grains. This resulted in a lattice curvature developing inside the grain which eventually leads to the grouping of the initially homogenous distributed GNBs when the lattice curvature reaches a critical value. Based on this model, new grains initially develop predominantly in the vicinity of the grain boundaries because of the higher constraints.

2.5.5.3 Strain-induced formation of UFGs

More recently, Sakai et al. [47] suggested a new model called strain-induced formation of UFGs that complements existing theory of grain subdivision. The author explained that existing subgrain/dislocation density-based models is unable to account for all the experimental results as observed in SPD. The existing model is unable to explain why fine grains initially develop heterogeneously and later homogeneously while some of the subgrains that are formed in early stages failed to transform into ultrafine grains (UFGs)

even at large strains. The grains formed at low temperatures are also found to be lower than the subgrains that first appear in the microstructure. In this new model, the change in misorientations with cumulative strain is divided into three stages. In the first stage, the misorientations increase rapidly followed by a small plateau at about 5° . The high angle boundaries (HABs) first appear near to the existing grain boundaries because of the constraint imposed by the neighboring grains similar to that of the lattice curvature model presented by Toth et al. In the second stage, the misorientations increases rapidly again beyond a certain critical strain, ϵ_c , with the development of MSBs or kink bands (in hcp materials) and HABs are found in the MSBs intersections where intersecting boundaries form microcrystallites. These HABs eventually transform into grain boundaries. Finally, in the third stage, the misorientations reach a saturation level and more MSBs are formed and UFGs spread homogeneously throughout the microstructures. In the third stage, the kinetic of UFGs is accelerated with increasing deformation temperatures. The critical strain ϵ_c and kinetic of UFGs formation depend on the material. For the case of AZ31, this critical strain values is around 0.1 and kink bands instead of MSBs appear in the grains.

2.5.6 Dynamic recrystallization mechanism of Mg

As discussed in the previous section on the various mechanism of grain refinement in SPD, it is clear that the grain refinement is considered to occur in a single step and is essentially a process of continuous dynamic recrystallization (cDRX). The occurrence of conventional discontinuous dynamic recrystallization (dDRX) or cDRX depends on the rate of dynamic recovery (DRV) and the migration velocity (mobility) of the grain boundaries.

dDRX generally occurs in hot working of materials above $\sim 0.5T_m$ of low to medium stacking fault energy (SFE) which exhibits low rates of DRV. For material with high SFE, DRV occurs easily but the formation of ultrafine grains requires an application of very high strains. In the case of SPD, however, cDRX process is observed to occur in materials of both low and high SFE, and at both warm and cold temperatures [47]. In addition, cDRX in high SFE occur at any values of T/T_m from zero to one.

Magnesium alloy is of low SFE but yet cDRX is the main DRX mechanism observed. Galiyev et al. [64] offer a possible explanation based on his compression studies of Mg-Zn-Zr alloys at a temperature of 523K (250°C) up to a total strain of 0.25. It was observed that small equiaxed grains formed in the vicinity of the pre-existing high angle grain boundaries and also twin boundaries in a necklace structure in coarse grains. This is because of the presence of cross-slip of a dislocation on non-basal planes can be activated near the high angle grain boundaries because of the high stress concentration.

Evidence of cDRX was also observed in the work of Yang et al and Xing et al. [65, 66] in the study of hot compression and multi-directional forging of AZ31 at a temperature of 673K ($0.73T_m$). Kinks bands were observed to develop in the grain interiors even at low strains (0.06~0.15) [65]. These kinks bands are of high misorientation and this misorientation increase with deformation which eventually forms the boundaries of the new grains at higher strains.

2.5.7 SPD processing of AZ31 alloy

The degree of grain refinement of AZ31B depends on many factors like deformation

temperature, strain rate, initial grain size, prior material processing, textures, and the type of severe plastic deformation which influence the strain paths. Processing of magnesium alloy is particularly challenging because of its poor workability due to the absence of sufficient operating slip systems at room temperature as discussed in details the introduction chapter. As such, processing of magnesium alloys are normally conducted at above 200°C and higher order slip system can be activated. Processing of magnesium alloy by equal-channel angular pressing (ECAP) using a 90° channel angle is particularly challenging because of the shear localization which can lead to segmentation type of cracking [44]. Premature cracking can be overcome at elevated deformation temperature above 300°C but result in insufficient grain reduction because of grain growth. Strategies to overcome cracking at lower deformation temperature can be overcome by using a larger channel angle (e.g. 110°). While performing an additional extrusion process before ECAP has shown to improve the formability and lead to further reduction of grain size [67]. Alternatively, it has been demonstrated that reduction of deformation temperature is highly effective means to reduce the average grain sizes [34, 66, 68] for hcp materials. The reason is attributed to increase in kink bands [66] and higher twinning which increases the sites for formation of new grains [34].

From the review of the available literature, there is a lack of guideline or explanation for the particular choice of deformation temperatures, and strain rates in each of the SPD process to achieve optimum grain refinement to achieve the smallest achievable grain size. This again will be highlighted in the later section which will review the current research in the understanding of the influence of temperature and strain rate using the Zener-Hollomon

parameter.

2.5.8 Microstructure of AZ31 after SPD

Examples of the microstructures of AZ31 alloy produced by the various SPD processes are illustrated in Figure 2.17. Microstructure from various SPD processed typically show a bi-modal distribution of grains sizes consisting of very fine grains of less than $0.1\ \mu\text{m}$ and coarse grains of between $1\text{--}6\ \mu\text{m}$ [34, 66, 69]. Coarser grains remain even at very high cumulative strain for most materials processed by SPD methods. It was believed that these grains are resistant the formation of micro shear bands and kink bands [47] which prevents the further grain fragmentation. It was observed that the ultrafine grains consist of large distortion with the absence of dislocation which is indicative of the high internal stress and the non-equilibrium state of the strain-induced boundaries produced by the SPD [47] (Figure 2.18).

Figure 2.17: (a) Optical image of the microstructures after ABRC to total strain of 5.0 and its corresponding TEM image [34] (b) Optical image of the microstructures after MDF to total strain of 5.6 and its corresponding TEM image [66] (c) SEM image of the microstructure after ECAP to total strain of 9.2 and corresponding TEM image [69]

Figure 2.18: Large distortion developed in a 304 stainless steel subjected to MDF to a strain of 6.4 determined by convergent beam Kikuchi line techniques [47]

2.5.9 Temperature and strain rate effect represented by the Zener-Hollomon parameter

The combined effect of temperature and strain rate can be expressed using the Zener-Hollomon equation or the Z-parameter given by:

$$Z = \dot{\epsilon} \exp\left(\frac{Q}{RT}\right) \quad (2.16)$$

Where Q is the relative activation energy, $\dot{\epsilon}$ is the strain rate, R is the gas constant. The above relation has been commonly used in the study of magnesium alloys where the

deformation behaviour depends on both temperature and strain rates. The Z-parameters can also be used to correlate the grain size produced from SPD processes [70]. The author approximated linear relation obtained from the plot of $\ln(d)$ against $\ln(Z)$ in the stir-friction processing of AZ31 specimen and found a similar trend to that of specimen processed by extrusion or tension (Figure 2.19).

Figure 2.19: Relationship between grain size and Zener-Hollomon parameter in specimen processed by FSP and extrusion or tension [70]

Li, et al. [71] conducted a study on the effect of Z parameter range from 22 to 66 (temperature range from 77 to 292K and strain rates from 10^{-3} to 10^3 s^{-1}) in the deformation of copper by uniaxial compression and found that high Z (>30) resulted in excellent grain size refinement and strength enhancement. At high Z, deformation twinning becomes the dominant mechanism of grain refinement with increasing fragmentation and shear banding of the nano-sized twin bundles. This mechanism may not be generic across all materials. It is also reasonable that higher Z could suppress dynamic recovery and promote grain subdivision.

2.5.10 Annealing and kinetics of grain growth of AZ31 after SPD

In the SPD of many materials, it is a common trend that the spectacular increase in strength occurs at the expense of ductility [42] while the improvement of both strength and ductility is challenging and not common. The room temperature ductility of the SPDed alloy is usually low due to the combination of high flow stress and low strain hardening effect. Annealing heat treatment is usually performed in order to improve the ductility of the alloy by process of recovery, recrystallization followed by grain growth. However, ductility and strength are mutually exclusive. Any improvement in ductility will result in a loss of strength due to the increase in the grain size after annealing. The UFGs have a strong propensity to growth during annealing because of very high stored energy introduced by the severe deformation process. As such, the study of grain growth kinetics during annealing after SPD is very important in order to avoid significant grain growth and to achieve a balance between strength and ductility.

The effect of annealing temperature and time on the kinetics of grain growth is often study using the equation developed by Burke and Turnbull (1952). It was deduced that the kinetics of grain growth is driven by the driving pressure that arises only from the curvature of the grain boundary and is given as [72, 73]:

$$D^n + D_0^n = kt \quad (2.17)$$

Where D is the average grain size after grain growth, D_0 is the average initial grain size, n is the grain growth exponent, t is the annealing time, and k is grain growth constant that can be determined from the Arrhenius equation in the form:

$$k = k_0 \exp\left(-\frac{Q_G}{RT}\right) \quad (2.18)$$

Where k_0 is a constant, Q_G is the activation energy for grain growth and R is the gas constant.

The grain growth rate can be determined by taking derivative of equation X with respect to t and taking natural log and can be written as:

$$\ln\left(\frac{dD}{dt}\right) = \ln\left(\frac{k}{n}\right) - (n-1)\ln(D) \quad (2.19)$$

By plotting of $\ln\left(\frac{dD}{dt}\right)$ against $\ln(D)$, the gradient of the slope is equivalent to $(n-1)$ and hence the grain growth exponent, n , can be determined. Similarly, $\ln(k)$ can be determined from the same plot. By taking natural log on both sides, equation x can be rewritten as:

$$\ln(k) = \ln(k_0) - \frac{Q_G}{RT} \quad (2.20)$$

By plotting of $\ln(k)$ against $1/T$, the activation energy, Q_G can be determined from the gradient of the slope.

Yang et al. [74] examined the isothermal annealing (493-503K) on hot (573K) compressed AZ31 samples to a total strain of 1.2 and found that the grain growth occurred continuously even at the start of the annealing process at the fine-grained regions. This observation is concluded from the observation of the effect of annealing time on the number of fine grains ($<10 \mu\text{m}$) measured per unit area (Figure 2.20a) which is difficult to observe in the measure of average grain size against annealing time (Figure 2.20b).

Figure 2.20: a) Effect of annealing temperature on the relationship between the number of fine grains with less than $10 \mu\text{m}$ in diameter per unit area, N , and annealing time. (b) Effect of annealing temperature on average grain size in the whole area with time [74].

Yang & Ghosh [34] studied the annealing of the UFG ($\sim 1.4 \mu\text{m}$) AZ31 alloy produced by alternate biaxial reverse corrugation (ABRC) process at deformation temperatures from 250 to 170°C to a total strain of 5.0. It was found that significant grain growth occurs after static annealing at 250°C while little growth at 200 °C (Figure 2.21).

Figure 2.21: Microstructure at annealing temperatures [34]

The thermal stability of the microstructures produced by the process of combination of extrusion and equal-channel angular pressing (EX-ECAP) was studied recently by Straska et al. [75]. The UFG ($\sim 0.9 \mu\text{m}$) was found to be very similar and hence thermally stable below 170°C while grains start to grow at temperatures around 190°C and 210°C (Figure 2.22) resulting in a bimodal microstructure.

Figure 2.22: Microstructure of AZ31 EX-ECAP (a) as-processed (b) after 1 h of annealing isothermal at 190°C [75]

Table 2.3 below shows the survey of activation energy determined from experimental

studies of annealed UFG AZ31 produced by various SPD processes. The activation energy is often compared to the activation energy values for grain boundary diffusion (Q_{gb}) in pure Mg (92kJ/mol), for lattice self-diffusion (Q_L) in pure Mg (135 kJ/mol) and for diffusion of Al in Mg-Al solid solution (143 kJ/mol) [76] to determine the likely grain growth mechanism. Presence of $Al_{12}Mg_{17}$ intermetallic phase and strong basal texture are common explanation for why the experimental activation energy for grain growth is higher than Q_{gb} [77]. While, the mechanism for grain growth, whether if it is mainly grain boundary diffusion or lattice self-diffusion, and the softening mechanism was shown to depends on annealing temperature range [75]. Straska et al. found abnormally low activation energy of 33 kJ/mol at the annealing temperature range from 210-400 °C. The authors highlighted two possible explanations from other studies. The first reason is due to be that due to a higher k_0 which lead to an underestimation of the k and Q . While the second reason is caused by the enhanced mobility of the grain boundaries in the non-equilibrium state of the ultra-fine grained materials produce by SPD which resulted in the reduction of the activation energy.

Table 2.3: Typical activation energy for grain growth, Q_g , and grain growth exponent, n

Typical activation energy for grain growth, Q_g , and grain growth exponent, n					
SPD Process	Annealing temperature range	Activation energy for grain growth, Q (kJ/mol)	Grain growth exponent, n	Grain size (μm) after SPD	Typical grain size (μm) after annealing
EX-ECAP [75]	170-500 °C (443 to 773K)	115 (170-210°C) 33 (210-400°C) 164 (400-500°C)	2 (assumed)	0.9	~1.0 to 2.0 (190-250°C, 1 h)
Hot Compression [74]	493 to 513K (220 to 240 °C)	125±10	-	5.0	~ 10.0 (493-513K, 27.8 h)
ACB (Accumulated Compression Bonding) [77]	623 to 723K (350 to 450 °C)	105.0	5	<1.0	10.0 (723K for 4 h)
ABRC [34]	200°C, 250°C	-	14.3 (200°C) 5.88 (250°C)	1.4	2-3 (200°C)

From the above review of UFG AZ31 alloy produced by various severe plastic deformation processes, it was shown that annealing resulted in an improvement of ductility better than that of the hot-rolled condition. However, this recovery of ductility occurred at the expense mechanical strength due to grain growth. Therefore, an optimized thermomechanical treatment should be examined to limit grain growth so as to maintain the strength enhancement achieved through SPD [45].

There are also limited studies on the stability of the fine grains in AZ31 alloy produced by constrained groove pressing processing. This deserves more investigation because

constrained groove pressing process is expected to produce different textures as compared to other SPD processes and texture is one of the factors that influence the grain growth [72]. The thermal stability of the grains at lower as well as elevated temperatures is also an important study and these influence the potential for superplastic properties.

2.6 Squeeze casting process (liquid metal forging)

Squeeze casting process, also known as liquid metal forging, is a near net-shaped casting technique that combines casting and forging into a single process whereby the melt is solidified under very high pressure within a closed die. There are two methods of squeeze casting process namely direct squeeze casting and indirect squeeze casting. Direct squeeze casting consists of pouring the melt directly into a preheated lower die while pressure is applied through the upper die/punch that comes down and shuts the die until the melt solidifies. Direct casting can be further classified into two types: with and without molten metal displacement depending on die design and punch movement as illustrated in Figure 2.23. Indirect squeeze casting is similar to conventional high pressure die casting whereby the melt is first transferred to a heated shot sleeve and a plunger is used to push the melt into the die cavity through a relatively large gating with an application of pressure. In both methods, the solidified parts are removed by ejector. One of the key advantages of squeeze casting process as compared to conventional die casting process is that it is generally more tolerable to low melt fluidity as die filling is assisted by the application of high pressure. Moreover, the absence of turbulence flow due to the relatively low melt velocity and high pressure eliminates porosity and result in parts having fine-grained microstructures with

superior mechanical properties.

Figure 2.23: Direct squeeze casting: (a) without melt displacement (b) with melt displacement

Figure 2.24: Indirect squeeze casting process

2.6.1 Process variables

Process parameter that affects the soundness of the part includes the level of applied pressure, holding time during which the pressure is being applied or the “dead time”, die temperature, and pouring temperature. For casting of magnesium and aluminium, the die temperature is usually held between 200°C to 300°C and the applied pressure varies from 50 to 150 MPa [78]. Other factors that influence the quality of the part include melt cleanliness and the design of the die which affects the melt movements.

2.6.2 Effect of pressure on solidification behaviour

For phase transformation, the relative stability of the system is determined by its Gibbs free energy (G):

$$G = H - TS \quad (2.21)$$

where H is the enthalpy, T is the absolute temperature and S the entropy of the system. The effect of temperature and pressure variation on the Gibbs free energy can be derived from classical thermodynamics equations [79] and is given by the equation:

$$\Delta G = -S\Delta T + V\Delta P \quad (2.22)$$

where V is the volume, ΔT is the change in temperature, and ΔP is the change in pressure.

Considering two phases α and β in equilibrium, from equation 2.6, 1 mole of both phases gives

$$\Delta G^\alpha = V_m^\alpha \Delta P - S^\alpha \Delta T \quad (2.23)$$

$$\Delta G^\beta = V_m^\beta \Delta P - S^\beta \Delta T \quad (2.24)$$

Since at equilibrium, $G_l = G_s$, therefore $dG_l = dG_s$ and rearranging equation 2.7 gives

$$\left(\frac{\Delta P}{\Delta T}\right)_{eq} = \frac{S^\alpha - S^\beta}{V_m^\alpha - V_m^\beta} = \frac{\Delta S}{\Delta V} \quad (2.25)$$

The above equation can be further simplified substituting ΔS using equation 2.5 to gives:

$$\left(\frac{\Delta P}{\Delta T}\right)_{eq} = \frac{\Delta H}{T_{eq}\Delta V} \quad (2.26)$$

The above equation is known as the Clausius-Clapeyron equation which describes the effect of pressure change on the phase diagram. The effect of pressure during solidification in squeeze casting can be deduced by considering the Clausius-Clapeyron equation rewritten in the following form [78]:

$$\left(\frac{\Delta T_f}{\Delta P}\right) = \frac{T_f(V_l - V_s)}{\Delta H_f} \quad (2.27)$$

where T_f is the equilibrium freezing temperatures, V_l and V_s are the specific volumes of the liquid and solid respectively, and ΔH_f is the latent heat of fusion. Substituting the appropriate thermodynamic equation for volume, the effect of pressure on freezing point may roughly be estimated as follows:

$$P = P_o \exp\left(\frac{-\Delta H_f}{RT_f}\right) \quad (2.28)$$

where P_o , ΔH_f and R are constants. Therefore, T_f should increase with increasing pressure.

The microstructure of squeeze cast component is strongly affected by the nucleation and growth of grains during the solidification under high pressure. Therefore, the understanding of nucleation process in squeeze casting process is crucial. Han et al. [80], proposed an expression for the heterogeneous nucleation during pressurized solidification of squeeze casting process which takes into account of the effect of pressure on nucleation activation energy ΔG_d and diffusion activation energy ΔG_{do} :

$$vI_{he} = 10^{42} K_{he} \times \exp\left[-\frac{bf(\theta)\frac{\sigma^3}{(\Delta G_v + \varepsilon P)^2} + \Delta G_{do} + \Delta V P}{K_B T}\right] \quad (2.29)$$

where $\dot{V}_{he}$ is the heterogeneous nucleation rate, σ is the surface tension, P is the applied pressure, ϵ is the volume change rate in the phase transformation from liquid to solid, K_B is the Boltzmann constant, θ is the contact angle between the embryo and the substrate, $b=16\pi/3$, T is the absolute temperature and ΔP is the activation volume. $f(\theta)$ and K_{he} are model parameters determined from experimental data.

The effect undercooling rate of on the nucleation rate under different pressure is shown in Figure 2.25. From this figure, increasing pressure shifted the peak nucleation rate to a lower undercooling which implies an accelerated nucleation rate during pressurized solidification.

Figure 2.25: Effect of pressure on nucleation rate relating to undercooling

2.7 Summary of literature review

- 1) From above discussion, it is clear that that low formability of magnesium alloy is a common research challenge. In general, ductility or formability can be improved by reducing the grain size and weakening the strong basal texture.
- 2) Severe Plastic Deformation (SPD) is an effective method for grain refinement of bulk metals. It is also promising for improving the formability of magnesium alloy.

However, achieving both high strength and high ductility by SPD is far less common as both are the properties are mutually exclusive of each other.

- 3) The study of SPD on wrought AZ31 sheet is very limited, particularly by using constrained groove pressing, due to insufficient understanding or effective processing means to achieve both grain refinement and superior mechanical properties.
- 4) SPD is also effective for reducing the grain size of as-casted magnesium alloy. Again, the study of SPD effect on alloyed or unalloyed squeeze-casted magnesium alloy is very limited. It has been highlighted that squeeze casting could be a viable potential alternative for the production of small to medium size magnesium alloy feedstock. As such, the effect of SPD on formability and mechanical properties enhancement is worth investigating.
- 5) Wrought AZ31 sheet will be the focus of this current research because of practical consideration since it is widely available and most commonly used alloy on the market. Wider use of magnesium sheet for press forming will be encouraged if the issue of low formability and high cost can be addressed.

Chapter 3 Experimental Techniques and Procedures

This chapter describes the experimental techniques and procedures used in this investigation. The experimental procedures were performed according to internationally recognized standards to ensure accurate, reliable and consistent results. The experimental procedures described here include material selection, sample preparation, severe plastic deformation technique (SPD) using constrained groove pressing (CGP), finite element simulation procedure, metallography, x-ray diffraction (XRD), electron backscattered diffraction (EBSD), transmission electron microscopy (TEM), and mechanical tensile testing. Some of the procedures are briefly explained again in later chapters to facilitate easy reading. Some of the later chapters may also describe procedures that are more specific to the individual study.

3.1 Material

AZ31 magnesium alloy, with a chemical composition shown in Table 3.1, was chosen as the material of this study. This is because the alloy is commonly used in automotive and aerospace industry. AZ31 possess a good combination of strength and ductility as compared to other alloys such as AZ61, ZK60 or AZ91. In addition, all the alloying elements are in solid solution with the Mg and hence the absence of intermetallic particles simplifies the study of deformation and strengthening mechanisms by SPD.

The hot-rolled AZ31 sheet (nominal thickness of 2.2 mm) was received in the annealed condition. This thickness value is commonly used in automotive and consumer

electronic applications. The yield stress of the annealed AZ31 is about 145-152 MPa, ultimate tensile strength is about 248-255 MPa, with an average elongation of 17-21% at room temperature [2]. The mechanical properties and specification of AZ31 of other tempered conditions can be found in the handbooks. The sheet was cut into square specimens of the dimension of 96 mm $\times$ 96 mm for the CGP experiments.

Table 3.1: Chemical composition (Wt. %) of AZ31B-O

Chemical compositions of AZ31 magnesium alloy (wt.%)							
Element	Al	Zn	Mn	Si	Fe	Cu	Mg
Mass (%)	2.95	0.6	0.24	0.06	0.02	0.05	Bal.

3.2 Constrained groove pressing (CGP) methods

The CGP method developed this research is a variant of the original method. As such, it is necessary to first explain the original CGP method developed by Shin et al. [51] as shown in Figure 3.1. In this method, the workpiece is compressed between a pair of groove and flat dies in a specific sequence. The groove angle is 45° while the groove pitch depends on the thickness of the plate. Optimization of the die design had been thoroughly investigated in another work [54] and the current dimensions described here were also commonly used in other work [81-83]. As shown in Figure 3.1a, during the first deformation pass, the workpiece is constrained and deformed between the lower and upper dies. The material mainly deforms between the grooves (shear zones) as a result of simple shear deformation, while the material outside the grooves experiences minimum deformation. In order homogenously deform the entire workpiece, it is necessary to first straighten the

deformed plate as shown in Figure 3.1c in the second pass and rotate the specimen by 180° (Figure 3.1d) before subjecting the workpiece to the same groove deformation as shown in Figure 3.1e. SPD method is a grain refinement technique through large strain deformation technique without significantly changing the initial workpiece geometry. As such, it is necessary to end the process by straightening the workpiece again as shown in Figure 3.1f. The above deformation sequence illustrated in Figure 3.1a-f constitute one complete deformation cycle in this original CGP method. The deformation cycle can be repeated as much as possible as long as the workpiece does not fracture. The effective strain, $\bar{\epsilon}$, is calculated by equation 2.10 shown in chapter 2 and estimated to be 0.58 after the first pass (Figure 3.1b). The total effective strain, $\sum \bar{\epsilon}$, accumulated in the shear zones increased to approximately 1.16 after the second pass (Figure 3.1c). Therefore, the total cumulative strain in the material after one cycle is 1.16.

