

SUMMARY

PROCESSING AND PROPERTIES OF HIGH PERFORMANCE 7075 AL AND AZ91 MG POWDER METALLURGY ALLOYS

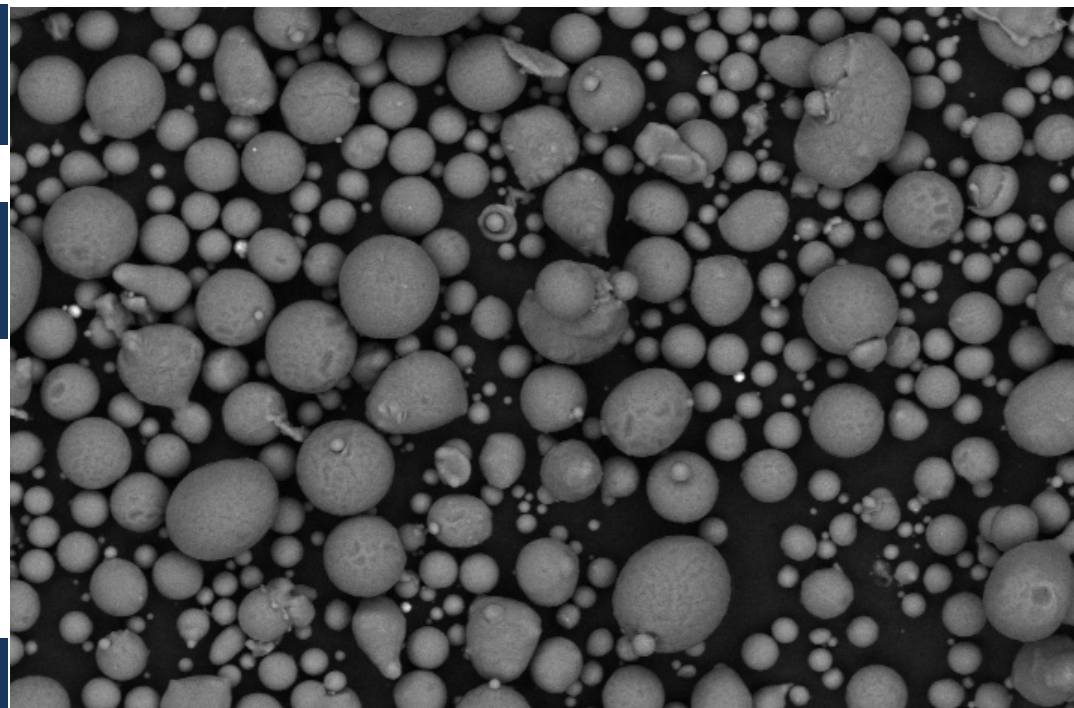
Aluminum (Al) and magnesium (Mg) alloys have received considerable attention over the past decades as potential materials of choice to achieve significant weight savings. Although the market for Al and Mg products continues to grow, many opportunities remain untapped because of the low stiffness and strength of Al and Mg alloys in comparison with ferrous alloys and some other structural materials. On the other hand, grain refinement is considered an effective way to increase the strength of metallic materials. In recent years, high-energy milling has been widely exploited for the production of nanostructured materials, and grain sizes with nanometer dimensions have been observed in almost all high-energy milled pure metals, metallic alloys, and intermetallic compounds. Although the processing and characterization of nanostructured Al alloys and composites by mechanical alloying has been the subject of many studies, studies on the high-energy milling of Mg alloys are scarce. It should also be considered that to be suitable for structural applications, the nanocrystalline Al and Mg powders produced by mechanical alloying should then be consolidated to bulk materials. The consolidation route can have significant effects on the microstructure and mechanical properties of the processed bulk product. However, to the best of our knowledge, there are no systematic studies comparing the effects of different consolidation routes on the microstructure and mechanical properties of the bulk products processed from mechanically alloyed Al and Mg powders.

The research work presented in this thesis was aimed to produce high-performance Al and Mg alloys via powder metallurgy using different powder processing techniques and consolidation routes and to understand the effects of consolidation route and its process variables through undertaking a comprehensive study of the microstructural and mechanical characteristics of consolidated alloys.

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PROCESSING AND PROPERTIES OF HIGH PERFORMANCE
7075 AL AND AZ91 MG POWDER METALLURGY ALLOYS



Doctoral Thesis

Processing and properties of high performance 7075 Al and AZ91 Mg powder metallurgy alloys

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TESIS DOCTORAL

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Processing and properties of high performance 7075 Al and AZ91 Mg powder metallurgy alloys

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TO MY FAMILY

TO ALL MY BELOVED FRIENDS

TO JOSE MANUEL

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Looking back at my PhD years at the Department of Materials Science and Engineering of Universidad Carlos III de Madrid (UC3M), I feel that things have run very smoothly for me. I owe this to all my dearest Spanish friends and colleagues at the Grupo de Tecnología de Polvos (GTP). Chicos, muchas gracias! Nunca olvidaré su amabilidad y Amistad.

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TABLE OF CONTENTS

ABSTRACT	1
RESUMEN	3
PREFACE	5
CHAPTER 1 MOTIVATION AND OBJECTIVES	11
1.1 Introduction	11
1.2 Research objectives.....	12
References.....	13
CHAPTER 2 LITERATURE REVIEW	17
2.1 Al and Al Alloys	17
2.1.1 7xxx series Al Alloys.....	17
2.2 Mg and Mg Alloys	18
2.2.1 AZ Mg Alloys.....	19
2.3 Fine-Grained and Nanocrystalline Materials	19
2.4 Powder Metallurgy (PM) of Al and Mg.....	21
2.4.1 Powder Metallurgy of Al.....	22
2.4.2 Powder Metallurgy of Mg	23
2.4.3 The PM Processing Routes	24
2.5 Powder Production.....	25
2.5.1 Atomization	25
2.5.2 Mechanical Grinding	26
2.5.3 Mechanical Alloying	26
2.6 Powder Compaction.....	28
2.7 Sintering.....	30
2.7.1 Solid State Sintering.	30

2.7.2 Liquid Phase Sintering.....	31
2.7.3 Sintering of Al PM Alloys.....	32
2.7.4 Sintering of Mg powders.	33
2.8 Field-Assisted Sintering Technique.....	34
2.9 Hot Deformation.....	36
2.9.1 Hot deformation behavior and constitutive analysis.....	36
2.9.2 Hot deformation behavior of PM alloys.	37
2.9.3 Workability and processing maps.	38
2.9.4 Hot compression.....	39
2.9.5 Extrusion.....	40
References.....	41
CHAPTER 3 MATERIALS AND EXPERIMENTAL PROCEDURE	51
3.1 Starting Materials.	52
3.1.1 Alumix 431D Premix.	52
3.1.2 AZ91 Mg Alloy Powders.....	52
3.1.2 Pressing Lubricant.	52
3.2 High-Energy Milling.....	52
3.3 Powder Characterization.....	53
3.4 Powder Compaction.....	54
3.4.1 Compressibility Studies.	54
3.4.2 Uniaxial Cold Compaction.....	54
3.5 Conventional Sintering.....	55
3.6 Field Assisted Hot Pressing (FAHP)	55
3.7 Uniaxial Hot Compression.....	57
3.7.1 The Effects of Relative Green Density.....	57
3.7.2 Hot Deformation Behavior.....	58
3.7.3 Processing Maps	59

3.8 Powder Extrusion	60
3.9 Characterization of Consolidated Materials.....	61
References.....	62
CHAPTER 4 SUMMARY OF RESULTS AND DISCUSSION FOR 7075 AL PM ALLOY	65
4.1 A 7075 Al PM Alloy: Alumix 431D Powder	65
4.2 Mechanical Alloying	66
4.3 Mechanically Alloyed Alumix 431D Powder	68
4.4 Analysis of the Compressibility.	70
4.5 Conventional Sintering.....	72
4.5.1 Effects of Sintering Temperature and Time.	72
4.5.2 Simultaneous Thermal Analysis (STA).	75
4.6 Field Assisted Hot Pressing (FAHP)	76
4.7 Effects of Green Density on the Hot Deformation of a 7075 Al PM Alloy.	79
4.8 Hot Deformation of a 7075 Al PM Alloy.....	79
4.8.1 PM Processing.....	80
4.8.2 Hot Compression Tests	81
4.8.3 Processing Maps.	81
4.8.4 Kinetics of Hot Deformation.	84
4.8.5 Microstructures of the Hot-compressed Specimens.	86
4.9 Hot Deformation of a Nanocrystalline 7075 Al PM Alloy.	88
4.9.1 PM Processing.....	88
4.9.2 Hot Compression Tests.	90
4.9.3 Processing Maps.	91
4.9.4 Microstructures of the Hot-compressed Specimens.	93
4.10 Hot Extrusion of a 7075 Al PM Alloy.	96
4.11 Hot Extrusion of a Nanocrystalline 7075 Al PM Alloy.	97