Figure 3.1: Schematic of the conventional groove pressing (CGP) process

The experimental setup is shown in Figure 3.2. The CGP process was performed using a 50 Ton hydraulic press (Figure 3.1a) using a pair of groove (Figure 3.2b) and flat dies (Figure 3.2c). The spacing of the groove, w , was 2 mm and groove angle, θ , was 45° . A constant press speed of 5.2 mm/s, equivalent to an initial strain rate of $\sim 2.3 \text{ s}^{-1}$, was used.

The pressing was conducted at elevated temperature. Heating of the dies was achieved using cartridge heaters. Before pressing, the dies were heated to the required temperature and allowed to stabilize for approximately 15 min before the start of the experiment. The dies were sprayed with water-based dispersion lubricant, Beruforge120AL, to reduce contact friction and for easy release of workpiece. The workpiece was placed on the lower die, with the upper die held close to the surface of the workpiece, and heated for 2 min to the required temperature before pressing. The required preheating time was determined by measuring a dummy sample inserted with a thermocouple and the accuracy of the temperature was within ± 2 K. After pressing, the workpiece was rapidly removed from the die and cooled in air. This process was repeated in each pressing step. For consistency, the workpiece was oriented such that its initial rolling direction was aligned parallel to the direction of the groove die in the first pass. The details of the deformation temperatures and sequences are described in the next section.

Figure 3.2: (a) Experimental setup on a 50 Ton hydraulic press, (b) groove dies and (c) flat dies

3.3 Deformation and temperature sequences

The modified CGP methods referred to as deformation sequence A (D_A) and B (D_B) are illustrated in Figure 3.3 and Figure 3.4. D_A method is similar to the initial concept by Shin, et al. [51] and this has been described in section 3.2. The only difference in this method was that the workpiece was rotated 90° (about the plate's normal direction) before the start of each deformation cycle. The intention is to introduce additional cross-shearing to accelerate the grain refinement and for preventing crack due to fatigue stress. In D_B method, the workpiece is orthogonally deformed between the groove dies four times before being straightened in the final step. The main difference between D_B and D_A methods is that D_B does not have any intermediate straightening of the workpiece during the deformation cycle. Similarly, the intention is to introduce more cross-shearing to accelerate grain refinement and to result in a higher cumulative strain using less pressing steps.

As summarized in Table 3.2, two pressing temperature sequence A (T_A) and B (T_B) were used in the study. In T_A method, the deformation temperature was progressively reduced after each cycle. The lowest deformation temperature was experimentally determined based on the workability of the material (to avoid fracture). The deformation temperature was maintained at 523 ± 2 K in the first cycle, 473 ± 2 K in the second cycle, and 423 ± 2 K in last two cycles. In T_B method, a constant deformation temperature was used for all the deformation cycles and the temperature investigated was between 473 ± 2 K and

573±2 K.

Figure 3.3: Schematic diagrams explaining the first two deformation cycles in D_A method Figure 3.4: Schematic diagrams explaining the first deformation cycle in D_B method

Table 3.2: Temperature sequence

Temperature sequence	Conditions
A	Progressive reduction in deformation temperature: <ul style="list-style-type: none"> Four deformation cycles: First cycle at 523±2 K, second cycle at 473±2 K, and last two cycle at 423±2 K (Chapter 4) Three deformation cycles: First cycle at 503±2 K and last two cycles at 453±2 K (Chapter 5,6,7,8, and 10)

B

Constant deformation temperatures:

- Four cycles: conducted at 473±2 K, 523±2 K, and 573±2 K (Chapter 4)

3.4 Simulation Procedures

In this study, the commercial FE implicit code, DEFORMTM 3D V11.0 was utilized to model and simulate the groove pressing process according to deformation paths D_A and D_B. The friction between the die and specimen interface was expressed by using the constant the friction model defined as follows:

$$\tau = mk = m \frac{\bar{\sigma}}{\sqrt{3}} \quad (3.1)$$

where τ is the shear stress, m is the friction factor, k is the shear strength and $\bar{\sigma}$ is the flow stress of the specimen material. To simplify the simulation analysis, plane strain condition was assumed. In order to simulate the actual rotation of the specimen in between the deformation passes, the lower and upper dies were rotated with respect to the specimen instead. This reduces the computational time and avoids convergence issues. The material properties of AZ31B-O were referenced from Takuda, et al. [84]. Table 3.3 shows the summary of the simulation parameters.

Table 3.3: FE Simulation parameters

Condition	Parameter	Descriptions
Material		AZ31B-O
Material properties		Rigid-plastic, $\sigma = K\epsilon^n \left(\frac{\dot{\epsilon}}{\dot{\epsilon}_0}\right)^m$ where
		$K(\text{MPa}) = 3.24 \times 10^5/t - 406, n = A \log\left(\frac{\dot{\epsilon}}{\dot{\epsilon}_0}\right)$
		+ B, $A = 0.016$, $B = 62.0/t + 0.053$, $m =$
		$-105/t + 0.303$ where t is the dimensionless

	temperature, $t = T(K)/1(K)$, and $\dot{\epsilon}_0 = 1 \text{ s}^{-1}$.
Specimen thickness	2.2 mm
Specimen dimension	96×96 mm
Friction condition	$m = 0.25$
No. of Elements	250,000
Punch Speed	5.2 mm/s
Time-step size	0.01 sec

3.5 Metallography

The microstructures of the workpiece before and after CGP was examined on the plane parallel to the plate's surface and its thickness cross-section. The workpiece was mechanically sectioned into smaller samples by a diamond precision cutter at 2000 rpm and feed rate of 0.1 mm/sec. The samples were cold mounted and polished by 1000 grit SiC paper followed by Struers polishing cloths using slurries of diamond particles (9, 3, and 1 μm) and oil lubricants. The polished samples were rinsed with alcohol and ultrasonic washed for a minute in a beaker of clean alcohol. The microstructures were revealed by chemical etching using picric acid solution (4g picric acid, 20ml acetic acid, 60ml ethanol and 20ml distilled water) for approximately 5 to 10 sec. Optical microscopy (OM) was performed using Olympus inverted optical microscope model GX51 at the magnifications of 500× and 1000×. The average grain size was determined by the linear intercept procedure according to ASTM E112 standard.

3.6 X-ray diffraction (XRD)

Samples of the dimension 20×20 mm were cut from the middle of the as-received (initial material) and CGP-processed plates for texture measurements by X-ray diffractometer. The surface of the samples was polished using 1000 grit SiC paper to remove

approximately 0.2-0.5 mm layer of the material. Measurements were performed on the ground surfaces. Incomplete pole figures of the basal $\{0002\}$, prismatic $\{10\bar{1}0\}$, and pyramidal $\{10\bar{1}1\}$ planes were collected over reflection angles from 30-39° and tilt angle up to 70° by Bruker D8 X-Ray Diffractometer using reflection geometry with the Cu-K α radiation at 40kV and 40 mA. Intensities of the diffraction peaks were then normalized and orientation distribution functions were calculated from the incomplete pole figures by using MULTEX 3.

3.7 Mechanical Testing

Tensile specimens were machined along the plates along the rolling and transverse direction. Two specimen sizes were used and prepared in accordance with ASTM E8M standard. The tensile specimen had a gauge length of 25 mm, width of 6 mm, and thickness of 1.2 mm. The sub-size tensile specimen has a gauge length of 12.5 mm, width of 3 mm and thickness of 1.2 mm. The smaller tensile specimen was used in the study in Chapter 8 because many replicates were required for the elevated tensile flow stress measurements and this reduced the material and cutting cost. Room temperature tensile tests were measured using Instron 5982 machine equipped with an extensometer at an initial strain rate of 1×10^{-3} . Elevated tensile tests were performed within a resistance furnace and equipped with a video extensometer under different temperatures (373 ± 2 to 523 ± 2 K) and initial strain rates (1×10^{-3} to 1.0 s^{-1}). The yield strength was taken as the 0.2% offset yield stress from the engineering stress-strain curve. The ductility was taken as the engineering strain at fracture and is referred to as elongation to failure. Hardness measurement was performed

across the thickness of the specimen using micro-Vickers hardness tester, Matsuzawa MMT-X3, using a load of 100g.

The mechanical anisotropy of the plate was investigated by room temperature tensile tests conducted at rolling, 45°, and transverse direction. The degree of anisotropy between in-plane and through the thickness is defined by the plastic strain ratio, r-value, and was calculated using strain values at 8% engineering strain for magnesium material [85]. The r-values at rolling, 45°, and transverse direction were calculated using the equation:

$$r = \frac{\varepsilon_w}{\varepsilon_t} = \frac{\varepsilon_w}{-(\varepsilon_l + \varepsilon_w)} \quad (3.2)$$

where ε_w , ε_t , and ε_l are the plastic strain values in the width, thickness, and length directions at 8% engineering tensile strain and volume constancy dictates that $\varepsilon_w + \varepsilon_t + \varepsilon_l = 0$. The average strain ratio, also known as normal anisotropy, was calculated by:

$$r_m = \frac{r_o + 2r_{45} + r_{90}}{4} \quad (3.3)$$

where r_o , r_{45} , and r_{90} are the r-values determined at rolling, 45°, and transverse directions. Planar anisotropy is used for determining the uniformity of the material during drawing process (“earing tendency”). This value is calculated from the equation:

$$\Delta r = \frac{r_o - 2r_{45} + r_{90}}{2} \quad (3.4)$$

3.8 Transmission electron microscopy (TEM)

A sample of the dimension 10×10 mm was cut from the plate and polished down to approximately 200 µm in thickness using 1200 grit SiC paper. Small discs of approximately 1 mm were punched from the polished sample with a mechanical puncher. These thin foils were furthered polished by a dual beam FIB (FEI xT Nova Nanolab 200, USA) to a thickness

of approximately 70 nm to 100 nm. Once the thin foil specimen was perforated, it was removed, lightly rinsed with alcohol and placed into the transmission electron microscopy (TEM) machine immediately. The thin foils were examined with a Philips CM 200, field emission gun operated at 200 kV.

3.9 Electron backscatter diffraction (EBSD)

The FESEM was performed using the Oxford Instrument HKL EBSD system operating at 20 kV with a working distance of 28 mm and a 70° tilt angle. The Channel 5 post-processing program from Oxford Instruments was used to analyze the EBSD data. The scanning step size used was between 0.03 μm and up to 0.1 μm depending on the grain size. To ensure reliable results, only EBSD mapping with successfully indexed pixels of above 70% was used. The high angle grain boundaries (HAGBs; misorientation $>15^\circ$) were depicted as black lines. The low angle grain boundaries (LAGBs; misorientations $>2^\circ$ and $<15^\circ$) were depicted by white lines.

Chapter 4 Finite element analysis of the strain uniformity in CGP process

The content of this chapter has been published in the below journal papers:

- K.S. Fong, D. Atsushi M-J Tan, B.W. Chua E. “Effect of Deformation and Temperature Paths in Severe Plastic Deformation Using Groove Pressing on Microstructure, Texture, and Mechanical Properties of AZ31-O” *Journal of Manufacturing Science and Engineering*, vol.137, (2015), pp. 051004-1-16

4.1 Introduction

Ideally, any severe plastic deformation (SPD) process should impart a large amount of strain uniformly throughout the material. This is not the case in many of the SPD processes, including ECAP [67, 86], HPT [87], ARB [88], and CGP [54, 89, 90], based on the analysis of the strain distribution from Finite Element Simulations and hardness measurements. Most of the current CGP research investigated the strain distribution based on the original method developed by Shin, et al. [51]. However, there exist other ways of deforming the plate, for example by changing its orientation and pressing sequences. This would induce a different total strain and strain distribution in the material.

This chapter investigates the effects of D_A and D_B methods on strain and stress distributions in the workpiece by 3D finite element (FE) analysis. In the original CGP method, the total cumulative strain can be easily determined by plane-strain assumption using equation 2.10. However, current D_B method is more complex due to the orthogonal deformation which introduces more cross-shearing. Hence, FE analysis is a useful tool for analyzing the total strain in this modified CGP process.

4.2 Effect of deformation sequence on strain distribution

The simulation results after one deformation cycle of D_A and D_B methods are shown in Figure 4.1 and Figure 4.2, respectively. It can be seen from the colour plots, which represent the effective strain values, that the strain distribution was clearly non-uniform in both methods. The values of the effective strain in each deformation pass of D_A and D_B methods are plotted in Figure 4.3 and Figure 4.4, respectively. These values were determined from the measurement points (~ 200) taken along the middle of the workpiece as indicated by the dotted lines in Figure 4.1 and 4.2. Table 4.1 summarizes the average cumulative strain after each deformation pass and its corresponding 95th percentile, 5th percentile and the spread between the two percentiles. As shown in Table 4.1, the average total cumulative strain after one cycle of D_A was approximately 1.3, with the 95th percentile and 5th percentile at 1.44 and 1.15 respectively. The spread between the two percentiles was 0.29. The average total cumulative strain after one cycle of D_B was approximately 2.47, with the 95th percentile and 5th percentile at 2.87 and 2.02 respectively. The spread between the two percentiles was 0.85. This result shows that one cycle of D_B method can impose a much higher total strain but result in a slightly higher amount of strain non-uniformity as compared to D_A method. By simple summation of the total strain in each cycle, D_A method can achieve a total cumulative strain of 5.2 when repeated to four cycles. This value is slightly higher than that estimated from the plane strain assumption (4.64) because it takes into account of the bending strains in the process. By similar estimation, D_B method when performed to a total of two cycles can achieve an average cumulative strain of 4.94. This value is similar to D_A method when performed to four cycles (5.2).

Figure 4.1: Effective strain distribution after one deformation cycle using method D_A

Figure 4.2: Effective strain distribution after one deformation cycle using method D_B

Figure 4.3: Plot of the effective strain distributions in the mid-section of the workpiece after each deformation pass in D_A

Figure 4.4: Plot of the effective strain distributions in the mid-section of the specimen after each deformation pass in D_B

Table 4.1: Average effective strain after each pass in one cycle of D_A and D_B

D_A				
Pass no.	average	95 th percentile	5 th percentile	spread
1	0.29	0.42	0.17	0.25
2	0.65	1.00	0.28	0.73
3	0.97	1.25	0.73	0.52
4	1.30	1.44	1.15	0.29
D_B				
Pass no.	average	95 th percentile	5 th percentile	spread
1	0.29	0.42	0.17	0.25
2	1.04	1.28	0.76	0.52
3	1.59	1.86	1.33	0.52
4	2.21	2.45	1.95	0.51
5	2.47	2.87	2.02	0.85

Figure 4.5 shows the results of the strain distribution along the thickness of the workpiece after one cycle of D_A . The non-uniformity of the strain in the shear zones (between the grooves) in D_A was contributed from the bending stresses due to the neighbouring constraints imposed by the un-deformed zones (outside the grooves). This bending imparted both tensile and compressive stresses near the top and bottom surfaces of the plate which contributed to the small amount of strain accumulation in the supposedly un-deformed zones. In order to understand the variation of stress state in the workpiece by method D_B , the deformation during the fourth pass is examined more closely as shown in Figure 4.6. The orthogonal deformation sequence without intermediate straightening was shown to impose a larger variation in stresses across the plate. Observation at the start, middle, and towards the ending stages of deformation (die closure) shows a “checkered-

like” pattern of compressive and tensile stresses which developed across the plate. There was also a higher spread of compressive and tensile stresses due to the stretching and bending of the material between the dies, in addition to the shear deformation which occurred between the 45° grooves.

The shape of the deformed workpiece is similar to a sine-wave profile with the highest profile being described as “crest” and lowest profile described as “trough”. In between the crest and trough is the “shear zone”. It can be seen from Figure 4.6 that there some regions of the previously formed crests (formed in the previous pass) were being compressed and stretched into troughs (in the current pass) and vice versa. Similarly, there were regions of crests or troughs that remain relatively un-deformed while some portion of the crests and troughs were subjected to shear deformation (between the 45° grooves). A small interaction of shear zones occurred in the regions of previously formed shear zones that were “re-shaped” into the current shear zones. To conclude, it can be stated that the higher total effective strain in method D_B was contributed by the higher amount of cross shearing and a significant amount of compressive and tensile strain which developed throughout the workpiece. This resulted in a higher cumulative strain in each deformation cycle by D_B method as compared to D_A method.

Figure 4.5: Effective strain distribution in the cross-section of specimen deformed according to deformation path D_A after (a) 1st pass, (b) 2nd pass, (c) 3rd pass, and (d) 4th pass

Figure 4.6: Maximum principal stress distributions in specimen deformed to D_B during the 4th pass at the (a) start, and (b) end of the pass, and expanded views at the (c) start, (d) intermediate, and (e) end of the pass.

4.3 Summary

- 1) Strain non-uniformity was observed in both deformation sequences A (D_A) and B (D_B). This was contributed by the bending stresses due to constraints imposed by the neighbouring un-deformed regions which imparted tensile and compressive stresses along the top and bottom surfaces.
- 2) Checkered-like” pattern of compressive and tensile stress was observed across the plate using method D_B as a result of the direct orthogonal deformation without intermediate straightening. This increased the total average effective strain in one deformation cycle (~ 2.4) of D_A as compared to D_A (~ 1.3).
- 3) The non-uniformity in strain by method D_B was found to be higher than D_A as seen from the spread of the lower and upper percentile of average strain values. This was due to the higher amount of tensile and compressive stresses due to more stretching of the material. D_B was found to be more effective as it required a lesser number of deformation cycles to achieve similar total average effective strain as compared to D_A .

Chapter 5 Effect of deformation and temperature sequences on microstructures and mechanical Properties

The content of this chapter has been published in the below journal paper/ conference proceedings:

- K.S. Fong, D. Atsushi M-J Tan, B.W. Chua E. “Effect of Deformation and Temperature Paths in Severe Plastic Deformation Using Groove Pressing on Microstructure, Texture, and Mechanical Properties of AZ31-O” *Journal of Manufacturing Science and Engineering*, vol.137, (2015), pp. 051004-1-16
- K.S. Fong, D. Atsushi M-J Tan, B.W. Chua, “Enabling wider use of Magnesium Alloys for lightweight applications by improving the formability by Groove Pressing”, *Procedia CIRP* 26 (2015), pp. 449 –454

5.1 Introduction

The development of severe plastic deformation (SPD) techniques for sheet geometry [77, 82, 91-93] was comparatively less as compared to bulk geometry [37, 38, 67, 75, 94-100]. This is probably because of the early SPD research, such as equal-channel angular pressing (ECAP), developed by V.M. Segal and co-workers in the mid-70s, and high-pressure torsion (HPT), derived from Bridgeman’s work and developed by R.S. Valiev and co-workers in the 80s [42], were initially demonstrated on non-sheet geometry. These SPD techniques show an exceptional degree of grain refinement and enhancement of mechanical properties [42], which subsequently generated greater research interest in these techniques apply to a wide variety of metallic materials.

It is important to note that many of the current SPD techniques such as ECAP and multi-directional forging (MDF) are only suitable for processing of bulk geometry, or only

applicable for lab-scale size as demonstrated by HPT. Among these techniques, ECAP is by far the most promising, with some commercialization to companies such as Honeywell, Matallicum, and Dynamic Motors [101]. In order to further advance the adoption of this technology, it is necessary to explore the benefits of SPD for sheet material. This is especially important for wrought magnesium alloy sheet because of its limited used as compared to cast magnesium alloy.

In recent years, ECAP was attempted on a plate [102] and thin sheet [103]. However, the result on grain refinement or mechanical properties were far from satisfactory. Another suitable SPD process for sheet geometry is accumulative roll bonding (ARB) [91]. However, ARB process is labour intensive. The process requires cutting, brushing and cleaning of the sheet surfaces before stacking together for repeated rolling. The process also leads to a strong basal texture similar to conventional sheet rolling process, which is a contributing factor to the poor formability in magnesium alloy.

On the other hand, constrained groove pressing (CGP) which was proposed by Shin, et al. [51] and demonstrated on aluminium is another attractive option for processing of sheet. This process is developed for sheet geometries, uses very simple die construction and has the opportunity for adaptation into rollers for continuous processing. Since the pioneering work by Shin et al., other researchers have investigated the process on a variety of materials such as brass, steel, and magnesium [54, 81, 83, 93, 104]. Generally, the research of this process on magnesium alloy is very limited and demonstrated little success in achieving very fine microstructure. This is because of the difficulties in SPD processing of magnesium alloy which has very poor workability at low temperature [67]. The poor

workability is further compounded by the nature of the die design in CGP, which imposes a comparatively lower hydrostatic pressure on the workpiece as compared to ECAP or HPT.

CGP process was chosen in this study because of the above advantages as discussed which suits our interest in achieving high strength and toughness magnesium sheet. Due to the practical challenges associated with the processing of magnesium alloy, a detailed experimental study should be performed to evaluate the suitability of CGP for magnesium alloy.

This chapter investigates the relationship between the microstructures and mechanical properties of AZ31 magnesium alloy processed by CGP using different deformation (D_A and D_B) and temperature sequences (T_A and T_B). The workpiece rotations were introduced during and between pressing steps promote cross shearing and delay in fatigue cracking. The mechanical properties are investigated by tensile tests and hardness measurements and these are correlated to microstructures and deformation textures.

5.2 Microstructures after different processing

Table 5.1 shows a summary of the tests performed in this study to systematically examine the influence of deformation and temperature sequences on the microstructures and mechanical properties. The detailed explanation of the deformation and temperature sequences can be found in chapter 3. These tests were planned in a way to allow useful comparison so that the influence of deformation and temperature sequences on the microstructure and mechanical properties can be revealed. For example, sample 1 (S1) and sample 6 (S6) were subjected to different deformation sequences A (D_A) and B (D_B) and

under the same temperature sequence B (T_B). Through a comparison of these two samples, it is possible to identify the influence of deformation sequence on microstructure and mechanical properties. Similarly, sample 2 (S2) to sample 4 (S4) were subjected to the same D_A and temperature sequence B (T_B) but with varying temperatures. From these samples, the influence of temperatures on the microstructures and mechanical properties can be examined. Lastly, a comparison between S2 and sample 6 (S6) will be discussed. These were carried out using the same T_A but different deformation sequence. As such, the influence of progressive reduction in temperature on microstructures and mechanical properties can be established.

Table 5.1: Summary of test samples subjected to different deformation and temperature sequences

Sample	Deformation Sequences	No. of cycles	Estimated total average strain	Temperature sequences
S1	D_A	4	5.2	T_A (first cycle: 523K; second cycle: 473; last two cycles: 423 K)
S2	D_A	4	5.2	T_B (473K)
S3	D_A	4	5.2	T_B (523K)
S4	D_A	4	5.2	T_B (573K)
S5	D_B	2	4.9	T_B (473K)
S6	D_B	4	9.9	T_A (first cycle: 523K; second cycle: 473; last two cycles: 423 K)

Figure 5.1 shows the initial microstructure of AZ31 received in the annealed condition. This condition is referred to as-received sample. The microstructures were observed at the thickness along the rolling (RD) and transverse (TD) directions. As shown in Figure 5.1a and b, the microstructures were fairly equiaxed and uniform in the RD and TD. The average grain size was determined by linear intercept method as $13.3 \pm 0.5 \mu\text{m}$.