4.11.1 PM Processing.....	97
4.11.2 Hot Extrusion.	97
4.11.3 Extruded Material.....	98
4.12 Partial Conclusions	101
References.....	102
CHAPTER 5 SUMMARY OF RESULTS AND DISCUSSION FOR AZ91 MG PM ALLOY	107
5.1 AZ91 Mg Alloy Powders.....	107
5.2 Mechanical Alloying	108
5.3 Mechanical Alloyed AZ91 Powder	109
5.4 Analysis of the Compressibility.	111
5.5 Conventional Sintering.....	114
5.5.1 Effects of Sintering Temperature and Time.	114
5.5.2 Effect of Sintering Atmosphere.	115
5.5.3 Microstructures of the Sintered Specimens.	116
5.5.4 Simultaneous Thermal Analysis (STA).	118
5.6 Field Assisted Hot Pressing (FAHP)	120
5.7 Hot Deformation of an AZ91 Mg PM Alloy.	124
5.8 Hot Deformation of a Nanocrystalline AZ91 Mg PM Alloy.....	126
5.9 Partial Conclusions	128
References.....	129
CHAPTER 6 CONCLUSIONS.....	133
PAPER AL I	
Optimisation of mechanical milling process for the production of AA7075 / (SiC or TiB ₂) composite powders	
PAPER AL II	
The microstructural evolution of a premixed Al-Zn-Mg-Cu powder through high-energy milling and subsequent isothermal annealing	

PAPER AL III

Compressibility characteristics of a nanostructured 7075 Al alloy powder produced by high-energy milling

PAPER AL IV

Hot deformation behaviour and flow stress prediction of 7075 aluminium alloy powder compacts during compression at elevated temperatures

PAPER AL V

Microstructural and mechanical characterisation of 7075 aluminium alloy consolidated from a premixed powder by cold compaction and hot extrusion

PAPER MG I

The microstructural evolution of a pre-alloyed AZ91 magnesium alloy powder through high-energy milling and subsequent isothermal annealing

PAPER MG II

An Investigation on the compressibility of a pre-alloyed Mg-Al-Zn powder

PAPER MG III

The effect of mechanical milling on the compressibility of a pre-alloyed Mg-Al-Zn powder

PAPER MG IV

Hot deformation behavior and workability characteristics of AZ91 magnesium alloy powder compacts – A study using processing map

PAPER MG V

Hot workability of nanocrystalline AZ91 magnesium alloy

ABSTRACT

Aluminum (Al) and magnesium (Mg) alloys have received considerable attention over the past decades as potential materials of choice to achieve significant weight savings. Although the market for Al and Mg products continues to grow, many opportunities remain untapped because of the low stiffness and strength of Al and Mg alloys in comparison with ferrous alloys and some other structural materials. On the other hand, grain refinement is considered an effective way to increase the strength of metallic materials. In recent years, high-energy milling has been widely exploited for the production of nanostructured materials, and grain sizes with nanometer dimensions have been observed in almost all high-energy milled pure metals, metallic alloys, and intermetallic compounds. Although the processing and characterization of nanostructured Al alloys and composites by mechanical alloying has been the subject of many studies, studies on the high-energy milling of Mg alloys are scarce. It should also be considered that to be suitable for structural applications, the nanocrystalline Al and Mg powders produced by mechanical alloying should then be consolidated to bulk materials. The consolidation route can have significant effects on the microstructure and mechanical properties of the processed bulk product. However, to the best of our knowledge, there are no systematic studies comparing the effects of different consolidation routes on the microstructure and mechanical properties of the bulk products processed from mechanically alloyed Al and Mg powders. The research work presented in this thesis was aimed to produce high-performance Al and Mg alloys via powder metallurgy using different powder processing techniques and consolidation routes and to understand the effects of consolidation route and its process variables through undertaking a comprehensive study of the microstructural and mechanical characteristics of consolidated alloys.