A detailed examination of sample S1 was performed to reveal the microstructure development after each cycle of CGP. The microstructures were observed at thickness along the RD as shown in Figure 5.2

Figure 5.1: Microstructures of the as-received AZ31 magnesium alloy (a) along the RD (b) and TD directions

Figure 5.2: Microstructure evolution of sample S1 subjected to D_A and T_A in the (a) first cycle (b) second cycle (c) third cycle and (d) fourth cycle

As shown in Figure 5.2a, the grain size was significantly reduced in the first cycle of CGP, which was carried out at 523 K and to an estimated total strain (ϵ_t) of approximately 1.3. The average grain size was determined as $6.3 \pm 0.5 \mu\text{m}$, which was an approximately 53% reduction of the initial grain size value. The microstructure after the first cycle was not homogenous due to incomplete dynamic recrystallization i.e., many fine recrystallized new grains are seen with larger grains from the initial microstructure. After the second cycle, processed at 473 K to $\epsilon_t \approx 2.6$, the average grain size decreased slightly ($\sim 8\%$) to $5.8 \pm 0.5 \mu\text{m}$ (Figure 5.2b). A more significant grain refinement ($\sim 43\%$) was seen in the third cycle, processed at 423 K to $\epsilon_t \approx 3.9$, where the average grain size was reduced to $3.3 \pm 0.5 \mu\text{m}$ (Figure 5.2c). After the fourth and final cycle, processed at the same temperature of 423 K to $\epsilon_t \approx 5.2$, the average grain size was decreased to $1.9 \pm 0.5 \mu\text{m}$ (Figure 5.2d). The final microstructure was fairly uniform although a few slightly larger grains can still be seen. The total percentage of grain refinement achieved after four cycles of CGP using methods D_A and T_A was approximately 86%.

Figure 5.3: Magnified view of the microstructures of sample S1 at the end of four cycles of CGP by D_A and T_A : (a) TD direction (b) RD direction

The microstructures, observed at the higher magnification, in sample S1 after four cycles of CGP by method D_A are shown in Figure 5.3. The variation of grain sizes in the regions near the upper, middle and bottom of the plate were also examined and shown in Figure 5.4. From Figure 5.3a-b, the microstructures are observed to be homogeneous in both RD and TD directions. The fine grains were between 0.6 to 1 μm while those the larger grains were between 3 and 5 μm . As shown in Figure 5.4a-d, the microstructures were observed to be fairly homogenous across the thickness of the plate which suggests that the grain refinement was uniform when repeated to four cycles despite some strain inhomogeneity in the process.

Figure 5.4: Microstructure of sample S1 observed at the cross-section of the thickness: (a) 30 μm ~ 130 μm from upper surface of the plate (b) in the middle of the plate and (b) 30 μm ~ 130 μm from lower surface of the plate

It is also important to understand the uniformity of the microstructure in the region between the “shear” and “un-deformed” zone where the strain was non-uniform as shown by the finite element simulation result in Chapter 4. Figure 5.5 shows the micrographs of sample S1 observed at the thickness plane at varying distances along the RD direction. The microstructures were observed over a distance of 4 mm which effectively covered the region between shear and un-deformed zone. From the micrographs, it is obvious that the grain refinement was fairly uniform even in the region where a high degree of strain non-uniformity was expected. From the above result, it can be concluded that the grain refining efficiency of CGP process is excellent when repeated to sufficient strain and the process is capable of producing homogenous fine-grained structures throughout the entire plate without fracturing the material.

Figure 5.5: Observation of the microstructure along the RD direction in sample S1 after four cycles of CGP by D_A and T_A : distance of (a) 1 mm (b) 2 mm, (b) 3 mm, and (d) 4 mm

from the middle of the plate

Figure 5.6 shows the microstructures of sample S1 to S6. The plot of their average grain size measurements is shown in Figure 5.7. Sample S2 to S4 were processed by the same D_A and T_B method at a different temperature from 473 to 573 K. The average grain size of sample S2 was $3.8 \pm 0.5 \mu\text{m}$, which was reasonably fine as compared to sample S1 ($1.9 \pm 0.5 \mu\text{m}$). As expected, increasing the deformation temperature resulted in significant grain coarsening as shown in sample S3 and S4 where the average grain sizes were 8.2 ± 0.5 and $21.6 \pm 0.5 \mu\text{m}$, respectively. The average grain size in sample S4 became much higher than the as-received sample due to the high deformation temperature which promoted significant grain growth.

Sample S2 and S5 were both processed using T_B at the same constant temperature of 473 K but with different deformation sequence D_A and D_B respectively. From the comparison of these two samples, sample S5 had a marginally smaller average grain size of $3 \pm 0.5 \mu\text{m}$ as compared to sample S2 ($3.8 \pm 0.5 \mu\text{m}$). This is interesting since grain refinement is usually a function of total average strain. However, sample S5 was processed to a lower total average strain (~ 4.9) as compared to S2 (~ 5.2) but resulted in marginally smaller average grain size. Although the differences in strain or grain size can be argued to be insignificant, it is most likely that the deformation sequence plays an important role which resulted in this differences in average grain size. The differences in grain sizes can be simply explained by the differences in exposure time of these samples at elevated temperature. The exposure time was different due to the difference in the number of pressing steps required in each of the deformation sequences. This exposure time includes preheating, straining, and

until removal of the sample from the die. Sample S5 was repeatedly pressed for 10 times (in two cycles) as compared to that of 16 times (in four cycles) in sample S2. As such, sample S5 exposure duration was shorter and had a lower opportunity for recovery and grain growth during preheating and post-deformation stages as compared to sample S2.

Figure 5.6: Comparison of microstructures of samples (a) S1 (b) S2 (c) S3, (d) S4, (e) S5, and (f) S6

Figure 5.7: Comparison of the average grain size of sample S1, S1-A (annealed), and S2-S6

Another comparison can be made between sample S6 (D_B and T_A to $\varepsilon_t \approx 9.9$ after four cycles) with sample S1 (D_A and T_A to $\varepsilon_t \approx 5.2$ after four cycles). The average grain size in sample S6 was $2.7 \pm 0.5 \mu\text{m}$ which was larger than sample S1 ($1.9 \pm 0.5 \mu\text{m}$). The average grain size did not decrease significantly in sample S6 despite its much higher of total average strain as compared to sample S1. This can be similarly explained by the sample's long exposure time at elevated temperatures. Sample S6 exposure time at elevated temperature was longer because more deformation passes were needed (20 times) as compared to sample S1 (16 times) which resulted in greater opportunity for grain growth.

In this study, sample S1 were furthered annealed at 453 K for 1h to investigate the degree of ductility recovery and changes in mechanical strength. As a result of this heat treatment procedure, the average grain size was found to increase from $1.9 \pm 0.5 \mu\text{m}$ to $7.9 \pm 0.5 \mu\text{m}$.

The above microstructures of samples S1-S6 show that the fine microstructure can be easily obtained in AZ31 magnesium plate by the CGP if appropriate processing conditions were adopted. Sufficiently fine and homogeneous microstructure can be achieved by using constant temperature (T_B) deformation approach provided that the temperature was maintained less than 523 K. Pressing at too high temperature can result in significant grain coarsening due to the larger thermal energy and driving force for grain boundary migration.

The development of microstructure can be complex due to the deformation and exposure time experienced by the material during each pressing step. The total exposure time at elevated temperature includes preheating, deformation and immediately after deformation. During preheating, the material is constantly subjected to the competing mechanisms of static recovery (SRV) and static recrystallization (SRX) driven by the stored energy introduced in the previous pressing step. During deformation, dynamic recrystallization (DRX) and dynamic recovery (DRV) are the dominating mechanisms, while metadynamic recrystallization (MDRX) may also occur immediately after deformation. The partially dynamic recrystallized microstructure typically contains regions with: (i) small dynamically recrystallized grains with zero dislocation, (ii) larger recrystallized grains with some dislocation and (iii) unrecrystallized structure with high dislocation [72]. When straining is stopped, various changes in the microstructure state can occur while the workpiece is still exposed to elevated temperature. In region (ii), recovery/growth of recrystallization nuclei may occur if dislocation density is below a critical value. Above this critical value, SRX will proceed. Fine grains in region (i) may continue to grow due to annealing. Region (iii) may experience SRV, SRX and subsequent

grain growth.

At higher temperatures, the kinetics for grain growth increases (during preheating and post-deformation) and likely overshadow the effect of grain refinement achieved through DRX during straining. This was evident in the sample S3 and S6 processed by using T_B at 523 K and 573 K respectively, where significant grain coarsening was observed. At 573K, it was observed that the microstructure consists of mainly coarse grains. Fine grains could still be achieved in sample S2 processed using T_B of 523 K because of the higher rate of the DRX and where grain growth was minimal. Progressive reduction in processing temperature using T_A was highly effective for obtaining very fine grain microstructures. It was possible to process the alloy at the lower temperatures (473 K) because of the better workability of the alloy as a result of grain refinement produced by earlier cycles. Processing at lower temperature results in further accumulation of dislocations within the grains which promotes further grain refinement by grain subdivision through the processing of continuous dynamic recrystallization [47]. The effect of twin-induced grain refinement may have accelerated grain refinement at the lower deformation temperature [34, 105-107]. The interaction of slip dislocations and twin boundaries increases the nucleation sites and subsequently led to the formation of finer DRX grains.

5.3 Texture development after different processing

Figure 5.8 shows the pole figures of as-received AZ31 magnesium alloy which displayed a strong basal texture $\{0002\}$ typical of a rolled magnesium sheet. Figure 5.9 shows the changes in the basal $\{0002\}$, prismatic $\{10\bar{1}0\}$, and pyramidal $\{10\bar{1}1\}$ pole

figures after each cycle in sample S1. Generally, the basal texture intensities were redistributed from ND towards RD-TD with increasing cycle of deformation. Similarly, the prismatic intensities which were initially observed to be randomly distributed around RD-TD were also redistributed towards ND in approximately the same direction as the shifting of the basal intensities. The basal texture intensity was decreased progressively from the first to third cycle but was marginally higher after the fourth cycle. The result suggests that a new texture was developed through CGP process whereby some of the grains had their c-axis, of the hcp structure, tilted away from ND towards the RD-TD. This change in texture was supposedly caused by shear deformation and interaction of slips and twinning which resulted in the formation of recrystallized grains with non-basal and basal orientations.

Figure 5.8: Pole figures of the as-received AZ31 magnesium alloy (a) prismatic (b) basal (c) pyramidal

Figure 5.9: Pole figures of sample S1 processed by D_A and T_A after (a) first cycle, (b) second cycle, (c) third cycle, and (d) fourth cycle

Figure 5.10: Final prismatic, basal, and pyramidal pole figures of samples (a) S1 (b) S1-A (annealed), (c) S2, (d) S3, (e) S5, and (f) S6

The final $\{0002\}$, $\{10\bar{1}0\}$, and $\{10\bar{1}1\}$ pole figures in sample S1 to S6 are shown in Figure 5.10. The texture and mechanical properties of sample S4 were not investigated because of significant grain coarsening and this study mainly focus on the texture and mechanical properties in the fine-grained alloy. From Figure 5.10a and b, it was observed from the pole figures of sample S1-A (after annealing) that the deformation texture was partially retained. The basal texture intensity was increased slightly as compared to the sample S1 but was still significantly weaker as compared to the initial alloy. Interestingly, the basal intensity in sample S6 (D_B and T_A) were distributed strongly in the middle of the pole figure and exhibited an intensity value much higher than that of the as-received sample. This was supposedly caused by the higher total straining and a larger amount of compressive and tensile stress in D_B method as compared to D_A method. Based on the estimation from finite element simulation (Table 4.1 in Chapter 4), the total cumulative strain in sample S6 can be estimated to ~ 9.9 as compared to 5.2 in sample S1. Furthermore, most of the straining in sample S6 was performed at lower temperatures of 473 K in the last two cycles. Compression along the ND of the plate could possibly activate extension twinning in grains which had their c-axis initially oriented away from ND. Activation of twinning can cause the grains to rotate such that its c-axis become align parallel to the loading direction [108]. Subsequent tensile strain along the RD-TD due to stretching was accommodated by basal slips which further strengthens the basal texture [109].

Sample S2 and sample S6 pole figures are shown in Figure 5.10c and Figure 5.10f. Both samples were processed to a similar total cumulative strain (5.2 in S2 and 4.9 in S5), by the same T_B (at 473K) method but with different deformation methods. Sample S6

exhibited a lower basal intensity of 2.5 magnitudes of random distribution (m.r.d) as compared to S2 which had a basal intensity of 3.8 m.r.d.

Furthermore, it was observed that the texture in S5 was significantly weaker as compared to S6. Both of the samples were processed using the same D_B method but with different temperature sequence. The lower basal texture seen in sample S5 as compared to sample S6 was due different processing temperature and total degree of straining. Sample S6 was processed to a higher cumulative strain and at a lower temperature in the last two cycles which encouraged higher basal slip and twinning activities and led to the strengthening of its basal texture.

5.4 Mechanical properties after different processing

Hardness variation along the thickness of S1 after each deformation cycle is shown in Figure 5.11. The measurements were taken from the top to the lower surface of the plate. The result shows that the hardness variation along the thickness was minimum especially at higher cycles. This implies that through thickness straining was uniform at higher cycle of deformation. Figure 5.12 shows the plot of the average hardness and grain size values against the average total average strain (determined by finite element simulation in chapter 4) in S1 after each cycle. From figure 5.11 and 5.12, the change in hardness after each cycle was found to be in good agreement with the grain size reduction. For example, the hardness was observed to increase sharply after the third cycle as compared to after the second cycle. This corresponds well to a higher reduction (~43%) in average grain size seen in the third cycle.

Figure 5.11: Hardness variations along the thickness of S1 after each deformation cycle

Figure 5.12: Plot of average hardness and grain size measured in S1 after each cycle against total average strain

Figure 5.13 shows the tensile true stress-strain curves measured in sample S1 processed after each cycle of CGP according to D_A and T_A . A comparison of the true stress-strain curves of the samples S1 to S6 is shown in Figure 5.14. The values of the yield stress, ultimate tensile strength and elongation to failure obtained from the stress-strain curves are shown in Figure 5.15. As shown in Figure 5.13, sample S1 strength was increased and elongation to failure was decreased with increasing cycle of CGP. After the second cycle, reasonable elongation to failure (~15-23%) can be maintained due to the higher deformation temperature which promoted SRV and SRX. The changes to yield strength, ultimate tensile strength and elongation to failure of S1 after four cycles of CGP and in the RD are approximately 46.8%, 1.7% and -64.8% as compared to the as-received sample. After annealing S1 (sample S1-A) at 473 K for 1h, elongation to failure was improved by 19% as compared to as-received sample. As expected, the yield strength and ultimate tensile strength were decreased after annealing, and the values were 11% higher and 12% lower than the as-received sample. The stress-strain curves of S1-A in the RD and TD became less anisotropic because of the annealing heat treatment. Basically, it is well known that strength and ductility are compromising properties which are affected by heat treatment. Other annealing conditions will be discussed in chapter 8 where a more optimum balance between ductility and strength was established.

From Figure 5.14, the stress-strain curves in the RD and TD of sample S2 and S5 are observed to be more anisotropic. The elongation to failure was significantly higher in RD than in TD. The higher ductility in RD was caused by the texture development in these

samples. This can be seen from their textures as shown in Figure 5.10 where the basal intensities were redistributed towards the RD than RD. This generally favours more basal slip along RD than TD direction [110] in the work-hardened material. Furthermore, Sample S2 exhibited a higher yield strength and elongation to failure as compared to sample S3. The lower ductility and strength in sample S3 was due to its larger average grain size. The yield strength, ultimate tensile strength, and elongation to failure of sample S2 were 21.9%, 9.1%, and 19.8% higher than the as-received sample. The improvement in ductility in both S1-A and S2 can be attributed to the lower textural strength, lower work-hardening and also fine microstructures. Fine grains are known to promote higher activities of non-basal slips as observed by Koike, et al. [17].

Another interesting observation that can be seen from the stress-strain curves in Figure 5.13 and Figure 5.14 is the occurrence of a yield point elongation in the sample after the 4th cycle and sample after annealing. This means that there exists a small plateau in the stress-strain curve after yielding. This phenomenon was associated with the relaxation of stress at the tips of twins when it meets the grain boundaries and propagate across the next grains [111]. From the analysis of the number of twins per grain, it was found that in the fine-grained magnesium alloy (5.1, 6.4 μm), the formation of approximately one twin per grain is a requirement for yield point elongation [111]. This basically makes it easier for the twins to propagate the full extent of the grain, halt at the grain boundaries and re-initiate and propagate in the adjacent grain. This is not possible in the coarse-grained material because of more twins per grain which are more likely to impinge onto each other.

Figure 5.13: True stress and strain curves of sample S1 after first to fourth cycle and after four cycle with annealing as compared to as-received AZ31 magnesium alloy in the (a) RD, and (b) TD

Figure 5.14: True stress and strain curves for different samples in the (a) RD and (b) TD

Figure 5.15: Yield strength, ultimate tensile strength and elongation to failure of the different samples in the (a) RD and (b) TD

To investigate the mechanical anisotropy of the CGP plate, the plastic strain ratio (r -value), normal anisotropy (r_m), and planar anisotropy (Δr) were determined from room temperature tensile tests. The comparison of the tensile properties and mechanical

anisotropy of AZ31 alloys under different processing conditions are shown in Table 5.2 and 5.3, respectively.

Table 5.2: Tensile properties of AZ31 alloy under different processing conditions									
Processing conditions	YS (MPa)			UTS (MPa)			Elongation to failure (%)		
	RD	45	TD	RD	45	TD	RD	45	TD
Normal rolling from hot extruded plate [40]	166.4	166.4	171.2	256.6	254.9	254.9	22.8	21.8	21.1
Differential speed rolling (DSR) from hot extruded plate [40]	145.5	158.9	176	259.2	258.5	259.2	25.5	24.6	23.1
As-rolled plate [85]	163	175	186	263	263	275	16	19	17
Annealed plate (current work)	172	143	138	259.7	197.3	248.4	19.0	20	22.3
CGP sample S1-A (current work)	191.5	165	174.9	266.3	173.7	264.5	23.4	13.3	21.7

Table 5.3: Plastic strain ratios, normal anisotropy and planar anisotropy of AZ31 alloy under different processing conditions					
Processing conditions	r-value			r_m	Δr
	RD	45	TD		
Normal rolling from hot extruded plate [40]	2.99	3.09	3.41	3.145	0.11
Differential speed rolling (DSR) from hot extruded plate [40]	1.85	2.47	3.27	2.515	0.09
rolled plate [85]	1.92	2.11	2.92	2.27	0.3
Annealed plate (current work)	1.49	1.23	0.94	1.2	-0.02
CGP sample S1-A (current work)	1.37	1.53	1.02	1.4	-0.3

From table 5.2, it can be seen that the annealed CGP plate exhibited a more significant improvement in both mechanical strength and ductility along the RD direction as compared to the, commercially available, rolled and fully annealed plates. The mechanical properties of the annealed CGP plate along the TD direction were more comparable as compared to the rolled and fully annealed plates. Unfortunately, the ductility of the annealed CGP plate was lower at the 45° direction as compared to all the other materials. This increased in anisotropy was due to the alignment of more grains towards RD and TD (which can be observed from the pole figure in Figure 5.10b) as resulted from the pressing procedure (180/90° workpiece rotation). Such grain alignment favours <a>-dislocation slip during tensile deformation at room temperature. As compared to normal rolling and differential speed rolling (DSR) from hot extruded plates, the CGP sample exhibited better strength properties but more comparable ductility in RD. The mechanical properties were also more comparable in the TD direction but significantly lower in the 45° direction.

In order to better understand the formability of sheet metal, the normal anisotropy (r_m) and planar anisotropy (Δr) were calculated from the plastic strain ratio (r-value). Plastic strain ratios were determined at 8% engineering strain for magnesium material [85]. The equations for calculating r_m , Δr , and r-value are shown in Chapter 3, section 3.7 of the experimental procedures. It is widely known that for cubic metals, a higher r-value indicates a better sheet formability [112]. However, the interpretation of r-value is the opposite for hexagonal metals. It was reported from deep drawing experiments of different magnesium alloys that a higher r-value was correlated to lower drawability [85]. This implied that a higher r-value will suggest a larger mechanical anisotropy and lower

formability. From Table 5.3, the r -value of the annealed CGP plate at the 45° was highest as compared to RD and TD. This was because of the lower ductility as shown from the tensile tests conducted along 45° . The annealed CGP plate was found to have a lower value of r_m when compared to rolled plate, but was marginally higher when compared to annealed plate. The value of Δr was found to be more negative in the annealed CGP plate as compared to the other materials. This indicates that the material was more susceptible to fracture when loaded at 45° . Generally, the r -values and values of r_m of the annealed CGP plate were much lower as compared to normal rolling and DSR from hot extrusion plate, which suggests a better formability in the CGP material. The value of Δr in the rolled plate was the highest which means that the material is more likely to draw-in nonuniformly (“earing tendency”) during deep drawing operation [112].

5.5 Summary

In this chapter, the effect of deformation and temperature sequence on the microstructure, texture and mechanical properties of AZ31 magnesium alloy by constrained groove pressing were systematically investigated. The main objective of this study is to investigate an optimum processing condition for obtaining fine-grained structure with enhancement mechanical properties. The following conclusions can be drawn:

- 1) Introducing workpiece rotation between cycles or during the deformation cycles, through deformation sequence A (D_A) or B (D_B) and progressively reduction in temperature (T_A), were found to be highly effective for producing fine to ultrafine-grained microstructures homogenously through the magnesium plate. Sample subjected

to D_A and T_A results in an improvement in yield strength and ultimate tensile strength by ~48.6% and ~1.7% respectively, while the elongation to failure decreased by ~64.8% as compared to the as-received sample. After annealing at 473 K for 1h, the changes to yield strength, ultimate tensile strength and elongation to failure are approximately +11%, -12% and +19% as compared to the as-received sample.

- 2) Deformation sequence D_B was found to be more effective as it requires a lower number of pressing to achieve a similar degree of total average strain. It was demonstrated that sample subjected to D_B and T_A can achieve a similar degree of grain refinement as compared to D_A and T_A .
- 3) Weakening in the basal texture was observed after each cycle of CGP in sample S1. In samples S1~S5, the basal intensities were redistributed away from ND towards RD-TD, while the prismatic and pyramidal intensities, which were initially distributed randomly around RD-TD, were shifted closer to the ND. The overall basal intensities and hence texture strengths were reduced after CGP as compared to the as-received sample.
- 4) Sample S6 exhibited an increase in basal strength as compared to the as-received sample. This was because of the higher degree of straining (~ 9.9) especially when most of the straining was carried out at a lower deformation temperature of 473 K in the last two cycles where basal slip and tensile twinning are the primary slip mechanisms.
- 5) Mechanical anisotropy in the annealed CGP plate (Sample S1-A) was determined and compared with commercial AZ31 plate and AZ31 plate subjected to different processing. The values of normal anisotropy ranked from highest to lowest: Normal rolling from hot extruded plate > DSR from hot extruded plate > rolled plate > annealed

CGP plate. > fully annealed plate. Generally, a low normal anisotropy value suggests a higher sheet formability in magnesium. The values of planar anisotropy ranked from highest to lowest: rolled plate> Normal rolling from hot extruded plate> DSR from hot extruded plate> fully annealed plate > CGP annealed CGP plate. A more positive planar anisotropy value suggests more non-uniform draw-in during deep drawing operation while a more negative value suggests a higher susceptibility towards fracture in the 45° direction of the plate.

Chapter 6 Dynamic recrystallization behaviour in CGP

The content of this chapter has been partially published in the below journal paper:

- K.S. Fong, D. Atsushi, M.J Tan, B.W. Chua, “Microstructure stability of a fine-grained AZ31 magnesium alloy processed by constrained groove pressing during isothermal annealing”, *Journal of Manufacturing Science and Engineering (Manuscript, MANU-16-1434, accepted for publication)*

The content in this chapter and in chapter 10 will be published in the follow papers

- K.S. Fong, M.J Tan, P. Farsid, S. Veena, Y.T. Tan, S.J. Bin F.L. Ng, “Influence of microstructure and recrystallization state on biocorrosion resistance of magnesium alloy processed by severe plastic deformation”. To be published in *Journal of Materials Research*

6.1 Introduction

Dynamic recrystallization (DRX) can occur readily during hot working of magnesium alloy, and therefore, this is useful for controlling of grain size to improve mechanical properties [113]. DRX and its influence on grain size are affected by processing conditions such as temperature and strain rate. [114-117]. This is commonly interpreted by using the temperature compensated strain rate Zener Hollomon (Z) parameter which relates temperature and strain rate to recrystallized grain size as represented by equation 6.1. Where $\dot{\epsilon}$ is the strain rate, T is temperature, R is gas constant, and Q is the activation energy for lattice diffusion of magnesium [76]

$$Z = \dot{\epsilon} \exp\left(\frac{Q}{RT}\right) \quad (6.1)$$

Mechanism of DRX is a subject of great importance and have been heavily reported over the years [64, 106, 118-121]. Galiyev et al. [118] investigated the dynamic

recrystallization behaviour of ZK60 at elevated temperatures and observed different operating mechanisms. It was reported that at low temperature, grain refinement was assisted by twinning, basal, and pyramidal $\langle c+a \rangle$ slip. At intermediate temperature, continuous dynamic recrystallization (cDRX) was dominant, whereby new grains were formed due to increasing cross-slip from basal to non-basal dislocations near the grain boundaries. At high temperature, nucleation of fine-grains occurred due to grain boundaries bulging and was controlled by dislocation climb. Ion et al.[119] described a mechanism known as rotation dynamic recrystallization (rDRX). It was reported that non-basal slips and $\langle c+a \rangle$ dislocations occurred at grain boundaries in Mg-08% Al alloy deformed at a temperature range of 425–600 K. This resulted in the formation and rotation of subgrain which subsequently developed into fine-grain with high angle grain boundary (HAGB) near the vicinities of the grain boundaries. In a more recent study by Yang et al. [120], it was observed that kink bands formed readily in AZ31 alloy at low strain which with continuous straining, led to the subdivision of grain in a manner similar to cDRX. Evidence of twin-induced DRX has also been reported [97, 106, 121]. Ma et al. [106] examined hot extruded AZ61 by electron backscatter diffraction (EBSD) and reported evidence of new grain formation at the sites of tensile $\{10\bar{1}2\}$ twin formation.

The growing interest in SPD processing of magnesium and its alloy is driven by the strength and formability enhancement through its exceptional grain refinement efficiency. In recent years, many papers investigated the recrystallization behaviours in SPD [69, 122-125] so as to understand its underlying grain refinement mechanism. Not surprisingly, different mechanisms have been observed. For example, it was reported that both

discontinuous dynamic recrystallization (dDRX) and cDRX were observed in accumulative back extrusion (ABE) process, which dominates in the early and later deformation stages respectively [123]. However, only cDRX was reported in equal-channel angular pressing (ECAP) process [69]. Several reports also indicate the role of rDRX and cDRX during SPD in processes such as accumulative roll bonding (ARB) [125], extrusion ECAP (EX-ECAP) [124] and cyclic extrusion compression (CEC) processes [122]. There are many factors that influence the recrystallization mechanisms such as the temperatures, strain rate, alloy composition and processing conditions. As such, depending on the processing conditions and techniques, the operating mechanisms can be different.

In the previous chapter, the effect of deformation and temperature sequence on the microstructure and mechanical properties were systematically examined and discussed in great detail. It was found that deformation and temperature sequence D_B and T_A were more effective in achieving fine-grained microstructure. Therefore, the objective of this chapter is to further investigate and discuss the mechanisms responsible for the grain refinement during CGP. The influence of temperature and strain rate on the recrystallized grain size was interpreted by Zener Hollomon (Z) parameter to establish the optimum processing window. With this knowledge, CGP under three cycles of pressing according to D_B and T_A was investigated. The microstructure evolution was examined by electron backscatter diffraction (EBSD) to characterize the grain boundary characteristics so as to understand the formation of subgrain and newly developed fine grain.

6.2 Experimental procedures

Single groove pressing tests were first performed to examine the influence of temperature and strain rate on average recrystallized grain size. The temperature and strain rate were varied from 423 ± 2 to 573 ± 2 K and from 0.1 to 10 s^{-1} , respectively. The samples for optical microscopy characterization were cold mounted, polished and chemically etched to reveal the microstructure. The microstructure and grain size were examined at the sheared zone (45° region) of the deform structure. The microstructures were examined at the thickness with the observation plane perpendicular to the transverse (TD) direction.

EBSD characterization of the microstructure was performed on the sample after each cycle of CGP. Three cycles of CGP were performed according to methods D_B and T_A . For clarity, the CGP pressing procedure and the dimensions of the groove die are presented again in Figure 6.1. The pressing temperatures were maintained at 503 ± 2 K in the first cycle and 453 ± 2 K in the last two cycles. The sample for EBSD characterization was prepared by mechanical grinding and polishing down to $1\text{ }\mu\text{m}$, followed by ion milling using JEOL cross-sectional polisher. The sample was immediately transferred into the Oxford Instrument HKL system for measurement to avoid oxidation. Microstructure was observed on the surface of the plate parallel to the rolling (RD) and transverse (TD) directions. Details of the CGP procedures and characterization techniques can be found in Chapter 3.

Figure 6.1: (a) Schematic of the CGP cycle (the black arrow indicates the initial RD with respect the grooves dies) and (b) dimensions of the workpiece after CGP

6.3 Relationship between Z parameter and grain size

Figure 6.2 shows microstructures observed in the sheared zone after a single groove pressing step at various temperature and strain rate. The sample that was groove-pressed at 423 K shows a heavily deformed structure (shear bands) with massive twinning (of lenticular morphology) at all strain rate. Very fine dynamic recrystallization (DRX) grain can be seen at some of the twinning sites as shown in Figure 6.3, which is an indication of twin-induced DRX. Twin interiors and boundaries are known to possess much higher distortion energy and therefore are favourable sites for nucleation of grains [117]. The plate groove-pressed at 423 K and 10 s^{-1} cracked partially due to excessive strain localization in these regions of the shear bands and heavy twinning.

As expected, twinning was not observed in the microstructures for the samples groove-pressed at higher temperatures from 473 to 573 K. This is because at temperature higher than 473 K, the critical resolved shear stress (CRSS) for prismatic slip becomes lower than CRSS for twinning ($\sim 3 \text{ MPa}$) [126]. And also when the temperature approaches 573 K, the CRSS for $\langle c+a \rangle$

slip (~ 6 MPa) become close to the CRSS for prismatic slip (~ 2 MPa) and basal slip (~ 0.5 MPa). Therefore, higher order slip systems can accommodate straining and more easily activated as compared to twinning. Incomplete dynamic recrystallization was also observed in the samples groove-pressed at 473 K and lower strain rate of 0.1 and 1 s⁻¹. The microstructure in these samples was heterogeneous, consisting of very fine recrystallized grains and larger grains from the initial microstructure. The microstructure of the sample groove-pressed at 473 K and 10 s⁻¹ exhibited homogenous fine grain structure. This indicates that the processing conditions are optimum because grain coarsening due to static recovery, static recrystallization and metadynamic recrystallization which may occur during preheating and/or immediately after straining are minimized. Generally, the average grain size increases with higher pressing temperature and the microstructure is less homogenous.

Figure 6.2: Microstructures observed in the samples grooved-pressed at different temperature and strain rate

Figure 6.3: magnified view of sample groove-pressed at 423 K and 10 s^{-1} ; arrows indicate fine recrystallized grains.

The relationship between temperature and strain rate and average grain size is examined using Zener-Hollomon (Z) parameter as shown in equation 6.1. In the calculation of the Z -parameter, the activation energy Q for lattice diffusion in pure magnesium is used (135 kJ/mol) [76]. Figure 6.4 shows the relationship between Z -parameter and recrystallized grain size. The slope of the line is given quantitatively by:

$$\ln d = 4.8 - 0.09 \ln Z \quad (6.2)$$

Figure 6.4: Plot of the relationship between grain size and Zener-Hollomon parameter in the sample subjected to single groove pressing

By using this relationship together with microstructures analysis shown in Figure 6.2, it is recommended that Z-parameters should fall within the range as indicated by the green dotted box in Figure 6.4. Z-parameters at the extreme end of the plot as indicated by the red dotted boxes should be avoided. Too high a Z parameter (low temperature and high strain rate) generally leads to a heavily deformed/ unrecrystallized structure which causes excessive strain localization and premature failure at repeated deformation. Using too low a Z parameter (high temperature and low strain rate) result in heterogeneous microstructure due to excessive grain growth during preheating and post-deformation.

6.4 Grain orientation map in each cycle of CGP

Based on the earlier findings, it is recommended that the processing temperature is reduced after each cycle to obtain very fine microstructure and carried out at a high enough

strain rate with keeping the temperature as low as possible. As such, current study was conducted using only three cycles of CGP which can achieve an average total strain of ~ 7.4 . The temperature in the first cycle was reduced to 503 K and repeated for another two cycles at 453 K. 453 K is the lowest possible temperature to avoid fracture. The strain rate chosen was approximately 2 s^{-1} (recommended between 1 to 10 s^{-1}).

Figure 6.5 shows the orientation mapping of the as-received sample and the samples after each cycle of CGP. Figure 6.6 shows corresponding average grain size distribution in these samples. From Figure 6.5a, the microstructure of the as-received sample consisted of coarse grain greater than $20 \text{ }\mu\text{m}$ and fine grain less than $10 \text{ }\mu\text{m}$ with an average grain size of $15 \pm 0.1 \text{ }\mu\text{m}$. The orientations of the grains were quite close to each other as indicated by the similarity of the grain colours. After the first cycle of CGP (Figure 6.6b), a more random grain orientation developed due to repeated straining and higher occurrences of dynamic recrystallization [108]. The microstructure was heterogeneous and displayed a typical appearance of a partial dynamic recrystallized microstructure because of the insufficient straining. Some of the dynamic recrystallized grains had grown in size due to the higher pressing temperature. From Figure 6.6a-b, it can be seen that most of the grains larger than $12 \text{ }\mu\text{m}$ in the as-received samples were reduced. Generally, a higher fraction of fine grains was observed (Figure 6.5b) and the average grain size was determined to be $3.3 \pm 0.1 \text{ }\mu\text{m}$.

The microstructure became more homogeneous after the second cycle of CGP as shown in Figure 6.5c. The frequency of fine grains of size less $2 \text{ }\mu\text{m}$ increased significantly as shown in Figure 6.6c and the average grain size was $2.4 \pm 0.1 \text{ }\mu\text{m}$. The grain boundaries were jagged with poorly-defined boundaries in the grain interiors. Interestingly, a strong

texture developed after the second cycle. Most of the grains were red in colour which indicates that their basal planes were oriented along the RD-TD direction. This suggests that basal slip dominated deformation occurred when the deformation temperature was reduced from 503 K to 453 K. This resulted in the rotation of the slip planes parallel to the loading direction, which predominantly lie along the in-plane direction.

The homogeneity of the microstructure improved greatly after the third cycle of CGP as shown in Figure 6.5d. Grain boundaries were observed to be well-defined with majority grains exhibiting a non-basal orientation, which was similar to the first cycle. This suggests a higher occurrence in non-basal slips in this cycle which promoted increased lattice rotation. It was reported that fine grain suppresses twinning [16], and increases cross slips at the grain boundary so as to satisfy grain compatibility [17]. The frequency of fine-grains less than 2 μm increased moderately as shown in Figure 6.6d and a final average grain size of $1.8 \pm 0.1 \mu\text{m}$ was obtained. This final microstructure consisted of submicron grains and fine grains in the range of 0.4-1.0 μm and 1.0-6.0 μm , respectively. The result indicates that the most significant grain refinement occurred in the first cycle while continued at a slower rate, but resulted in a more homogeneous microstructure, at higher cycles of CGP.

Figure 6.5: Orientation maps (FESEM-EBSD) of (a) as-received sample and CGP samples after (b) first cycle, (c) second cycle, and (d) third cycle.

Figure 6.6: Grain size distributions; (a) as-received sample, and CGP sample after (b) first cycle, (c) second cycle, and (d) third cycle.

6.5 Texture in each cycle of CGP

The textures of the as-received sample and samples after each cycle of CGP determined from the microtexture analysis by EBSD are shown in Figure 6.7. Figure 6.7a shows the pole figure of the as-received sample which exhibited a typical rolling texture whereby the basal peak intensities were located near the center and spread towards RD. After the first cycle of CGP (Figure 6.7b), the basal intensities were redistributed away from center towards the RD-TD directions, and the maximum intensity was reduced from 11.0 to 5.0 multiples of random distribution (m.r.d). The prismatic intensities, which initially located around the RD-TD, were shifted closer to ND. This weakening/or randomization of the texture can be attributed to the repeated shear strain accommodated by non-basal slip modes which leads to the formation of new grains through dynamic recrystallization (DRX) of non-basal orientation. A similar texture weakening/randomization was also reported by T. Al-Samman and G. Gottstein during hot compression of AZ31 alloy when deformed at a much higher temperature and a lower strain rate of 673 K and 10^{-4} s^{-1} respectively [117]. The authors attributed this to the higher activities of DRX which were assisted by pyramidal and prismatic slips. The texture randomization through the formation of non-basal DRX and subsequent preferential growth of these grains due to long exposure time at elevated temperature cannot be neglected [127, 128]. In CGP, the high straining facilitates DRX while repeated deformation at elevated temperature led to the growth of non-basal grains as seen in Figure 6.5b.

Similar to the observation of the grain orientation map in Figure 6.5c, the basal intensity strengthened significantly after the second cycle of CGP as shown in Figure 6.7c. The basal intensities were realigned to the middle of the pole figure, while the prismatic

intensities were weakly distributed around the RD-TD. The maximum basal intensity increased from 5.0 to 25 m.r.d. This texture strengthening was supposedly caused by the reduction in deformation temperature from 503 K to 453 K whereby there is a change from non-basal slip to basal slip and twinning. The complex interactions between basal slip and twinning contributed to the strong basal texture in the microstructure. As explained by the simulation study in Chapter 4, the plate processed by method D_B was subjected to compression along the plate ND and tensile stretching along the RD-TD, in addition to shear deformation. It is well-known that grains which have their c-axis initially perpendicular to the compression direction can undergo large lattice rotation due to tensile twinning and this can cause the c-axis to realign almost parallel to the compression direction [129, 130]. On the other hand, tensile strain along the RD-TD are accommodated by basal slip which increases basal plane alignment along the loading direction [109].

Interestingly, the basal texture decreased again after the third cycle of CGP as shown in Figure 6.7d. The maximum basal intensity decreased to approximately 4 m.r.d which was slightly lower than that in the first cycle. Both the basal and prismatic intensities were distributed around RD-TD. The average grain size was reduced significantly after the second cycle. Further CGP cycle, in the already fine-grained structure, likely promoted cross-slip from basal to non-basal planes at the grain boundaries in order to satisfy stress compatibility [17]. Therefore, DRX facilitated by non-basal slip resulted in the weakening of the basal texture.

Figure 6.7: Pole figures of (a) as-received sample and CGP samples alloy after (b) first cycle, (c) second cycle, and (d) third cycle.

6.6 Grain boundary characteristics

The grain boundary maps and misorientation plots after each cycle of CGP are shown in Figure 6.8 and Figure 6.9, respectively. In Figure 6.8, the low-angle boundaries (LAGB) in the range of 2-15° are delineated by white lines and the high-angle boundaries (HAGB) above 15° are delineated by black lines. The magnified views of the grain boundaries indicated by red circles in Figure 6.8a-c are shown in Figure 6.8d-f.

From Figure 6.8a and Figure 6.8d, it can be seen that a majority of the grains were observed to be bounded HAGB after the first cycle. Some of the grain interior displayed a higher density of LAGB. This observation agrees well with the misorientation distribution plot after the first cycle as shown in Figure 6.9, whereby the frequencies of low (<15°) and high misorientation angles (>70°) were higher as compared to that of the as-received sample. From Figure 6.8b and Figure 6.8e, LAGB increased significantly in the microstructure after the second cycle of CGP. These LAGB were distributed almost uniformly throughout the microstructure. This observation agrees well with the sharp increase in low misorientation

frequencies which occurred at the expense of high misorientation frequencies as shown in Figure 6.9. After third CGP cycle, the microstructure exhibited a lower fraction of LAGB in the grain interior as shown in Figure 6.8c and Figure 6.8f. This explains the decreased in low misorientation frequencies and corresponding increased in high misorientation frequencies as shown in Figure 6.9. The result indicates that most of LAGB from second CGP cycle had developed into fine grains bounded by HAGB after third CGP cycle through DRX.

Figure 6.8: Grain boundary maps of the CGP samples after (a) first cycle, (b) second cycle and (c) third cycle; LAGB and HAGB are delineated by white ($2-15^\circ$) and black ($>15^\circ$) lines

respectively; Magnified view of the grain boundary maps indicated in the red circles in (a to c) are shown in (d to f).

Figure 6.9: Misorientation distribution plots of the as-received sample and samples after each cycle of CGP

6.7 Mechanical properties

The measurements of the stress-strain curves in the RD direction of the as-received sample and samples after each cycle of CGP are shown in Figure 6.10. The elongation to failure in RD direction after the first cycles was increased from 18.8 ± 1.7 to $25 \pm 1.4\%$. However, the elongation to failure in the TD direction was marginally reduced from 20.8 ± 0.8 to $18.7 \pm 1.1\%$. This anisotropy was attributed to the changes in texture whereby

more grains are more favourably aligned along the RD than TD direction for slip. Generally, ductility was maintained was because of the reduction in strain hardening effect by SRX which occurred readily during the pre-heating and post-deformation stages of the forming cycle at the higher forming temperature. After the first cycle, the yield strengths in the TD and RD directions were increased from 140 ± 9 and 175 ± 4 MPa to 205 ± 10 and 217 ± 6 MPa. The stress-strain curve became increasingly anisotropic after the second cycle. The elongation to failure became significantly lower in the TD ($4\pm 0.5\%$) as compared to the RD ($24\pm 0.4\%$) direction due to the development of a strong basal texture as shown in Figure 6.7c. The yield strengths in the TD and RD directions were increased to 212 ± 15 and 240 ± 11 MPa, respectively. After the third cycle, the elongation to failure in TD and RD directions were decreased drastically to $0.9\pm 0.1\%$ and $1.6\pm 0.1\%$, respectively, due to the significant strain hardening which promoted brittle crack nucleation and plastic strain instability [131]. The yield strengths in the TD and RD directions were increased to 223 ± 6 and 243 ± 4 , respectively.

The above result suggests that CGP repeated to three cycles was necessary to produce more homogenous microstructure whereby some of the fine grains were completely recrystallized and were free of subgrain/dislocation structures. However, the severely low ductility limits practical applications. Therefore, post-annealing treatment is necessary to recover the ductility. This was investigated and discussed in the later chapter.

Figure 6.10: True stress-strain curves of as-received sample and sample after each cycle of CGP in the (a) Rd and (b) TD.

6.8 Dynamic recrystallization behaviour

From the observation of grain boundary maps after the first cycle, as shown in Figure 6.8a, it can be seen that many of the LAGB were densely located within larger grains. These LAGB are microbands (MB) which are essentially dislocation boundaries and a form of geometrically necessary boundaries (GNB) [56, 130, 132, 133]. Some of these LAGB propagated through the grain interior as indicated by the white and black arrows in Figure 6.8d, and resulted in the formation of subgrain boundaries. Furthermore, it was observed that the fine grains (in Figure 6.5b) were bounded by HAGB and were close to the size of the subgrains observed in Figure 6.8a. This observation suggests that new grains were formed through the process of continuous dynamic recrystallization (cDRX) [64, 134]. cDRX is essentially a recovery process, whereby strain-induced dislocations re-arrange by glide/climb into subgrain boundaries with LAGB. Repeated straining increases the misorientation of LAGB leading to the formation of fine grains bounded by HAGB. In addition, fine grains with high misorientation (Figure 6.5b.) were observed near the vicinity of large grain boundary as indicated by the blue arrows in Figure 6.8a which suggests that

rotational dynamic recrystallization (rDRX) was responsible. In rDRX, fine grain develops continuously as a result of minor sub-grain migration, and dynamic recovery adjacent to the severely distorted grain boundaries as a result of grain compatibility stresses. rDRX commonly occurs at a lower deformation temperature [119] and is associated with the higher activities of non-basal slips at the grain boundaries. It is worth mentioning that no recrystallized grains were observed along pre-existing grain boundaries in a “necklace-like” manner due to grain boundary bulging through discontinuous dynamic recrystallization (dDRX) [116, 118, 123]. Grain boundary budding occurs mainly at higher temperatures ($>300\text{ }^{\circ}\text{C}$), where the activation energy for plastic flow approaches the activation energy for volume self-diffusion [126].

After the second cycle of CGP, a higher fraction of LAGB was observed throughout the microstructure. Continuous straining at a lower temperature of 453 K increased the dislocations density in the grains and resulted in a higher fraction of LAGB/subgrains. Further straining in the third cycle resulted in a higher fraction of fully recrystallized fine grains as observed in Figure 6.8c. Most of the subgrains with LAGB in the second cycle developed into fine grains with HAGBs through cDRX. In both the second and third cycle, because of the smaller grain size and higher constraints imposed by the neighbouring grains, most of the LAGB were observed to propagate through the grain interior. This observation suggests that grain subdivision through cDRX was dominant the last two cycles when the grains were small as compared rDRX which was observed in the first cycle when the grains were large.

6.9 Summary

- 1) Constrained groove pressing (CGP) to three cycles using method D_B and under reducing deformation temperature from 503 to 453 K was effective for producing homogeneous fine-grained microstructure in AZ31 magnesium plate. The average grain size was $1.8 \pm 0.1 \mu\text{m}$ and contained submicron grains in the range 0.4-1 μm . A significant grain refinement was observed in the first cycle but became moderate in the second and third cycle.
- 2) A cyclic change in texture was observed under each cycle of CGP. This was caused by a change in the active slip systems from non-basal to basal slip and twinning and vice versa due to the change in processing temperature and grain size. Dynamically recrystallized grains of non-basal orientations resulted in the weakening of the basal texture as seen in the first and second cycles.
- 3) The maximum yield strength was $243 \pm 4 \text{ MPa}$ in the RD direction. However, the elongation to failure was drastically reduced to $1.6 \pm 0.1\%$. Optimization of the annealing heat treatment is necessary and will be discussed in the later chapter.
- 4) Continuous dynamic recrystallization (cDRX) was found to be the dominant grain refinement mechanism, whereby misorientation of LAGB increased continuously during straining which eventually led to the formation of fine grains bounded by HAGB with high misorientation. Rotational dynamic recrystallization (rDRX) was observed mainly in the first cycle when the average grain size is larger.

Chapter 7 Thermal stability of CGP microstructure

The content of this chapter has been published in the below journal paper:

- K.S. Fong, D. Atsushi, M.J Tan, B.W. Chua, “Microstructure stability of a fine-grained AZ31 magnesium alloy processed by constrained groove pressing during isothermal annealing”, *Journal of Manufacturing Science and Engineering (Manuscript, MANU-16-1434, accepted for publication)*

7.1 Introduction

The severely deformed material produced by SPD often contains fine grains with high lattice distortion and internal stresses. As such, the strain-induced fine grain boundaries migrate easily when exposed to high temperatures, resulting in rapid grain growth. In recent years, the grain growth kinetics of SPD materials have been investigated by several authors [73, 75, 77, 135, 136]. Young et al. [136] examined the activation energies (Q) by isochronal and isothermal annealing of the twin roll cast AZ31 alloy after ECAP and FSP. It was suggested, from the comparison of activation energies, that the ECAP (154 kJ/mol) resulted in better microstructural thermal stability than the FSP (42-82 kJ/mol) in the temperature range of 673-773K. Kim et al. [135] investigated the activation energy of AZ31 alloy after ECAP by isochronal annealing. The activation energies were measured to be 70.1, 24.5, and 114.3 kJ/mol in the temperature ranges of 473-523, 523-673 K, and 673-773 K. Straska et al. [75] also reported a similar activation energies in the low, intermediate, and high temperatures annealing of the as-cast AZ31 alloy after extrusion and equal-channel angular pressing (EX-ECAP). In another study by Ma et al, [77], the activation energy of AZ31 alloy processed by ACB was found to be 105 kJ/mol in temperature range 623-723K. It can be

seen from these studies that the activation energies are strongly dependent on, not only the range of annealing temperature, but also the material texture and grain boundaries characteristic resulted from different processing. Therefore, the aim of this study is to clarify the microstructure stability of fine-grained AZ31 magnesium alloy produced by constrained groove pressing. This technique is attractive because of its simple processing and tool design. The process is also possible to scale-up by adapting it into rolling process. The temperature range chosen in this study is between 473 and 623 K, where hot forming is usually performed, to examine the grain growth kinetics and determine the activation energy.

7.2 Experiment procedures

Magnesium alloy plate was subject to three cycles of CGP. The deformation method used was “D_B”. The pressing sequences and deformation temperatures under each cycle are described in details in Chapter 3. Tensile test were conducted using a gauge length of 25 mm, width of 6 mm, and thickness of 1.5 mm that were machined along the initial rolling (RD). The isothermal annealing heat treatments were conducted using an electric furnace, and the temperature fluctuation is controlled to be within ± 2 °C. The samples, of dimension 10×10 mm, were sectioned from the plate after three cycles of CGP. These samples were annealed at temperatures ranging from 473 to 623 K in different time from 10 to 180 min. After annealing, the samples were removed from the furnace, and quenched in water to preserve the microstructures. A minimum of two samples were used in each annealing condition.

Electron backscattered diffraction (EBSD) was performed on the sample after three cycles of CGP, with the observation plane parallel to RD-TD directions. The surface was prepared by mechanical grinding, polishing down to 1 μm , and ion milling using JEOL cross-sectional polisher. The sample was immediately transferred into the Oxford Instrument HKL system for measurement to avoid oxidation. Microstructure was observed on the surface of the plate parallel to the rolling (RD) and transverse (TD) directions. Details of the CGP procedures and characterization techniques can be found in Chapter 3.

7.3 Microstructure after CGP

The microstructures of as-received and CGP-processed AZ31 alloy after first, second, and third cycle are shown in Figure 7.1a-d. From Figure 7.1a, the initial microstructure in the as-received material was found to be equiaxed and the average grain size was $15 \pm 1 \mu\text{m}$. A significant grain refinement can be seen in the first cycle, in which the average grain size was reduced significantly from $15 \pm 1 \mu\text{m}$ to $5 \pm 1 \mu\text{m}$ as shown in Figure 7.1b. However, the microstructure was heterogeneous, because of higher pressing temperature and insufficient straining. After the second cycle, the microstructure homogeneity was improved significantly, and average grain size was decreased to $3.8 \pm 1 \mu\text{m}$. The grain boundaries became increasingly jagged due to higher internal stresses in the material. After the third cycle, the final average grain size was reduced to $1.8 \pm 1 \mu\text{m}$ as shown in Figure 7.1d.

Figure 7.1: Microstructure of the (a) as-received, and CGP-processed AZ31 alloy after (b) first, (b) second, and (d) third cycle

Figure 7.2a shows the inverse pole figure (IPF) map of AZ31 alloy after three cycles of CGP. The final microstructure was observed to be bimodal, and consisted of both fine and large grains in the range of 0.4-1.0 μm and 1.0-6.0 μm respectively. The grains possessed different crystallographic orientation because of the repeated shear deformation and dynamic recrystallization during CGP. The microstructure also exhibited a wide spread of grain misorientation as seen in the misorientation distribution plot in Figure 7.2b. A misorientation peak was seen at around 86° and this indicates that some of the grains may have been originated from extension twinning [106]. The twin lost their lenticular morphologies due to twin boundary migration followed by coalesce and the growth of twin

during large straining. Furthermore, a significant misorientation peak was also observed at around 3° , which suggest a high fraction of low angle grain boundaries (LAGB) in the microstructure. This distribution of LAGB (in the range of $2\text{--}15^\circ$ as delineated in white lines) are depicted in the grain boundary map shown in Figure 7.2c. These LAGB are essentially subgrains and dislocation boundaries that developed in the grains during large straining [137]. This suggests that the formation of new grains of HAGB occurred continuously from subgrains of initially LAGB, through the process of continuous dynamic recrystallization (cDRX) [64, 134].

Further details of the microstructure were revealed by the grain orientation spread shown in Figure 7.2d. The component estimates the extent of deformation by measuring the degree of orientation change between every pixel in the grain and the grain's average orientation. As expected, strain anisotropy was present in the microstructure after CGP, due to inhomogeneous straining and the different rate of dynamic recovery and recrystallization in the process. The higher deformation (colored green to red) regions basically coincide with grains with a higher density of LAGB (Figure 7.2c), while the low deformation regions (colored blue) are located within larger grains which had recrystallized and grown in size.

It is well known that the recrystallization in the hot working of magnesium alloy is strongly dependent on temperature and strain rate [113, 115]. In this work, the strain rate was kept constant, and fine grains were primarily achieved by reducing the deformation temperature. High shear strain had to be imparted in the material in order to produce homogeneous grain refinement throughout the plate. At the same time, deformation had to be performed at the lowest possible temperature, without initiation of cracks in the material.

The current method of pressing, using a 90° workpiece rotation (orthogonal pressing), was found to be effective in achieving high cumulative strain using a lesser number of pressings. Fatigue cracking was also avoided, which occurs more easily in the conventional CGP [51] due to the repeated tensile stresses in the same material regions; regions between the undeformed and shear zone in this process [138].

Figure 7.2: EBSD measurement of the microstructure after CGP: (a) orientation map, (b) misorientation distribution profile, (c) grain boundary map (LAGB in the range of 2-15° were delineated by white lines and HAGB above 15° were delineated by black lines) and (d) grain orientation spread map (highest in red)

7.4 Texture and mechanical properties

Figure 7.3a shows the pole figures of as-received material which displayed a typical rolling texture with a dominant basal texture {0002} component. The initial maximum basal

intensity was 11.0 MRD (multiples of random distribution). After three cycles of CGP, a redistribution of the basal intensities away from the normal direction (ND) towards the rolling (RD) and transverse direction (TD) could be observed (Figure 7.3b). The prismatic intensities which were initially observed to be randomly distributed around RD-TD had also redistributed more towards ND. The basal texture was significantly weakening with the maximum basal intensity reduced to 4 MRD.

Figure 7.3: Pole figures of the (a) as-received and (b) CGP-processed alloy

The stress-strain curves of the as-received and CGP-processed AZ31 alloy after first to third cycle are shown in Figure 7.4. After three cycles of CGP, the yield strength in the RD and TD increased from 175 ± 4 to 243 ± 4 MPa and 141 ± 9 to 223 ± 6 MPa, as compared to the as-received material. Significant work hardening after the third cycle caused a sharp decrease in elongation to failure in both RD and TD, from 19 ± 1.7 % to 1.6 ± 0.1 % and 1 ± 0.1 % respectively. The stress-strain curves are observed to be anisotropic, whereby elongation and yield strength are lower in the TD than RD. This anisotropy in mechanical properties is attributed to the initial rolling texture of the magnesium sheet which favors

deformation along the RD. Such anisotropy in the stress-strain curves was also similarly reported in the ARB process of AZ31 alloy [91, 125].

Figure 7.4: True stress-strain curves of the as-received and CGP-processed AZ31 alloy after first to third cycle along the (a) RD, and (b) TD directions

7.5 Abnormal grain growth during annealing

The thermal stability of the microstructures after CGP processing was investigated by isothermal annealing at temperatures in the range from 473 to 623 K for different time from 10 to 180 min. Figure 7.5 and Figure 7.6 shows the optical micrographs of annealed microstructures and the corresponding grain size distribution plots normalized by the average grain size. The microstructures at 120 min were not drastically different from 180 min and hence were omitted to make the presentation more concise. As shown in Figure 7.5, grain growth was found to be heterogeneous from 473 to 573 K, resulting in the development of both small and large grains in the microstructure. This was due to the difference in the strain energy as seen in Figure 7.2d which resulted in different driving force for grain growth during annealing. A few abnormally large grains were visible in the samples annealed at 673 K for longer duration. To qualitatively determine if abnormal grain growth

had occurred, the normalized grain size distribution were examined [72, 139]. During normal grain growth, the grains coarsen uniformly and the shapes of the normalized grain size distribution remain consistent with annealing time. In the case of abnormal grain growth, only a few grains increase significantly in size as compare to the average and this result in a loss of self-similarity, whereby the width of the distributions becomes broader with longer annealing time. As shown in Figure 7.6, the normalized grain size distribution at annealing temperatures from 473 to 573 K and different time remained log-normal despite the heterogeneous microstructure. This suggests that the numbers of small and large grains in the microstructures were almost equal. The width of the distribution also remained nearly the identical over different annealing time, which suggests normal grain growth. At 623 K, the width of the distribution increased after 120 min and slightly shifted to one side which is a clear indication of abnormal grain growth.

To understand the above observation, X-ray diffraction analyses were performed on the annealed samples. Figure 7.7 shows the relation between the peak intensity ratio of (0002)/(10-11) against annealing time for different temperatures measured by X-ray diffraction analysis. The ratio of (0002)/(10-11) was found to increase significantly with annealing time for temperatures from 473 to 573 K. This indicates a strengthening of the basal texture during normal grain growth. Interestingly, the ratio of (0002)/(10-11) was significantly weaker with annealing time at temperature of 623 K as compared to the lower annealing temperatures. This observation suggests that non-basal grains increases at the expense of basal grains during abnormal grain growth, which caused the ratio of (0002)/(10-11) to decrease. This observation was also similarly reported during static annealing of a

hot-rolled AZ31 magnesium alloy sheet [127]. It was suggested that non-basal grains had faster grain growth kinetic and consumed the surrounding basal grains. Humphrey et al. [72] had also explained that if a grain of a different texture orientation is present, the differences in misorientation will introduce boundaries of higher energy and mobility, promoting preferential grain growth. In the current study, it is postulated that the compounded effect of an accelerated grain growth at higher temperatures together with the presence of non-basal grains in an environment of basal grains, increases the propensity for abnormal grain growth.

Figure 7.5: Microstructures at different annealing temperatures and time

Figure 7.6: Superposition of normalized grain size distributions at (a) 473 K, (b) 523 K, (c) 573 K and (d) 623 K for different annealing time

Figure 7.7: Relationship between texture and annealing time at different temperatures: (a)

473 K, (b) 523 K, (c) 573 K and (d) 623 K

7.6 Grain size and hardness after annealing

Figure 7.8a and b shows the variation of hardness in samples at different annealing temperatures for different time and the corresponding variation in average grain size, respectively. For all the annealing temperatures, the decrease in hardness was found to be most rapid in the first 10 min, while becoming more gradual at longer duration. This observation corresponds well with the rapid increase in grain size in the first 10 min as compared to the longer time. The above observation suggests that recrystallization occurred rapidly in the first 10 min due to the rapid annihilation of dislocation, while subsequent grain growth occurs at a slower pace, and is mainly driven by high grain boundary energies of the fine-grained structures. It should be noted that despite the rapid grain growth, the grains remained reasonably fine ($< 8 \mu\text{m}$) at all annealing temperatures and for time less than 30 min.

Figure 7.8: Plot of (a) hardness against time, and (b) average grain size against time at different temperatures

7.7 Grain growth kinetic

Grain growth kinetic was analyzed by using equation proposed by Burke and Turnbull [140]. It was deduced that the grain growth is primarily driven by the driving pressure that arises only from the curvature of the grain boundary and its kinetics can be described by the general equation:

$$D^n + D_0^n = kt \quad (7.1)$$

Where D is the average grain size after grain growth, D_0 is the average initial grain size, n is the grain growth exponent, t is the annealing time, and k is grain growth constant that can be determined from the Arrhenius equation in the form:

$$k = k_0 \exp\left(-\frac{Q}{RT}\right) \quad (7.2)$$

Where k_0 is a constant, Q is the activation energy for grain growth and R is the gas constant. Based on Burke and Turnbull analysis, n is theoretically equivalent to 2. In practice, n is well above 6.2, and varies with temperature and composition. Several factors such as second-phase pinning, texture, and solute drag on boundaries have been attributed to the higher n values [72].

To determine n , the average grain size data as shown in Figure 7.8 were used in this analysis. Average grain size measurements were performed on at least three different locations on each sample. By taking derivative respect to t and natural logarithm, eq. (7.1) can be re-written as:

$$\ln\left(\frac{dD}{dt}\right) = \ln\left(\frac{k}{n}\right) - (n-1)\ln(D) \quad (7.3)$$

The n values at different temperature was determined from of the slopes of the plots of $\ln(dD/dt)$ against $\ln(D)$ as shown in Figure 7.9a. Therefore, the n values were calculated to

be 3.8, 4.2, 6.9, and 6.8 at 473, 523, 573, and 623 K respectively. n is observed to be larger at higher temperatures. A higher n values at higher temperature suggests a change in the grain growth kinetic due to a stagnation of grain growth. This is likely due to abnormal grain growth and development of a stronger texture which reduces driving pressure for grain growth [72, 141]. It was also suggested that grain boundary pinning due to the presences of second-phase particles at higher temperature can lead to a higher n value [142].

To work out the activation energy, Q , equation (7.2) was used and by taking natural log, the equation takes the form:

$$\ln(k) = \ln(k_0) - \frac{Q}{RT} \quad (7.4)$$

The k values were first determined from the slopes of the fitted lines from the plot of $D^n - D_0^n$ against t using equation (7.1) as shown in Figure 7.9b. Here n is taken as a constant value and is equal to 5.4 based on the average of n values calculated. The k values were then substituted into equation (7.5) and this allowed the plot of $\ln(k)$ against $1/T$ to be established as shown in Figure 7.9c. Q was then determined from the slope, $-\frac{Q}{R}$, of the plot and was estimated to be 27.8 kJ/mol.

The Q obtained in this study is considerably lower than that for lattice self-diffusion in pure Mg ($Q_L=135$ kJ/mol) [143], and for grain boundary diffusion in pure magnesium ($Q_{gb}=92$ kJ/mol) [144]. In our temperature range of 473-623 K, $Q = 0.3Q_{gb}$ and closely match the value determined by Straska et al. [75] ($Q = 0.36Q_{gb}$), Kim et al. [135] ($Q = 0.27Q_{gb}$), and Wang et al. [145] ($Q=0.28Q_{gb}$). In these studies, n was assumed to be equal to 2. If the same n value were used in current computation, the activation energy will be slightly smaller, but does not change the conclusion that activation energy is abnormally low. Since

n is known to be much higher in most alloys, and especially in fine-grained materials [72], the estimation of Q in this work was preferably based on the average n value.

Figure 7.9: Plot of $\ln(dD/dt)$ against $\ln(D)$ (a), $D^{5.4} - D_0^{5.4}$ against annealing time (b), and $\ln K$ against $1000/T$ (c)

Different views have been offered to explain why Q value is much lower. Wang et al. [145] attributed the abnormally low Q to un-recrystallized grains with non-equilibrium grain boundaries which enhanced atomic mobility. Kim et al. [135], however, reported that such non-equilibrium boundaries were absent and attributed the low Q value to the invalid assumption of constant k_o (eqn. 7.2). It was reasoned that k_o should decrease with increasing temperature since k is related to diffusivity and dislocation density is a factor affecting k_o . In the present study, un-recrystallized microstructure was also not observed. The

microstructure after three cycles of CGP contains only well-defined grains and subgrains boundaries (Figure 7.2c). Subsequent annealing only resulted in further grain coarsening with well-defined grain boundaries and without any observation of un-recrystallized structures (Figure 7.5). Hence, the argument of enhanced atomic mobility of the non-equilibrium boundaries cannot explain the low Q value in this study. Therefore, it is more likely that k_o is not constant and this is because the dislocation density decreases with increasing temperature which caused an underestimated Q . Furthermore, it is observed that most of the fine grains contained LAGB which were essentially subgrains and dislocations remained in the structure due to incomplete dynamic recovery and recrystallization (Figure 7.2a-d). This increased the strain anisotropy and the driving force for grain growth, which explains the rapid increase in grain size during annealing and low Q value.

7.8 Summary

The grain growth kinetics were examined at the temperature range from 473 to 623 K, and for 10 to 180 min. This temperature range is the typically used in the hot forming of magnesium and annealing process. Hence, the understanding of microstructure stability at these temperatures is important. The results are as follows:

- 1) The microstructure after three cycles of CGP contained fine and large grains in the range of 0.4-1.0 μm and 1.0-6.0 μm , respectively. From the grain boundary map and misorientation distribution, the microstructure was found to contain a high fraction of low angle grain boundaries (LAGB). These were subgrains and dislocations which remained in the microstructure due to incomplete dynamic recovery and

recrystallization. This also resulted in the strain anisotropy as indicated from the grain orientation spread (GOS) map.

- 2) Abnormal grain growth occurred at 623 K as observed from the micrographs and indicated in the normalized grain size distribution. From the X-ray diffraction analysis, it was found that the peak intensity ratio of (0002)/(10-11) was significantly lower at 623 K as compared to the lower temperatures. This suggests an increase in non-basal grains at the expense of basal grains during abnormal grain growth.
- 3) From the analysis of the grain growth equations, the activation energy was estimated to be 27.8 kJ/mol. This activation energy was considerably lower as compared to the activation energy for lattice self-diffusion and grain boundary diffusion in pure magnesium. The result also suggests that despite the lower microstructure stability and rapid grain growth in the CGP-processed alloy, the resulting grains remained smaller than the as-received material and especially at the shorter annealing time.

Chapter 8 Effect of CGP and short duration post-annealing on tensile flow behaviour at elevated temperature

The content of this chapter has been published in the below journal paper:

- *K.S. Fong, D. Atsushi, M.J Tan, B.W. Chua, “Tensile flow behaviour of AZ31 magnesium alloy processed by severe plastic deformation and post-annealing at moderately high temperatures”, Journal of Materials Processing Technology, vol. 246 (2017), pp.235–244*

8.1 Introduction

Forming of magnesium alloys is commonly performed at elevated temperature because of its poor room temperature formability, in which plastic deformation is limited to basal slip and mechanical twinning. In automotive manufacturing, magnesium alloy sheets are typically hot stamped at high temperature close to 623 K [146] where higher order prismatic and pyramidal slips are active due to the significant reduction in their critical resolved shear stresses (CRSS) [105]. For more complex panels shape forming, superplastic forming is commonly employed. This process is typically performed at above 623 K where additional deformation mechanism by grain-boundary-sliding (GBS) can occur [147, 148] to bring about a significant enhancement of formability. Forming of magnesium sheet at high temperature escalates the manufacturing cost because of various reasons such as complex heating system, slow cycle time, high energy consumption, and the need to remove solid lubricant after forming operation. Therefore, lowering the processing temperature of magnesium alloy by formability improvement to achieve complex shape forming is highly

desirable.

Many efforts have been devoted to improving the formability of magnesium alloys using methods such as severe plastic deformation (SPD) [75, 98, 149-151], asymmetric rolling (ASR) [152, 153], cold pre-forging [154], and cyclic bending-unbending (CBU) [155]. SPD particularly attracts a lot of attention because of its ability to impart large plastic strain in bulk metallic material without significantly changing workpiece geometry [45]. These techniques are capable of producing ultrafine-grain in the range of submicrometer and nanometer microstructure which lead to superplastic properties [156-158]. Equal-channel angular pressing (ECAP) [159, 160] and high-pressure torsion (HPT) [161] are among the most promising SPD methods for achieving fine grains and superplasticity in magnesium alloys. For examples, low-temperature superplasticity (LTSP) was achieved in ZK10 after ECAP where an elongation to failure of 550% was measured at a temperature of 473 K and initial strain rate of $1 \times 10^{-4} \text{ s}^{-1}$ [160]. It was reported that deformation mechanisms lie in the transition region from GBS at low strain rates to viscous glide dislocation at high strain rates. In another work, both LTSP (e.g. 760% at 423 K and of $1 \times 10^{-4} \text{ s}^{-1}$) and high strain rate superplasticity (HSRSP) (e.g. 860% at 573 K and of $1 \times 10^{-2} \text{ s}^{-1}$) were achieved in AZ91 processed by HPT [161]. The rate controlling deformation mechanisms was attributed to GBS during HSRSP and the glide-dislocation creep accommodated by GBS during LTSP. Despite these recent achievements, application of these materials into hot stamping or superplastic forming remains challenging. This is because ECAP is difficult to apply to large and thin sheet geometry, while HPT is only limited to small specimen. With this consideration, other SPD techniques such as accumulative roll bonding (ARB) [92] and

constrained groove pressing (CGP) [51] should be investigated because of their suitability for direct processing of magnesium sheet. However, reports on tensile flow behaviours at moderately high temperatures of magnesium alloy processed by these techniques are limited. Therefore, the purpose of this study is to evaluate the effect of SPD using CGP and post-annealing on the tensile ductility of AZ31 alloy at moderately high temperatures from 373 to 523 K. The aim is to determine the activation energy, strain rate sensitivity, and identify the deformation mechanism.

8.2 Experimental procedures

The experimental material was the AZ31 magnesium alloy plate of a thickness of 2.2 mm and size of 96×96mm. The magnesium plates were subjected to three cycles of CGP using method D_B at different temperatures. The details of the deformation and temperature sequences were explained in Chapter 3. It was determined from finite element simulations under Chapter 4 that the estimated total cumulative strain after three cycles of CGP using method D_B was approximately 7. This total strain consists of shear strain imparted in the material in the shear zones, and a combination of both tensile and compressive strain imparted in the material between the “shear” and “undeformed” zones.

As shown from the earlier studies, the yield strength of the as-processed CGP sample (CGP) was found to be improved significantly but possessed very low ductility as compared to the as-received samples at room temperature. As such, a post-annealing heat treatment was necessary to improve the ductility and strain hardening ability. The optimum annealing condition was investigated by performing a series of annealing tests at different temperature

from 463 K to 573 K at annealing duration from 0.5 to 60 min. The relationship between hardness and average grain size was also investigated at short annealing duration. All the annealing were carried out by “conduction technique” in which the samples were rapidly pressed between a pair of preheated flat dies. The heating rate in this technique was measured around 100 K/sec, which was significantly higher than that achievable in the furnace (1 K/sec). The total annealing duration included the time needed for the samples to reach the required annealing temperature. Therefore, conduction technique ensured that the sample was rapidly heated and precisely maintained at the desired temperature which was especially crucial for short annealing duration.

As shown in the later section, this optimized annealing condition was determined as 473 K over a short duration of 3 min. This annealing condition resulted in a good balance between yield strength and ductility without inducing excessive grain growth. In this work, the mechanical properties at moderately high temperatures were examined in the post-annealed CGP sample mainly in the rolling direction (RD) to minimize the number of experiments and to simplify the discussion. This sample condition is designated as CGP-A in the remaining discussion.

For the uniaxial tensile tests, bar specimens with a gauge length of 12.5 mm and width of 3 mm were machined along the rolling direction (RD) of the samples. Tensile tests were carried out at room temperature (RT) to evaluate the mechanical properties of the as-received, CGP, and CGP-A samples. The mechanical properties of the CGP-A sample were evaluated at moderately high temperatures (373, 423, 473, and 523 K) under different initial strain rates (1×10^{-3} , 1×10^{-2} , 1×10^{-1} , and 1.0 s^{-1}). Instron 5982 machine equipped with a non-

contacting video extensometer and a resistance furnace controlled with $\pm 2\text{K}$ was used for these tests. The furnace and the clamping fixtures were first preheated and stabilized to the required temperature for 1h before the start of the test. Each tensile specimen was then loaded into the furnace, preheated and stabilized for an additional time of 5 min to reach the required temperature prior to the tensile test. The temperatures, preheating, and stabilizing time was checked by inserting a small thermocouple wire into the gauge section of a dummy tensile specimen prior the experiments. Two tensile specimens were used for each test condition. The microstructures and fracture surfaces were examined using optical microscopy (OM) and scanning electron microscope (SEM) respectively.

8.3 Optimized annealing heat treatment

In Chapter 7, the microstructure stability of the CGP sample was investigated. It was found that grain growth was rapid in the as-processed material due to high dislocation density and strain anisotropy which increased the driving force for grain boundary migration at elevated temperatures. It was also observed that the average grain sizes were relatively fine over short annealing duration. Therefore, additional studies were carried out to first examine the variation of the hardness and grain size at temperature close to the recrystallization temperature (half the melting point) of magnesium alloy and at short annealing time.

Figure 8.1 shows the plot of the relationship between the hardness and average grain sizes obtained by annealing the CGP samples over different temperature of 463-493K and time of 0.5-15 min. Generally, the ratio of yield strength to hardness is known to be around

3.45 in coarse grain material and reported to be around 3.0 in fine-grained material [162].

As expected, the hardness values decreased and average grain size increased with increasing annealing time. The slopes of the curves decreased at annealing time longer than 5 min. The average grain size in the sample annealed at 493 K was significantly larger than that in samples annealed at lower temperature of 463 and 473 K. The average grain size in the samples annealed at 463 and 473 K were also quite similar especially at longer time. Hardness and ductility are well-known to be compromising properties. Therefore, the above observation suggests that annealing temperature should be minimized to around ~ 473 K and over shorter time of ~ 5 min.

Figure 8.1: Plot of the relationships between hardness and average grain size of the CGP samples annealed at temperature of (a) 463 K, (b) 473 K and (c) 493 K over different duration.

To confirm the idea heat treatment condition, the mechanical properties of the CGP sample after different temperature and time were examined, and these results are shown in Figure 8.2. Figure 8.2a shows the mechanical properties of the CGP samples annealed at different time from 1 to 60 min. The mechanical strength decreased sharply after 1 min of annealing possibly due to the non-uniformity in the material when heat-treated at a too short time. A good balance between strength properties and elongation to failure were seen in the samples annealed at 3 and 5 min. Therefore, annealing time of 3 min was chosen because of its smaller average grain size.

Figure 8.2b shows the mechanical properties of the CGP samples annealed at different temperature at a fixed annealing time of 3 min. This result further confirms that the optimum temperature should be closed to 473 K. Figure 8.3c shows the comparison of the mechanical properties obtained in different tensile directions in the CGP samples annealed at 473 K and 3 min. Anisotropy in the mechanical properties existed in the samples due to the development of texture after CGP which remained after annealing. The properties in the RD direction were better than as compared to other directions, due to the favourable alignment of the basal planes for slips.

Figure 8.2: Relationships between yield strength, ultimate tensile strength and elongation to failure of the GGP samples at different annealing conditions; (a) Annealing temperature at 473 K over different duration, (b) Annealing temperatures from 473 to 573 K over short annealing duration of 3 min (c) Mechanical properties along different tensile directions for samples annealed at 473 K for 3 min.

8.4 Microstructure and room temperature properties

The microstructures of the as-received, CGP and CGP-A samples observed on the surface plate are shown in Figure 8.3a-c. As shown in Figure 8.3a, the initial microstructure of the as-received sample contains coarse and fine grains of sizes from 5 to 50 μm with an average grain size of around $13 \pm 0.5 \mu\text{m}$. A homogeneously fine-grained microstructure was obtained after the CGP processing as shown in Figure 8.3b, and the average grain size was reduced by approximately 86% to $1.8 \pm 0.5 \mu\text{m}$. This microstructure contains ultrafine grains and fine grains sizes from 0.4 to 1 μm and from 1 to 3 μm , respectively. After annealing, the

average grain size increased by approximately 50% to $3.5 \pm 0.5 \mu\text{m}$ as shown in Figure 8.3c.

The final microstructure appears bi-modal and equiaxed.

Figure 8.3: Microstructures of as-received (a), after three cycles of CGP (CGP) (b), and after three cycles of CGP with post-annealing heat treatment (CGP-A) (c).

For a comparison of the mechanical properties at room temperature, the true stress-strain curves of the as-received, CGP and CGP-A samples measured at the initial strain rate of $1 \times 10^{-3} \text{ s}^{-1}$ are plotted in Figure 8.4. The CGP treatment shows an improved yield strength of $267.5 \pm 2.5 \text{ MPa}$ but lower elongation to failure of $7.9 \pm 0.1\%$. This corresponds to a 55% improvement in yield strength but 70% reduction in ductility as compared to the values for the as-received sample. This low ductility is associated with plastic strain instability and propagation instabilities which commonly limits homogeneous plastic deformation in the ultrafine-grained structure [131]. Fine-grained polycrystalline metals typically exhibit

limited strain hardening capability due to a lower amount of lattice dislocation storage capability in the grain interior during plastic deformation. Furthermore, as shown in EBSD measurements in Chapter 6, the grains retained dislocations (LAGB) after CGP processing. This further limited the amount of addition dislocation that can be accommodated during tensile tests.

With annealing, recovery proceeds by rearrangement of dislocations and annihilation of dislocations follow by grain growth. By using the optimized annealing condition, excessive grain growth was minimized. Therefore, the CGP-A sample retained relatively fine grains and exhibited a good balance between ductility and yield strength. The CGP-A sample exhibited a lower yield strength of 230 ± 3.0 MPa but better elongation to failure of $30.5 \pm 0.2\%$. The mechanical properties were also better as compared to the as-received sample where the yield strength and elongation to failure were 172 ± 1.0 MPa and $27.5 \pm 0.2\%$ respectively. This higher yield strength is attributed to the fine microstructure. Due to the higher fraction of grain boundaries, the stress require to propagate dislocations across the grain boundaries also increase, which leads to an increase in yield strength in accordance with the famous Hall-Petch relation. Another contribution to the higher yield strength comes from the remnant dislocations in the microstructure due to the short annealing heat treatment. The improvement in ductility can be attributed to the additional non-basal slips activated at the grain boundaries due to compatibility stresses as observed by Koike et al. [17] in the fine-grained AZ31 after ECAP and post-annealing.

(a)

Figure 8.4: Flow stress curves of the as-received, CGP, and CGP-A samples at room temperature and strain rate of $1 \times 10^{-3} \text{ s}^{-1}$

8.5 Tensile flow behaviour at elevated temperatures

The true stress-strain curves of the CGP-A samples obtained from the uniaxial tensile tests measured at different temperatures and initial strain rates are plotted in Figure 8.5. The flow stress shows a typical dependency both initial strain rate and temperature, in which the mean stress decreases with increasing temperature and decreasing initial strain rate. At room temperature and 373 K, flow stress increased to a maximum value due to strain hardening and decreased abruptly until failure with very minimum necking. At a temperature of 423 K and higher, flow stress also increased to a maximum value, but subsequently decreased more gradually until fracture, resulting in a more noticeable peak stress. Obvious necking was seen in the tensile specimens when deformed at these temperatures. The appearance of peak stress is a typical characteristic of dynamic recrystallization (DRX), which occur close to the peak stress and follow by the softening of the flow stress until fracture [47]. The elongation to failure generally increases with increasing temperature and decreasing initial strain rate. The maximum elongation to failure was $100 \pm 2.5\%$ obtained at 523 K and 1×10^{-3}

3 s-1.

Figure 8.5: Flow stress curves of the CGP-A sample at different temperatures (RT-523 K) and strain rates of 1 s^{-1} (a), 10^{-1} s^{-1} (b), 10^{-2} s^{-1} (c), and 10^{-3} s^{-1} (d).

The strain hardening ability of the material was evaluated by the strain hardening exponent (n) and is commonly expressed by the well-known empirical stress-strain Holloman's (power) law: $\sigma = K\epsilon^n$, where K is the material coefficient, σ is the true stress, and, ϵ is the true strain. The n values were measured from the slope of $\log \sigma - \log \epsilon$ plots in the uniform region. The variation of the n values under different deformation conditions for the CGP-A sample is shown in Figure 8.6. As expected, the value of n decreases with increasing deformation temperature and decreasing initial strain rate. This decrease in the

strain hardening ability is due to the increase in the softening effect as a result of accelerated dynamic recovery (DRV) at higher deformation temperatures and lower initial strain rates. It is worth mentioning that the flow stress reached a steady state immediately after yielding when tested at 523 K and $1 \times 10^{-3} \text{ s}^{-1}$. This is because DRV had increased significantly to balance off strain hardening and imply that DRV is the main restoration process [72].

Fig. 5

Figure 8.6: Variation of strain hardening exponent, n , of the CGP-A sample at different deformation conditions.

8.6 Fractography and surface morphology

The microstructures observed immediately prior to tensile tests, in the gauge section of the tensile specimens along the loading direction, just after preheating and stabilizing period to various temperatures are shown in Figure 8.7a, c, e, and g. For low temperatures from 373 to 423 K, no significant grain growth is observed (Figure 8.7a and c) and the average grain sizes are similar to that of the CGP-A microstructure (Figure 8.3c). As expected, grain growth occurred in the tensile specimens during preheating and stabilizing to higher temperatures. The average grain sizes increased to 3.7 and 5.6 μm at 473 and 523

K, respectively (Figure 8.7e and g). The microstructures remained bimodal and equiaxed prior the tensile tests. Microstructures observed along tensile loading direction near the fracture tip of the tensile specimens at different temperatures from 473 to 523 K and initial strain rate of $1 \times 10^{-3} \text{ s}^{-1}$ are shown in Figure 8.8b, d, f, and h. At 373 K, the numerous elongated coarse grains are observed while fine grains remain fairly equiaxed (Figure 8.7b). It is apparent from the shape of the flow stress curve, shown in Figure 8.5d, that there was no noticeable peak stress and that the flow stress decreased abruptly until fracture almost immediately after reaching a maximum stress value. This indicates that there no grains that were formed by DRX, which will often lead to a softening and gradual decrease in flow stress until failure. The increase in elongation to failure is a mainly a result of higher slip activities. At a higher temperature of 423 K, an obviously higher fraction of finer grains was generated due to DRX with some elongated coarse grains remaining in the microstructure as shown in Figure 8.7d. This agrees well with the observation of peak stress as seen in Figure 8.5d. The presence of elongated grains suggests that DRX was partially complete while the fine grains are formed by the mechanism of continuous dynamic recrystallization (CDRX) [163]. When the temperature increases to 473 K, no elongated coarse grains are observed (Figure 8.7f). DRX occurred readily and resulted in a fine microstructure at the fracture tip as compared to the CGP-A sample (Figure 8.3e). At the maximum temperature of 523 K, higher static recovery and grain growth occurred during the preheating stage. DRV subsequently became the main restoration process. The average grain size at fracture tip at 523 K is similar to the microstructure just before tensile test (Figure 8.7g and h).

Figure 8.7: Microstructures observed immediately prior to tensile tests after heating and stabilizing to 373 K (a), 423 K (c), 473 K (e), and 523 K (g). Microstructures observed near the fracture tip tested at 373 K (b), 423 K (d), 473 K (f) and 523K (h) at strain rate of $1 \times 10^{-3} \text{ s}^{-1}$.

Figure 8.8 shows the SEM images of the fracture morphology of the CGP-A tensile

specimens deformed at RT-523 K under the initial strain rate of $1 \times 10^{-3} \text{ s}^{-1}$. For the sample tested at room temperature (Figure 8.8a), the fracture surface contains a small fraction of dimples and of varied sizes and depth. Some regions are relatively flat with little dimples and contains some cleavage facets, while stretches along longitudinal direction. These observations suggest that the sample failed by shearing which is an indication of a ductile-brittle fracture mode commonly seen in magnesium alloy with moderate ductility at room temperature [164]. As temperature increases to 373-423 K (Figure 8.8b-c), the fracture surface exhibits more dimples of both equiaxed and oval shapes with a lower fraction of the sheared surfaces. Some enlarged dimple holes are observed in the sample tested at 423 K. At temperatures from 473 to 523 K (Figure 8.8d-e), the fracture surfaces are mainly dominated by dimple structures. These dimples are large and deep due to grain growth at higher temperatures [165]. This is because the voids nucleate at the larger grain boundaries which subsequent coalescence and growth in size. The above results indicate a transition from ductile-brittle to ductile failure mode with increasing deformation temperatures.

Figure 8.8: Fracture morphology of CGP-A samples deformed at RT (a), 373 K (b), 423 K

(c), 473 K (d), and 523 K (e) at strain rate of $1 \times 10^{-3} \text{ s}^{-1}$.

8.7 Deformation mechanism at elevated temperature

To further understand the deformation mechanism of the CGP-A samples, the apparent activation energy (Q) were determined from the tensile tests using the following equation [166]:

$$Q = NR \frac{\partial \ln \sigma}{\partial (1/T)} \quad (8.1)$$

Where σ is the flow stress, N is the stress exponent ($N=1/m$), m is the strain rate sensitivity exponent, R is the universal gas constant, and T is the deformation temperature. The m values were determined from constant strain rate tests as defined by the slope of the double logarithmic plot of flow stress versus strain rate [167]:

$$m = \left. \frac{\partial \ln \sigma}{\partial \ln \dot{\epsilon}} \right|_{\epsilon, T} \quad (8.2)$$

Figure 8.99a shows these plots of the $\ln \sigma - \ln \dot{\epsilon}$ plot for the CGP-A sample. The flow stress was selected at a fixed strain of 0.1 in the uniform deformation region. As stated in Figure 8.9a, the strain rate sensitivity exponents increased from 0.03 to 0.14 from temperature of 373 to 523 K. Generally, a higher m value improves the necking resistance which leads to an increase in the elongation to failure [156]. The m values obtained from this study were lower than that required for superplasticity ($m \approx 0.5$) [156], in which deformation can be significantly enhanced through grain boundary sliding (GBS) mechanism and intergranular sliding within grains [157]. This m -values suggest that climb-controlled dislocation creep could be a dominant deformation [168] process. The apparent activation energy (Q) was estimated from the slopes of $\ln \sigma - 1000/T$. Figure 8.9b shows

the plot of $\ln \sigma - 1000/T$ curves at various temperatures and initial strain rates. The apparent Q value in the CGP-A alloy tested at 423-523 K with the initial strain rates of 1×10^{-3} - 1.0 s^{-1} was estimated to be $123.6 \text{ kJ mol}^{-1}$, which is higher than the value for pipe diffusion of magnesium (92 kJ mol^{-1}) [76] and closer to the value for lattice self-diffusion of magnesium (135 kJ mol^{-1}) [143]. Thus, deformation could be well described by the climb-controlled dislocation creep associated by lattice diffusion. The Q value obtained in this study was comparable to the strain rate test method reported by Somekawa, et al. [169] at higher temperature from 573 to 623 K (128 kJ mol^{-1}), and very close to the creep test result reported by Hyun and Kim [170] at temperature from 423 to 473 K at high stress level ($123.9 \text{ kJ mol}^{-1}$). The materials used in both studies were AZ31 alloy annealed sheet with larger initial grain sizes (~ 48 - $56 \mu\text{m}$). Both authors attributed the deformation mechanism to be climb-controlled dislocation creep controlled by lattice diffusion. This comparison also shows that the CGP-A treatment did not significantly alter the deformation mechanism despite the finer initial grain size.

Figure 8.9: Variation of strain rate sensitivity exponent, m (a), and activation energy curves, $\ln \sigma$ vs. $1/T$ (b), of the CGP-A sample at different deformation conditions.

In this work, CGP with post-annealing was found to be an effective technique for producing fine-grained structures in difficult-to-work AZ31 magnesium plate and resulted in better mechanical properties at room temperature. This process is relatively easy to perform, as compared to ECAP which is sensitive to die design causing potential segmentation failure [67, 157]. The tooling design is also simpler as compared to ECAP for processing of plate geometry, which is prone to buckling [103]. Although the CGP-A microstructure was fine, superplastic-like ductility was not observed at low temperature possibly due to the low thermal stability of the grains at elevated temperatures. The average grain size increased by approximately 90% in the CGP-A alloy as compared to that in CGP alloy. The average grain size was further increased by approximately 60% after preheating and stabilizing at 523 K prior tensile tests. This low thermal stability of the microstructure is due to the large straining (~ 7.0) of the alloy in the CGP processing, which induced large stored strain energy and increased the driving force for grain growth. Thus, competitive grain growth during tensile deformation limits grain boundary sliding mechanism for achieving large elongation.

8.8 Summary

The tensile flow behaviour was investigated on AZ31 alloy, processed by constrained groove pressing and post-annealing, from room temperature to moderately high temperatures under different initial strain rates. The following results were obtained.

- 1) Room temperature tensile test revealed that the constrained groove pressed alloy has a yield strength and elongation to failure of 267.5 ± 2.5 MPa and 7.9 ± 0.1 % at the initial strain rate of $1 \times 10^{-3} \text{ s}^{-1}$. With post-annealing at 473 K for 3 min, the elongation to failure

was improved to $30.5 \pm 0.2\%$ with a decreased in yield strength to 230 ± 3.0 MPa. As compared to the as-received alloy, the yield strength and elongation to failure of the constrained groove pressed and annealed alloy were improved by approximately 34% and 11%, respectively.

- 2) The maximum elongation to failure measured was $100 \pm 2.5\%$ at a temperature of 523 K and initial strain rate of $1 \times 10^{-3} \text{ s}^{-1}$. Dynamic recovery was the main restoration process at this deformation condition. Homogenous and large dimples were observed on the entire fractured surface. This suggests that ductile fracture occurred by nucleation, coalescence, and growth of voids.
- 3) Strain rate sensitivity values increased from 0.03 to 0.14 when temperature was increased from 373 to 523 K. The apparent activation energy tested at 423-473K with initial strain rates $1-1 \times 10^{-3} \text{ s}^{-1}$ was estimated to be $123.6 \text{ kJ mol}^{-1}$, and is close to the value for lattice self-diffusion of magnesium. This suggests that climb-controlled dislocation creep was the dominant deformation mechanism controlled by lattice diffusion. Despite the relatively fine grain size in the constrained groove pressed and annealed alloy, superplastic-like properties were not observed, and this was supposedly due to the low thermal stability of the microstructure.

Chapter 9 Microstructure and mechanical properties of AZ31 alloy prepared by squeeze casting and CGP

The content of this chapter has been published in the below conference proceedings:

- 1) *K.S. Fong, D. Atsushi, M.J Tan, B.W. Chua, M.K. Ho, “Effect of Severe Plastic Deformation on Microstructure of Squeeze-cast Magnesium Alloy AZ31 Plate”, AIP Conference Proceedings 1769, 200005 (2016)*

9.1 Introduction

Several studies of SPD on wrought magnesium alloys using techniques such as equal-channel angular pressing (ECAP), high-pressure torsion (HPT), accumulative roll bonding (ARB), multidirectional forging (MDF) and groove pressing (GP) with different degree of the properties enhancement have been reported [65, 67, 91, 96, 171]. In comparison, the study of groove pressing on magnesium alloy, and especially using as-cast alloy as the starting material is far limited [82, 93]. Groove pressing has many advantages such as low tooling cost, easier processing for thin sheet, and relatively scalable to a larger format. Moreover, unlike other sheet processing techniques such as ARB, the productivity is higher because it does not require a delicate process of cutting, cleaning and stacking and is not prone to edge cracking.

In a recent paper by the authors [40], it was shown that the magnesium sheet processed by warm rolling from cast alloy and subsequent annealing leads to an improvement in the sheet formability. It was reported that significant texture weakening occurred as a result of large orientation spread in the recrystallized grains. This work suggests that using as-cast

alloy as the starting material could be a means to control the texture development in subsequent thermomechanical processing because of the more random initial texture.

In this study, squeeze casting is employed as a method of preparing small size (96×96 mm) and thin (4 mm) AZ31 magnesium plate. In squeeze casting process, the molten metal solidifies under pressure and result in a porosity-free component with better mechanical properties as compared to other casting methods. The application of pressure also leads to a large undercooling which increases the nucleation rate and formation of finer microstructure [78]. To further improve the properties of the squeeze-casted magnesium alloy, the plate is subjected to homogenization and SPD using groove pressing. The aim of this paper is to examine the effect of SPD by groove pressing on the microstructure of AZ31 Mg alloy plate produced by squeeze casting.

9.2 Experimental procedures

In the squeeze casting process, a commercial AZ31 Mg alloy ingot was melted in a graphite crucible using an electric resistance furnace and protected by a constant flow of argon gas. The molten mixture was held at 983K for 5 min before casting as illustrated in Figure 9.1. The melt was manually transferred into the die (reservoir) preheated to 523K (Figure 9.1a). The melt was immediately pressed by a punch, preheated to the same temperature of 523K, at the speed of 200 mm/sec and forging force of 180 Ton (Figure 9.1b). Due to this forging action, the melt was squeezed and transferred horizontally into the middle die cavity to form the plate of dimension of 96 mm × 96 mm × 4 mm. The excess melt was allowed to overflow into opposite cavity. The punch was held in position for 45

sec before ejecting the squeeze-cast part (Figure 9.1c). The solidified “melt reservoir” and “melt overflow” were subsequent cut away from the part to be recycled while leaving behind the desired plate specimen (Figure 9.1d). Additional grinding was performed on the top and bottom surfaces to reduce the thickness of the plate from 4 mm to 2 mm. This melt transfer technique has an advantage over direct squeeze casting for making relatively thin and small size plate which has small melt volume. In direct squeeze casting, small melt volume can lead to quick solidification and poor flow-ability which can cause insufficient mould filling.

Figure 9.1: Schematic diagrams illustrating the procedures used in the squeeze casting process for forming the Mg plate: (a) Transferring of melt into preheated die, (b) Application of forging force by the punch, (c) Ejecting the squeeze-casted part and (d) Cutting the plate from squeeze-casted part and recycling of scrap

The magnesium plate obtained from squeeze casting was subsequently used as the starting material in the constrained groove pressing (CGP) experiments. Before CGP, a partial homogenization heat treatment was carried out at a temperature of 723K for 5hr [172]. The deformation method used here was method D_A as described in details in Chapter 3. CGP was performed to two cycles under decreasing temperature from 543K to 493K. Microstructure examinations were performed on initial and as-processed plates in the x-z planes. Hardness was measured across the thickness of the specimen using micro-Vickers

hardness tester using a load of 50gf.

9.3 Microstructures after squeeze-casting and homogenization

Figure 9.2(a) shows the optical image of the microstructure of the AZ31 Mg plate obtained after squeeze casting which is observed to be dendritic with heavy segregation of intermetallic phases. The dendritic cells are generally finer than those in gravity casting. This is because of the higher nucleation rate during solidification as a result of large undercooling and faster heat transfer under application of pressure in the squeeze casting process [78]. The structure of the squeeze-cast AZ31 Mg alloy was examined to consist of solid solution δ -phase (Mg), intermetallic γ -phase ($\text{Mg}_{17}\text{Al}_{12}$) phases, intermetallic ϕ -phase ($\text{Mg}_{21}(\text{Al}, \text{Zn})_{17}$), eutectic ($\delta+\gamma$), and AlMn-based particles [173]. Heavy segregation of phases is likely to reduce the hot workability of the alloy during the groove pressing. Therefore, a partial homogenization heat treatment was performed to dissolve these phases into the alloy matrix to improve its workability [172]. As shown in Figure 9.2(b), majority of the intermetallic phases were dissolved after the heat treatment and an equiaxed grain structure was developed. Furthermore, the average grain size after homogenization is approximately 39 μm and these grains are observed to be slightly larger than the initial dendritic cells.

Figure 9.2: Optical images of the microstructure observed in the x-z plane (a) in the squeeze-casted AZ31 Mg alloy (b) squeeze-casted AZ31 Mg alloy after partial homogenization heat treatment

9.4 Microstructures after CGP

Figure 4 shows the observations of the microstructure after the first and second cycle of groove pressing at 543K and 493K respectively. In the first cycle, the microstructure is heterogeneous with numerous recrystallized fine grains observed in the initial coarse grain structure. The average grain size of the microstructure is approximately 12.5 μm and consists of coarser grains in the range of 30-40 μm and finer grains in the range of 1~10 μm . In the second cycle, the microstructure becomes less heterogeneous with a larger fraction of fine grains observed. Coarser grains can still be seen in the microstructure due to incomplete dynamic recrystallization. The average grain size is considerably reduced, by approximately 88%, from the initial value of 39 to 4.7 μm . Further groove pressing cycle at lower temperature was not possible because of material fracture. The average Vickers hardness of the squeeze-casted Mg alloy and squeeze-cast Mg alloy after the first cycle, and second cycle were measured to be 59, 61, and 74 respectively.

Figure 9.3: Optical images of the microstructure of squeeze-casted & homogenized AZ31 Mg alloy after (a) first cycle at 543K, (b) second cycle at 493K

9.5 Summary

- 1) AZ31 Mg plate, with dimensions $96 \text{ mm} \times 96 \text{ mm} \times 4 \text{ mm}$, was successfully formed by squeeze casting process using the novel melt transfer technique. The squeeze-cast & homogenized plate was further subjected to two cycles of groove pressing at the temperature of 543K and 493K.
- 2) After CGP, the grain size was significantly reduced by 88% from 39 to 4.7 μm . The final microstructure was heterogeneous due to incomplete dynamic recrystallization and insufficient straining of the material. Additional groove pressing cycles by optimization of the processing parameters are necessary in order to obtain a more homogenous microstructure. The final hardness increases by 25% which suggests that the yield strength possibly improved as a result of the grain refinement and work hardening.

Chapter 10 Bio-corrosion resistance of Magnesium alloy after CGP

The partial content of this chapter has been accepted in the below conference:

- *S.J. Bin, Y.T. Tan, K.S. Fong, M.J. Tan, Effect of severe plastic deformation and post-annealing on mechanical properties and bio-corrosion rate of AZ31 magnesium alloy. International conference on the technology of plasticity, ICTP 2017, 17-22 September 2017, Cambridge, United Kingdom*

The content of this chapter to be published in the below journal paper:

- *K.S. Fong, M.J Tan, P. Farsid, S. Veena, Y.T. Tan, S.J. Bin F.L. Ng, “Influence of microstructure and recrystallization state on biocorossion resistance of magnesium alloy processed by severe plastic deformation”. To be published in Journal of Materials Research*

10.1. Introduction

The research in magnesium alloys for use as biomedical implant is gaining importance in recent years because of the material's bio-absorbability, excellent biocompatibility and stress-shielding properties [174]. Currently, most of the common metal implant used today include titanium and stainless steels which have high corrosion resistance coupled with good mechanical strength and fracture toughness [175]. However, limitations such as the release of toxic ions [176] and particularly, stress shielding effect due to the mismatch of elastic moduli can promote instability in the implant and impede bone growth in vivo [177].

Magnesium and its alloys, on the other hand, is a remarkably lightweight material (density of 1.74 g/cm^3) that is 3 times less dense compared to titanium. Unlike current metallic biomaterials, oxidation of magnesium promotes magnesium ions, which is essential

to the metabolism of a human body and secretion of insulin, aiding in the healing process of the bone [178]. It also prevents the need for a second surgery to remove the implant that can cause discomfort to the patient. More importantly, the elastic modulus, as well as the yield strength of magnesium, is closer to that of natural bone, which aids in the stimulation of bone growth. However, the high corrosion rate of magnesium alloys can cause a rapid loss in its mechanical strength of the fixation plate before the bone healing process [179]. Furthermore, the dissolution of hydrogen gas beneath the skin is a major concern in developing magnesium implants [180]. This can be uncomfortable for the patient and also unsightly.

Due to the above concerns, several corrosion protection techniques have been investigated. These can be broadly classified under mechanical (machining), chemical (coating), and physical (surface modification) methods [179]. Grain refinement by severe plastic deformation (SPD) is attractive because it can lead to improvement in strength and influences the corrosion resistance of magnesium alloys. However, contradicting results have been reported so far even for the same alloy class. For example, it was reported that equal-channel angular pressing (ECAP) of AZ31 cast alloy resulted in finer grain structure and better corrosion resistance as compared to AZ31 rolled alloy [181]. However, friction stir processing (FSP) of AZ31 alloy resulted in the fine and bimodal microstructure but increased the corrosion rate by three times [182]. Some other researchers also reported a decrease in corrosion rate [93] and comparable or increase in corrosion rate [183, 184] by SPD. Therefore, it is important to understand the effect of SPD on the corrosion resistance of magnesium alloy. The thermomechanical treatment and material used in this study are

constrained groove pressing (CGP) with and without post-annealing and AZ31 magnesium alloy. This study will attempt to understand the influence of the microstructure state on the corrosion resistance of AZ31 magnesium alloy.

10.2. Experimental method

10.2.1. Material

Plates of size 96 mm x 96 mm with 2.2 mm thickness were machined from hot-rolled AZ31 magnesium alloy sheet received in annealed condition. The chemical composition of this alloy is shown in Table 3.1 in Chapter 3. The plates were subjected to three cycles of CGP at elevated temperature from 503 to 453 K to achieve fine grain size. The details of the processing steps and illustration of the CGP were thoroughly explained in Chapter 3. For the corrosion study, samples of size 10 mm x 10 mm and 20 mm x 20 mm were cut from the central part of the sheets for immersion test and electrochemical test respectively. Some of the CGP-processed samples were also post-annealed in air at 473 K for 15 min and 30 min.

10.2.2. Immersion test

All the surfaces of the samples were polished by 1200 grit SiC paper to ensure the same surface roughness for the corrosion tests. The final thickness of the samples was approximately 1.2 mm. Before the immersion tests, the samples were ultrasonic washed with acetone, dried in air and weighted. The immersion duration chosen were at 24, 48, and 168 h and the corrosion medium used was Hank's solution which contains minerals that

were close in composition and concentration to human body. The details of its compositions are listed in Table 10.1. The solution volume (SV) was chosen at 6.7 times the total surface area (SA) of each sample as recommended by Yang et al. [185]. It was reported that a low SV/SA increased the pH value of the solution leading to an under-estimation of the corrosion rate. This effect can become negligible if a high enough SV/SA value of 6.7 is chosen. A minimum of two samples were used in each condition to take into account of the measurement errors. After reaching the required duration, the samples were removed from the solution, rinsed with de-ionized water and air dried for SEM and XRD measurements. After measurements, the corrosion product was removed using a solution containing 200 g chromic trioxide and 10 g of silver nitrate in 1000 ml of distilled water. The washing duration was kept constant at 1 min for the samples immersed up to 48 h and 2 min for samples immersed for 162 h. The duration was observed to be sufficient for complete removal of the corrosion product without affecting the integrity of the samples. The samples were subsequently washed with acetone and air-dried before measuring the weight loss. Two repeats of the immersion measurements were performed. The average corrosion rate, P_w (in mm/year) is then calculated by equation 10.1 [174, 186, 187], where Δw is the weight loss (in mg/cm²/day).

$$P_w = 2.1\Delta W \quad (10.1)$$

Table 10.1: Component and concentration of Hank's balanced salt solution from BiowestTM

Component	Concentration (g/l)
CaCl ₂	0.18
MgSO ₄ -7H ₂ O	0.1
KCl	0.4
KH ₂ PO ₄	0.06
NaHCO ₃	0.35
NaCl	8.0
Na ₂ HPO ₄	0.048
D-glucose anhydrous	1.0
water	989.9

10.2.3. Characterization of microstructure and corrosion product

Optical Microscopy (OM) was used to examine the microstructures of the different sample conditions. The samples were cold mounted, polished and etched in picric acid mixture to reveal the microstructure. The grain size was measured using line intercept method according to ASTM E112 standard.

Electron backscatter diffraction (EBSD) analysis was also performed on the CGP sample. For this analysis, a high resolution backscattered electron based orientation microscopy and transmission Kikuchi diffraction (TKD) was conducted using an Oxford system with an attached Carl Zeiss AURIGA® CrossBeam® field emission gun scanning electron microscopy (FEG SEM) workstation. The microstructure of the CGP samples was

also observed using a TEM equipped with a field emission gun (Philips CM 200, Netherlands). All the TEM and TKD samples were prepared using a dual beam FIB (FEI xT Nova Nanolab 200, USA), and the thickness of the specimens was estimated to be around 70 to 100 nm.

Scanning electron microscopy (SEM) was used to observe the morphology of corrosion product immediately after the immersion test just before removal of the corrosion product for weight loss measurement. Energy dispersive X-ray spectroscopy (EDS) and X-ray diffraction (XRD) were also performed on the samples for identification of composition of the corrosion product found on the surfaces.

10.2.4. Electrochemical Test

Electrochemical tests were conducted using a potentiostat and a standard three-electrode system in an electrochemical test cell with Hank's solution as the electrolyte. The counter electrode was a high-density graphite rod; reference electrode was a saturated calomel electrode (SCE); and the working electrode was the metal specimen, covered with an electrochemical mask exposing an area of 1 cm². The open circuit potential (OCP) was measured for one hour before potentiodynamic polarization was conducted at a scan rate of 1 mV/s. Tafel fitting was used to obtain the corrosion current density (i_{corr}) from the polarization scan. Each sample condition was measured three times to ensure the consistency of results obtained.

10.2.5. Tensile test

Specimens for tensile testing were cut along the rolling direction of the plate into a gauge length of 25 mm x 6 mm x 1.5 mm, in accordance with ASTM E8M Standard. Tensile tests were conducted with an initial strain rate of $3 \times 10^{-3} \text{ s}^{-1}$. The yield strength was taken at 0.2% offset stress from the engineering stress-strain curve and elongation to failure was taken at engineering strain at fracture.

10.3. Microstructures and mechanical properties after CGP and annealing

Figure 10.1 shows the micrographs of the as-received sample, CGP sample, and CGP samples after post-annealing at 473 K for 15 and 30 min. The corresponding mechanical properties are shown in Figure 10.2. Table 10.2 summarizes the different material conditions and their average grain sizes and mechanical properties. The grain size evolution and grain refinement mechanism of AZ31 alloy during CGP have already been discussed in detail in chapter 5 and 6. The present study utilized the same technique and demonstrated a similar degree of grain refinement. As shown in Figure. 10.1 & table 10.2, the average grain size was reduced to $1.6 \pm 0.5 \text{ }\mu\text{m}$ from an initial value of $15 \pm 0.5 \text{ }\mu\text{m}$ after three cycles of CGP by the process of strain induced dynamic recrystallization. The post-annealed CGP samples show a marginally increased in grain size from $1.6 \pm 0.5 \text{ }\mu\text{m}$ to around 3.4 ± 0.5 and $4.8 \pm 0.5 \text{ }\mu\text{m}$ after 15 and 30 min, respectively. As shown in Figure 10.2 and Table 10.2, the yield strength and ultimate tensile strength increases significantly after CGP from $175 \pm 4 \text{ MPa}$ to $243 \pm 4 \text{ MPa}$ and $264 \pm 1 \text{ MPa}$ to $310 \pm 4 \text{ MPa}$, respectively. The increased in mechanical strength was associated with finer grain structure and significant strain hardening effect. As such, the as-processed material has a low ductility of $1.6 \pm 0.01\%$ from an initial value of

18.7±0.02%. As expected, the yield strength and ultimate tensile strength both decreased with increasing annealing duration with a corresponding improvement in ductility as a result of static recrystallization and recovery. A maximum elongation to failure of 22.4±0.02% was obtained in the sample after 30 min of annealing. This sample has a yield strength and ultimate tensile strength of 206±0.6 MPa and 273±0.1 MPa respectively, which is a minor improvement as compared to the as-received sample.

Figure 10.1: Optical micrographs of (a) as received sample, (b) CGP sample, (c) CGP sample after 15 min annealing at 473 K and (d) CGP sample after 30 min annealing at 473 K.

Figure 10.2: Mechanical properties of the different samples.

Table 10.2: Summary of material conditions, average grain sizes and mechanical properties

Label	Conditions	Average grain size (μm)	Yield strength (MPa)	Ultimate tensile strength (MPa)	Elongation to failure (%)
As-received	As-received AZ3	15.0±0.5	175±4.2	264±0.7	18.7±0.02
CGP	After three cycles of CGP	1.6±0.5	243±3.7	310±3.5	1.6±0.01
CGP-15	CGP and annealed at 473 K for 15 min	3.7±0.5	216±1.3	285±0.9	16.8±0.01
CGP-30	CGP and annealed at 473 K for 30 min	4.8±0.5	206±0.6	273±0.1	22.4±0.01

EBSD was carried out to characterize the extent of deformation and to understand microstructure state in the CGP samples. Figure 10.3 shows the dislocation density obtained from kernel average misorientation (KAM) and grain orientation map measured from EBSD technique. KAM component calculates the average misorientations between all neighbouring points within the kernel which is useful for estimating the extent of deformation and dislocation density. The dislocation density was found to be approximately $5 \times 10^{13} \text{ m}^{-2}$. This value is significantly higher as compared to annealed state ($\sim 10^{11} \text{ m}^{-2}$) and the extreme end of the severely deformed state ($\sim 10^{15} \text{ m}^{-2}$) [188, 189]. This value is also close to the dislocation density ($\sim 1.6 \times 10^{13}$) obtained by combine extrusion and equal channel angular pressing (EX-ECAP) technique of SPD in AZ31 alloy [75] which has a similar degree of grain refinement. From Figure 10.3, it is also observed that there are recrystallized grains with nearly zero dislocation (blue colour). This is also similarly observed from the TEM image as shown in Figure 10.4. The image shows a grain with high dislocation density next to grain with nearly zero dislocation density.

Figure 10.3: Dislocation density measured from kernel average misorientation (KAM) by

EBSD analysis

Figure 10.4: Bright-field TEM image of the CGP sample

10.4. Corrosion rate

Figure 10.5 shows the corrosion rate (in mm/year) of the various sample conditions (as summarized in Table 10.1) after 24, 48 and 168 h immersion in Hank's solution. For the samples after 24 h, the corrosion rates measured in the as-received, CGP, CGP-15 and CGP-30 samples were found to be 0.38 ± 0.18 , 0.48 ± 0.3 , 0.4 ± 0.04 and 0.49 ± 0.02 mm/year. It can be said that there were no noticeable differences in the corrosion rate among these samples after 24 h, as these values are similar and within the limits of experimental error. The difference in corrosion rate was more evident after 48 h. The as-received sample shows better corrosion resistance as compared to all other sample conditions. At the longer duration of 168 h (7 days), the influence of the material processing state on corrosion rate was more clearly established. The average corrosion rate of the CGP sample was 2.8 ± 0.2 mm/year which is marginally higher than the as-received sample at 2.6 ± 0.3 mm/year. It can be argued that both samples have similar corrosion rate because of the limits of experimental errors.

The corrosion rates in both annealed CGP samples (CGP-15 and CGP-30) are significantly higher than that of the as-received and CGP samples. The corrosion rates of CGP-15 and CGP-30 were 3.5 ± 0.26 and 3.8 ± 0.5 mm/year, respectively. Therefore, annealing decreases the corrosion resistance by a factor of ~ 1.5 as compared to the as-received sample.

The result suggests that the CGP sample without annealing exhibits a similar degree of corrosion resistance despite the very fine grain size. Therefore, the thermomechanical treatment increases the strength of the alloy without a significant deterioration of its bio-corrosion resistance.

Figure 10.5: Average corrosion rate (mm/year) of AZ31 alloy for the different conditions after 24, 48 and 168 h immersion in Hank's solution.

10.5. Electrochemical corrosion behaviour

The electrochemical corrosion behaviours were examined by potentiodynamic polarization technique. The polarization curves obtained from the different samples are shown in Figure. 10.6.

According to the mixed potential theory by Wagner and Traud [190], the sum of currents from anodic reactions (oxidation processes) must be equal to the sum of currents from cathodic reactions (reduction processes) for an electrode under open-circuit conditions. The potential that this situation occurs is called the corrosion potential (E_{corr}). At E_{corr} , the anodic current density is equal to the cathodic current density, resulting in a net current density of zero. The anodic current density at E_{corr} is the corrosion current density (i_{corr}). Corrosion can be described by the flow of electrons between the anodic and cathodic areas and its kinetic depends on the rate of oxidation and reduction chemical reactions as described by the simplified chemical equations below:

The corrosion current density (i_{corr}) and corrosion potential (E_{corr}) were estimated from the intersection of the lines extrapolated from the Tafel slopes of the anodic (oxidation) and cathodic (reduction) branches of the polarization curves. These values are summarized in Table 10.3.

Comparison of the i_{corr} and E_{corr} values can provide a rough indication of the corrosion rates. Generally, lower i_{corr} and more positive E_{corr} indicates better corrosion resistance [114, 191]. Out of these two values, i_{corr} is widely considered as the most important parameter in defining the corrosion performance [192]. From table 10.3, the average i_{corr} value is observed to be lower and E_{corr} is higher in the as-received sample as compared to the CGP sample and CGP samples with annealing. This suggests that the as-received sample has a

better corrosion resistance than other samples, although the values are relatively close to each other within the limits of experimental errors. It is worth mentioning that the electrochemical results from the polarization experiments (after 1 hour immersion) agree well with the immersion test results at 24 hours. Both techniques indicate that the corrosion rate of as-received and of as-processed samples (with and without annealing) are fairly similar at the beginning.

Although electrochemical techniques are widely used to measure the corrosion rate of metals, it may not be the most suitable measurement technique for magnesium. It has been reported that corrosion rate determined from extrapolation of the tafel region of the polarization curves can deviate from the corrosion rate determined from mass loss and hydrogen evolution by as much as 48-96 % [193]. The reason is because the potentiodynamic polarization technique is a short-term test while weight loss or hydrogen evolution are both long-term measurements. The build-up of corrosion product which occurs during long-term measurement can significantly affect corrosion rate. Moreover, dissolution of magnesium alloy is more of a chemical reaction rather than electrochemical which implies that potentiodynamic polarization technique underestimates the total corrosion. Anodic reaction of magnesium alloy increases the concentration of Mg^{2+} in the aqueous solution and amount of H_2 gas evolved. This continued hydrogen evolution on the Mg surface consumes electrons that would have otherwise flowed through the potentiostat, resulting in an underestimation of the corrosion rate. Nevertheless, the electrochemical measurements in this current study are found to agree well with the weight loss measurements from immersion tests. Both methods indicate that corrosion resistance of the

AZ31 alloy after CGP was marginally reduced (although insignificant), and only significantly reduced after annealing.

Different degree of passivation was also observed in all the samples. This was shown by the discontinuity of the polarization curves as indicated by the arrows in Figure 10.6. This is supposedly caused by the formation of corrosion product which adhered strongly to the surface and protecting it from further anodic reaction [194]. This corrosion product is usually unstable and will subsequently break down due to pitting thus allowing the anodic reaction proceed normally. Passivation and pitting corrosion in magnesium alloy were also commonly reported in the literature [192, 195, 196].

Table 10.3: Summary of the mean corrosion current density and corrosion potential from potentiodynamic polarization curves

Sample	I_{corr} (A/cm ²)	E_{corr} (V vs. SCE)
As-received	8.0×10^{-06}	-1.41
CGP	1.5×10^{-05}	-1.48
CGP-15	2.0×10^{-05}	-1.45
CGP-30	1.0×10^{-05}	-1.43

Figure 10.6: Potentiodynamic polarization curves of as-received, CGP, CGP-15 and CGP-30 samples

10.6. Surface morphology

The surface morphology the samples after 24, 48 and 168 h immersion in hank's solution are shown in Figure 10.7. XRD analysis of corrosion product deposited on the surfaces is shown in Figure 10.8. After 24 h immersion, all the samples were covered with a uniform layer of cracked film and with a small presence of white particles. EDS analysis shows minerals consisting of P, Na, Cl, and Ca were deposited on the surfaces for all the samples. These minerals likely came from the hank's solution which were deposited on the surfaces and reacted with magnesium during corrosion. The compositions of the corrosion products were confirmed by XRD and determined as $\text{Mg}(\text{OH})_2$, MgCl_2 , $\text{Mg}_3(\text{PO}_4)_2$, and $(\text{Ca})_{10}(\text{PO}_4)_6(\text{OH})_2$ (hydroxylapatite). The white compound is known to be a form of magnesium apatite containing both $\text{Mg}_3(\text{PO}_4)_2$ and $(\text{Ca})_{10}(\text{PO}_4)_6(\text{OH})_2$ as reported by Song et al. [197] and H. Kuwahara et al. [198]. The thin layer of film is $\text{Mg}(\text{OH})_2$ which act as an initial barrier against corrosion. However, this film is unstable in chloride solution. The Mg on the film can react with chloride to MgCl_2 which is highly soluble [199], causing the film to crack or flake off. Thus, exposing a fresh surface of the substrate to the corrosion medium which increases the corrosion rate. From the XRD patterns, an increase peaks around $69 - 71^\circ$ was seen in the CGP, CGP-15 and CGP-30 samples and these peaks which corresponds to $\text{Mg}(\text{OH})_2$. This suggests that the CGP and post-annealed samples had a higher dissolution of Mg which result in a possibly thicker and denser layer of $\text{Mg}(\text{OH})_2$ as compared to the as-received sample. As such, the weight loss can be more significant after removal of the

corrosion product. Generally, the CGP, CGP-15 and CGP-30 samples were observed to have more blocky magnesium apatite adhering to the surfaces. After 168 h immersion, all the samples were covered with a thick and dense layer of $\text{Mg}(\text{OH})_2$ film with visible cracking and with thick and blocky magnesium apatite adhering to the $\text{Mg}(\text{OH})_2$ film.

Figure 10.7: SEM images and EDS analysis of as-received (a), CGP (b), CGP-15 (c) and CGP-30 (d) samples after 24 h, 48 h and 168 h immersion in hanks solution.

Figure 10.8: XRD patterns of the as-received (a), CGP (b), CGP-15 (c), and CGP-30 (d) samples after 24 h and 168 h immersion in hanks solution.

10.7. Microstructure state and its influence on corrosion rate

Some studies have suggested that fine-grained microstructure can improve the bio-corrosion resistance of magnesium alloy. Sunil et al. [93] reported an improvement in corrosion resistance after CGP performed at higher deformation temperatures and attributed it to the enhanced wettability of the surface due to the fine-grained ($\sim 7\mu\text{m}$) microstructure. This enhanced wettability was found to increase the rate of deposition of hydroxylapatite onto the material surface during the early corrosion stage which protected the surface from further corrosion attack. However, it is important to note that their immersion test was conducted using supersaturated simulated body fluid (SBF 5 $\times$) solution. It is worth

mentioning that this may significantly accelerate the rate of deposition of hydroxyapatite and resulted in more uniform coverage of the surface by the hydroxyapatite which may lead to an overestimate the corrosion performance. Furthermore, the state of the microstructure (lattice defects and stresses due to lattice distortion) and grain orientation can influence the corrosion behaviour differently. It is well known that dynamic recrystallization and recovery in magnesium alloy is strongly dependent upon strain rate and temperature which influences the grain size, grain orientation and degree of density dislocation [113, 200]. It is possible for two material with similar average grain size to have different corrosion rate as a result of the different processing treatments. This was shown in the work by Hamu et al. [183], where similar grain size was achieved in AZ31 alloy by conventional extrusion and ECAP. However, the corrosion rate of the ECAP sample was higher than conventional extruded sample because of higher dislocation density due to the higher deformation strain. Aung et al. [201] similarly reported that defects in the form of twins can greatly reduce the corrosion resistance of AZ31 alloy and a coarser grain microstructure without twinning, obtained through heat treatment, had a better corrosion resistance. All the work point to the importance of microstructure state towards corrosion resistance. Particularly, a defect-free structure could benefit corrosion more significantly than average grain size alone. It is worthy to note that current work aims to achieve high strength magnesium alloy with for implant application. This was achieved by subjecting the alloy to CGP at low temperatures (458 K) which is close to the recrystallization temperature of the alloy ($0.5T_m$, where $T_m = 903$ K) to generate fine grains by dynamic recrystallization so as to increase the strength. Repeated deformation at this temperature for the last two cycles generates dislocation which

rearranges into fine grain by the process of continuous dynamic recrystallization [47, 65, 134]. After the final cycle of CGP, dislocation was retained in the final microstructure due to insufficient dynamic recovery as shown in EBSD and TEM analysis in Figure 10.3 and 10.4. Short annealing treatment was performed to recover the ductility while balancing the decrease in yield strength by minimizing grain growth. However, the corrosion resistance of the CGP-15 and CGP-30 was lower than the as-received and CGP sample. This is supposedly due to the insufficient recovery of the dislocation concomitant with grain growth which worsens the corrosion properties. As shown in Figure. 10.3 and 10.4, there was strain inhomogeneity due to the CGP process as a result of the incomplete dynamic recrystallization. Due to localised stress at the interface between these two grains, in the regions between high dislocation density and very low dislocation density, the corrosion rate can be accelerated. These phenomena encourage the reaction of Mg alloy with the corrosive media, hence increase the corrosion rate despite the fact that small grain size should decrease the corrosion rate

10.8. Summary

AZ31 magnesium alloys were subjected to severe plastic deformation via constrained groove pressing (CGP) and were subsequently annealed at 473 K for 15 and 30 min to assess its bio-corrosion resistance. The influences of the processing condition on the mechanical properties and bio-corrosion behaviours were measured and discussed.

- 1) Highest yield strength of 243 MPa and ultimate tensile strength of 310 MPa were measured on the constrained groove pressed sample, but with low ductility of 1.6 %.

Best combination strength and ductility were measured on the CGP sample annealed for 15 min, where the yield strength, ultimate tensile strength and elongation to failure were 216 MPa, 285 MPa, and 16.8 %, respectively.

- 2) Weight loss measurements after 24 h and 48 h showed little noticeable differences in the corrosion rate as compared to 168 h (7 days). After 168 h, the corrosion rate of CGP processed sample (2.8 ± 0.2 mm/year) was found to be similar to the as-received sample was slightly better but comparable to the as-received alloy (2.6 ± 0.3 mm/year). The corrosion rates were found to be significantly higher in both the post-annealed CGP sample. The highest corrosion rate was 3.8 ± 0.5 mm/year in the CGP sample after 30 min annealing, which was a factor of ~ 1.5 higher than the as-received sample. This is supposedly due to incomplete recovery of the dislocation concomitant with grain growth.
- 3) From the comparison of the corrosion current density and corrosion potential measured by potentiodynamic polarization technique from does not show a significant difference in the corrosion rates. However, the trend shows good agreement with the weight loss measurements determined by immersion tests, with better corrosion resistance in the following sequence: as-received > CGP > CGP after 15 min annealing > CGP after 30 min annealing.
- 4) Thicker and denser corrosion products (hydroxyapatite) were observed on the surfaces of the CGP and CGP with annealing samples as compared to the as-received sample. This contradicts the suggestion that higher adhesion of hydroxyapatite can shield the surface and improve the corrosion resistance.

- 5) From the EBSD a high dislocation density of 5×10^{13} was measured in the CGP sample

Furthermore, from the observation of the EBSD and TEM images, there are presences of grain that had fully recrystallized with zero dislocation density next to deformed grain with high dislocation density. This created region of localized stress at the interface between the grains which is attributed to the generally higher corrosion rate seen in the CGP sample.

- 6) Currently, the higher corrosion rate despite fine grains makes it unsuitable for implant application. To overcome this, processing at a higher temperature or lower number of cycles should be explored to determine if fine grain with low dislocation density can lead to improve corrosion resistance.

Chapter 11 Conclusions and suggestions for future work

The work presented in this study has shed light on deformation behaviour during severe plastic deformation (SPD) via constrained groove pressing (CGP) using a modified deformation path and also post material behaviour of AZ31 magnesium alloy. These studies successful highlighted the potential of the process to achieve higher strength and ductility AZ31 magnesium alloy, which still remain as one of the most widely used alloys in the industry, particularly in automotive industry. The implication is of great importance for the future lightweight initiative to reduce weight and improve fuel consumption and reduce carbon footprint. The work brings a step towards mass production of magnesium alloy by SPD. Moreover, it could motivate the further studies on the process improvements for various applications and developments on the analytical modelling. The conclusion and future work are as follow:

11.1 Conclusions

Numerical studies were performed to investigate the difference in the two deformation paths examined in this research, namely deformation path A, (conventional method) and path B (a modified method by repeated orthogonal pressing). It was observed that strain inhomogeneity in the workpiece existed in both technique with deformation path B being larger than path A. It was determined that deformation path B resulted in higher straining ($\epsilon_t \sim 2.4$) than deformation path A ($\epsilon_t \sim 1.3$) with less pressing. This was due to higher tensile and compressive stresses as a result of direct groove deformation without intermediate

straightening.

Base on the numerical studies, comprehensive experiments were performed to investigate the effect of deformation paths and temperature conditions on the microstructure evolution and mechanical properties. These are strongly influenced by the degree of dynamic recrystallization and dynamic recovery in the process. It was found that decreasing deformation temperature in each cycle was effective in the formation of fine (1-2 μm) and ultra-fine grains ($\sim 0.5 \mu\text{m}$), which benefited strength but reduces ductility. Maintaining constant deformation temperature near the recrystallization temperature of the alloy could achieve fine grain ($\sim 4 \mu\text{m}$) while maintaining ductility but with marginal improvement in strength. Deformation paths B and reducing temperature conditions resulted in the finest microstructure and highest mechanical properties and were thus investigated in greater detail.

From EBSD characterization of the microstructure evolution, it was observed that grain refinement occurred through continuous dynamic recrystallization through the rearrangement of dislocation boundaries of low-angle boundaries into subgrain and eventually fine grain with high-angle boundaries. Development of ultra-fine grains near the vicinity of grain boundaries suggested the role of rotational dynamic recrystallization in early deformation.

Microstructure stability of the material after CGP found to be low due to the rapid grain growth during isothermal annealing. From the kinetic study, the activation energy value was determined to be low (27.8 kJ/mol) found to be close to equal-channel angular pressing of the same alloy from literature, and its underestimation was attributed to the

reduction of dislocation density during annealing.

Short annealing was found to benefit both the mechanical strength and ductility of the alloy after CGP at room temperatures while keeping the grain fine ($\sim 3\mu\text{m}$). It was found that that dynamic recrystallization could occur in the fine-grained alloy at a relatively low temperature of 423 K. The deformation mechanism at elevated temperature was primarily driven by dislocation climb creep controlled through lattice diffusion. The relatively fine-grained microstructure did not produce superplastic-like ductility but did result in enhanced ductility in which dynamic recovery was observed as the main restoration process.

Thin AZ31 magnesium plates were successfully formed by squeeze casting process and subjected to CGP for grain refinement. The grain size was significantly reduced but remained heterogeneous due to incomplete dynamic recrystallization and insufficient straining of the material. The process demonstrates the potential of using this combined thermo-mechanical processing approach to prepare small batch of thin magnesium plate with improved properties for potential application such a biomedical bone plates.

Lastly, the effect of CGP on bio-corrosion resistance of AZ31 alloy was examined. It was found that the corrosion resistance does not drop significantly while the mechanical strength was improved substantially. For example, this can positively work together with calcium phosphate coating prepared by pulse electrodeposition, as reported by other researchers, to improve both the mechanical and corrosion properties of magnesium bone plates used in certain orthopaedic surgery that are subjected to higher stress loading. Nevertheless, there are rooms for further improvements to expand into future potential applications and will be explained in the future work.

11.2 Future studies

11.2.1 Scale-up by rolling or progressive stamping

Severe plastic deformation techniques are known to be of lower productivity and incurred higher cost due to the need for repeated processing and at warm temperatures for difficult-to-deform metals such as magnesium alloys. This limitation is a barrier to entry into cost-sensitive products such as consumer electronics. Continuous processing is, therefore, an important consideration for reducing processing time and cost. Various continuous processing have been proposed such as continuous repetitive corrugating and straightening (RCS) [53], ECAP-conform [202] and continuous shear deformation process [203]. However, these are not sufficiently demonstrated on larger sheet or continuous strip of larger widths and for difficult-to-deform magnesium alloy. One approach to improve the productivity of CGP is by implementing the grooves designs into rollers that are orthogonally arranged to induce the same cross groove deformation which was demonstrated in this research. Annealing heat treatment can be performed by a series of flat rollers through contact heating at the last station. For continuous strips, progressive stamping is promising. It is also possible to directly form the product shape at the last few stations. This progressive stamping approach is very promising for manufacturing of bone plates for medical implants. Both techniques require heating up the rollers and die plates using cartridge heaters with appropriate insulation or water cooling channels to minimize heat transfer to sensitive machines components.

11.2.2 Further studies on superplasticity behaviour through SPD

Forming of magnesium sheet are typically performed by superplastic forming at high temperature of 673 K [147, 148, 204] or by hot stamping which requires the tools and part to be heated to as high as 723 K [205] in order to produce parts of medium to high complexity. This greatly increases the processing cost, productivity and lubrication challenges. In Chapter 8, formability and deformation mechanism of AZ31 alloy at warm temperatures range from room temperature to 523 K have been investigated and discussed in details. This study suggests that formability at room temperature can be improved while maintaining the mechanical strength but does not lead to low-temperature superplasticity (LTSP) or high strain rate superplasticity (HSRSP) behaviour. This was caused by the low thermal stability of the microstructure due to the high dislocation density that remained in the microstructure which accelerated grain growth. SPD techniques such as equal-channel angular pressing (ECAP) and high-pressure torsion (HPT) demonstrated excellent LTSP or HSRSP for magnesium alloys [94, 158, 160, 206-209]. However, it is worth mentioning that these techniques cannot be scaled up and mainly demonstrated on an alloying system that forms precipitates at elevated temperatures which improve the thermal stability of the microstructure, while AZ31 magnesium alloy sheet is still the most widely used material in automotive. In this case, formability is of greater importance as compared to improving the mechanical strength. Further studies should be conducted to examine the effect of processing at above recrystallization temperatures where dynamic and static recovery can occur more easily during CGP. This approach will still lead to the formation of fine grains ($< 10\mu\text{m}$) but not resulting in the higher mechanical strength.

11.2.3 Further studies on the enhancement of bio-corrosion resistance

Magnesium alloys are known to possess excellent biocompatibility which makes it very attractive for medical implants application [174]. However, problems such as inadequate strength and rapid corrosion need to be addressed for orthopaedic implants. The strength should not fall too rapidly with respect to degradation rate in order to have sufficient time for the injury to heal [179, 210, 211]. Coating is the most promising option to slow down the degradation rate of magnesium alloy. However, sometimes cracks or defects will appear on the coating over time leading to accelerated localized corrosion [179]. And also, due to the concern with toxicity effect of some magnesium alloys, especially those that contain aluminum or heavy metal elements which may affect the nervous system of the body [212], there has been a growing interest in the development of magnesium alloys which composed of non-toxic elements that are commonly needed in human body. It has been discussed in chapter 10 that SPD has the potential of improving the corrosion resistance of magnesium alloy through grain refinement while minimizing dislocation density. For future studies, development of other SPD techniques such as accumulative roll bonding (ARB) and ECAP for Mg-Zr or Mg-Ca alloys prepared from casting should be explored to develop a cheaper alternative method of preparing the material and enhancing its corrosion resistance.

Appendix: Fatigue crack growth behaviour of fine-grained AZ31 alloy

The content in this appendix is through collaboration with University of Oxford. I would like to acknowledge Dr Enrico Salvati and Prof. Alexander M. Korsunsky for their guidance and allowing the usage of their fatigue test fixture to conduct the tests as required. The content has been published in the below journal papers:

- E. Salvati, H. Zhang, K.S. Fong, X. Song, R.J.H Paynter, A.M. Korsunsky, “Fatigue and Fracture behaviour of AZ31B Mg alloy plastically deformed by Constrained Groove Pressing in the Presence of Overloads”, *Procedia structural integrity*, Vol. 2, 2016, pp. 3772-3781
- E. Salvati, H. Zhang, K.S. Fong, X. Song, R.J.H Paynter, A.M. Korsunsky, “Separating plasticity-induced closure and residual stress contributions to fatigue crack retardation following an overload”, *Journal of the Mechanics and Physics of Solids*, Vol. 98 (2017), pp. 222–235

A.1. Introduction

An ideal structural material should possess high strength with sufficient ductility together with high fatigue resistance and fracture toughness [42] which can be possibly achieved through grain refinement. The aim of this study is, therefore, to characterize fatigue resistance of AZ31 magnesium alloy processed by constrained groove pressing (CGP) technique of grain refinement through severe plastic deformation (SPD). The initial material was AZ31B-O plates that had been subjected to four cycles of CGP using deformation path D_A under decreasing deformation temperature. The process details and further information regarding the microstructure, texture and mechanical properties are covered in chapter 3 to

5. Compact Tension (CT) samples were machined from the CGP processed alloy and subjected to cyclic loading to determine the Fatigue Crack Growth Rate (FCGR). Tests were carried out under loading control at two different load ratios ($R=0.1$ and $R=0.7$) in order to evaluate material's sensitivity to mean loading stress. The material response to the occurrence of an anomalous load during a constant amplitude fatigue test was also examined. Two tests with overloads (OL) applied during the crack propagation under baseline load ratio test conditions. In addition, an underload (UL) was also studied in the case of $R=0.1$. Furthermore, a comparison of the fatigue resistance was made between the initial and CGP-processed alloy tested at $R=0.1$. The outcomes of the experimental parts are discussed below.

A.2. Fatigue test procedure

Miniature Compact Tension (CT) specimen, of length 35mm and thickness of approximately 2 mm, was machined from the CGP-processed plate for fatigue testing. The details of the sample geometry are shown in Figure. 11.1 [213]. The cyclic fatigue loading test, for evaluation of the fatigue crack growth rate (FCGR), was carried out using a servo-controlled hydraulic fixture with a load capacity of up to 20 kN. The CT specimen was subjected to a constant (baseline) amplitude loading at the frequency of 7Hz. Crack initiation its length was precisely monitored and measured using an optical microscope system capable of producing images at 1024x1024pixels resolution (pixel size of around 1 μ m). The fatigue test setup and the fatigue load history are shown in Figure. 11.2a-d.

Figure A- 1: Compact tension sample geometry.

Figure A- 2: (a) Fatigue Crack Growth Rate (FCGR) setup; (c-d) fatigue loading history

The CGP samples were subjected to different fatigue load history for this study. The sample labelled as “DA1” was subjected to cyclic loading at constant amplitude as illustrated in Figure 11.2b (without OL). A load ratio of $R=0.1$ was used and the load range was between 0.87kN ($F_{\max}$) and 0.087kN ($F_{\min}$). Another set of experiments were performed using a different load ratio of $R=0.7$ with a load range of between 0.87 kN ($F_{\max}$) and 0.69 kN ($F_{\min}$). These samples were labelled as “DA2” and “DA3” and the fatigue loading history is illustrated in Figure 11.2c (without OL). Sample named “DA UL1” was tested at the same constant amplitude cyclic loading (fatigue baseline) as sample “DA1” but with an application of a single underload (UL) at the point of time after a crack length increased to 4.5mm. The magnitude of the F_{UL} was -1.2 kN and the loading sequence is shown in Figure 11.2d. The CGP samples labeled as “DA OL1” and “DA OL2” were subjected to the load ratio of $R=0.1$ and 0.7, respectively, and with a single OL applied when the crack length reached 9 mm. These fatigue loading sequences are shown in Figure 11.1b-c. The ratio of the OL and maximum cyclic load was chosen as 1.5. As such the magnitude of the OL was determined as 1.3 kN (FOL). An additional sample using the initial as-received material (AZ31B-O) was subjected to the same loading sequences as CGP sample “DA1” for comparison of the fatigue crack propagation rate so as to determine the influence of SPD on the alloy’s fatigue resistance. Table 11.1 shows the summary of tests conducted.

Table A- 1: Summary of fatigue loading sequences for different test samples

Samples	Load Condition	Load ratio, R	$F_{\max}$ (kN)	$F_{\min}$ (kN)	F_{UL} (kN)	F_{OL} (kN)
DA, As-received	Constant amplitude	0.1	0.87	0.087	N.A	N.A
DA3/DA2	Constant amplitude	0.7	0.87	0.69	N.A	N.A
DA OL1	Constant amplitude with single overload (OL)	0.1	0.87	0.087	N.A	1.3
DA UL1	Constant amplitude with single underload (UL)	0.1	0.87	0.087	-1.2	N.A
DA OL2	Constant amplitude with single overload (OL)	0.7	0.87	0.69	N.A	1.3

A.3. Fatigue test results and discussion

The plot of fatigue crack growth rate (FCGR), da/dn , against stress intensity factor (SIF) range, ΔK , is shown in Figure 11.3. The SIF range was calculated based on mode I crack propagation by using the equation proposed by Murakami [214] as shown in Equation 11.1, where a is the crack length and σ is the range of uniaxial stress.

Figure A- 3: Fatigue crack growth rate for different load sequences (superimposed fitting of Paris's law)

$$\Delta K = \Delta \sigma \sqrt{\pi a} \quad (\text{A.1})$$

As shown in Figure 11.3, the stage II crack propagation stage can be well represented by Paris's law in equation 11.2. Table 11.2 shows the summary of coefficients C and m for the two load ratios as determined by fitting the experimental data points using equation 11.2.

$$\frac{da}{dn} = C \Delta K^m \quad (\text{A.2})$$

Table A- 2: Summary of Paris's coefficients for different load ratio

Load ratio, R	C, m/(cycle MPa $\sqrt{m}$)	m
0.1	2.34×10^{-10}	3.07
0.7	2.85×10^{-9}	2.41

The coefficient m represents the slope of the FCGR vs SIF range curve. From the fitting of the experimental data points with equation 11.2, a higher load ratio shows a marginally larger m value which indicates steeper curve. However, the m values determined for the different load ratios are considered to be very close, which suggests that the load ratio does not significantly affect crack growth rate behaviour. What was significantly changed was the fatigue threshold value. A higher mean load (at $R=0.7$) was found to decrease the fatigue threshold value from $\sim 12.4 \text{ MPa}\sqrt{m}$ (at $R=0.1$) to $\sim 4.2 \text{ MPa}\sqrt{m}$. This generally indicates the crack initiated more easily by a factor of ~ 3 by increasing the mean stress (mean value of the maximum and minimum applied load) by $\sim 63 \%$.

It can also be observed from Figure 11.3, that there were no noticeable differences

between the experimental data points in as-received alloy and CGP-processed materials at $R=0.1$. This indicates that the fatigue crack growth rate and behaviour of the fine-grained material were similar to the coarse-grained material. This result is interesting since fine-grained materials are known to have a lower resistance to fatigue crack growth rate [215]. This is because the plastic deformation zone ahead of the crack tip is usually larger than the average grain size and therefore has a higher damage accumulation. With regards to this finding, it is interesting to understand how the fatigue performance of CGP processed AZ31 alloy compares with that processed by other SPD techniques. Such studies were however limited [100, 216, 217]. Kim et al. [217] investigated the influence of equal-channel angular pressing (ECAP) on the fatigue performance of as-extruded AZ31 alloy and found that ECAP reduced the fatigue crack growth rate (higher resistance to crack growth) but lowered the fatigue endurance limit. The lowered fatigue endurance limit was attributed to the poor resistance to crack initiation which was linked to the reduction in yield strength due to texture softening after ECAP, where the basal planes were strongly aligned 45° to the extrusion direction [99]. It was furthered postulated that the effect of crack nucleation was more dominant than the fatigue crack growth rate which resulted in the overall decrease in fatigue endurance limit. However, this was not the case in CGP-processed alloy where the yield strength increased ($\sim 47\%$) as a result of the grain refinement and there were no texture softening (basal planes were randomly tilted towards the RD and TD redirection). The details of these results can be found in Chapter 5. The largely similar fatigue threshold values $\sim 12.4 \text{ MPa}\sqrt{m}$ for both the as-received and CGP alloy strongly suggest that both materials have similar resistance to crack initiation and thus similar fatigue performance. Hence, grain

refinement associated with yield strength enhancement is important to maintain equivalent or better fatigue performance.

The effects of overload and underload were further investigated on the CGP samples. A sudden OL was found to retard the crack propagation for both load ratio conditions. This is expected as crack retardation are known to occur by primary mechanisms such as crack closure and compressive residual stress. The crack closure mechanism is associated with the contact of the crack flank during unloading stage of the OL cycle which reduces the effective crack opening displacement and the stress intensity factor at the crack tip. Compressive residual stress mechanism well-known as OL can significantly impose a very large compressive residual stress ahead of the crack tip which impedes crack propagation due to a smaller mean stress. It was found that the FCGR retardation for $R=0.1$ persisted longer than for $R=0.7$. Crack arrest was also observed in sample “DA OL2” at $R=0.7$ after the OL as shown in Figure 11.4. The crack was arrested for approximately 2000 cycles before crack initiated again and continue to propagate. UL does not show a remarkable effect on the FCGR, where only a very brief crack acceleration occurred, as shown by the square markers in Figure 11.3. It can be concluded that UL has a less significant effect in terms of crack propagation as compared to OL.

Figure A- 4: Crack arrest detail at R=0.7 in the event of an overload

A.4. Summary

- 1) The fatigue crack growth rate between the as-received (initial) and CGP-processed alloy tested at the load ratio R=0.1 was found to be similar. It can be stated that there was no significant alteration in the fatigue resistance due to the thermo-mechanical treatment.
- 2) The fatigue crack growth threshold, ΔK_{th} , was reduced from 12 to $4.2 \text{ MPa}\sqrt{m}$ when the load ratio was increased from R=0.1 to R=0.7. The coefficients C and m in Paris's law were fitted experimentally. C and m were determined as 2.34×10^{-10} and 3.07 in R=0.1 and 2.85×10^{-9} and 2.41 in R=0.7. These values are considered very close which can also be observed from the slopes of the FCGR curves.
- 3) Application of a sudden overload OL resulted in crack growth retardation in the fine-grained material at both load ratios. In the case of R=0.7, crack arrest up to approximately 2000 cycles before the crack nucleation and subsequent propagation continued.

- 4) Underload was applied in the baseline fatigue test conducted at $R=0.1$. This resulted in a slight acceleration in crack growth rate but only lasted briefly before going back to the original steady-state behaviour. The rather quick restoration steady-state fatigue crack growth rate revealed that UL had only minor effect as compared to OL in the fine-grained material.

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