The raw materials used for this study were a commercially available premixed Al–Zn–Mg–Cu powder, i.e. Alumix 431D with a chemical composition equivalent to 7075 Al alloy, and two different kinds of AZ91 Mg alloy powder produced by mechanical grinding and atomization. Mechanical alloying was then optimized to produce nanostructured 7075 Al and AZ91 Mg alloy powders with favorable microstructural, morphological, and particle size characteristics. The nanocrystalline 7075 Al (crystallite size 30 nm) and AZ91 Mg (crystallite size 25 nm) alloys produced by mechanical alloying showed good thermal stability, which retained their crystallite sizes under 100 nm after having been isothermally annealed at high temperatures for up to 4 h.

Fully dense products were directly consolidated from the as-received and mechanically alloyed powders by field-assisted hot pressing (FAHP). Pressing temperature was found to have significant effects on the microstructures and hardness of the bulk samples processed by FAHP technique. Thanks to the low pressing temperature and short processing time used, the bulk alloys consolidated from the nanostructured 7075 Al and AZ91 Mg powders exhibited ultra-fine grain structures and very high hardness values.

Uniaxially cold pressed compacts were used to study the sintering response of the as-received and mechanically alloyed powders. Based on the obtained results, the optimum sintering temperature and time for each powder were determined. Besides, studying the effect of sintering atmosphere revealed that the AZ91 compacts are more responsive to sintering in the nitrogen atmosphere than the argon atmosphere.

Hot compression tests were performed to study the hot deformation behavior and workability characteristics of the as-received and mechanically alloyed powders. To this end, the data obtained through the hot compression of powder compacts were analyzed to develop processing maps. Strain was found to have important effects on the processing maps of all powders. The developed processing maps successfully identified the optimum conditions for hot deformation of each powder, which were then employed for the production of bulk products by hot extrusion.

Hot extrusion without canning and degassing was used to produce full density alloys from the as-received and mechanically alloyed powders. The microstructures and mechanical properties of the extrusion products were carefully studied. The obtained results confirmed that the hot extrusion without canning and degassing can be considered as an advantageous technique for consolidation of the Al-based and Mg-based powders.

RESUMEN

En las últimas décadas han adquirido mucha relevancia las aleaciones de Aluminio (Al) y Magnesio (Mg) como potenciales materiales mediante los que conseguir importantes reducciones de peso. Pese a que el mercado de productos de Al y Mg sigue creciendo, existen numerosas oportunidades sin explotar a causa de la baja rigidez y resistencia de sus aleaciones en comparación con las aleaciones base hierro y otros materiales estructurales. Por otro lado, el afino de grano es una vía eficaz para mejorar la resistencia en los materiales metálicos. En los últimos años, la molienda de alta energía se ha empleado para la fabricación de materiales nanoestructurados, y tamaños de grano de escala nanométrica en muchos metales, aleaciones y compuestos intermetálicos. Pese a que el procesamiento y caracterización de aleaciones y compuestos base Aluminio y fabricados por aleación mecánica han sido objeto de numerosos estudios, no ocurre lo mismo con las aleaciones base Mg. También se debe considerar que las posibles aplicaciones de los materiales nanocristalinos de Al y Mg como materiales estructurales, son en forma de material consolidado macizo. Las vías de procesamiento tienen efectos significativos sobre la microestructura y propiedades mecánicas del material macizo. Sin embargo, no existen estudios sistemáticos que comparen entre sí distintas vías de consolidación y su influencia en la microestructura y propiedades mecánicas de materiales obtenidos a partir de polvos fabricados por aleación mecánica. El trabajo de investigación desarrollado en esta tesis, tiene como objetivo la producción de aleaciones de Al y Mg de altas prestaciones, utilizando distintas vías de procesamiento del polvo y distintas rutas de consolidación con sus variables de proceso, a través de un extenso estudio de la microestructura y las características mecánicas de las aleaciones consolidadas.

La materias primas utilizadas han sido un polvo premezclado comercial, la calidad Alumix 431D con una composición química equivalente a la aleación de aluminio 7075 y dos polvos distintos de la aleación AZ91 de magnesio, obtenidos por molienda mecánica y atomización, respectivamente. El proceso de aleación mecánica se optimiza para obtener polvos de 7075 Al y AZ91 Mg con una microestructura, morfología y tamaño de partícula adecuados. Las aleaciones nanocristalinas de 7075 Al (tamaño de dominio cristalino de 30 nm) y AZ91 Mg (tamaño de dominio cristalino de 25 nm) obtenidas por aleación mecánica, mostraron una buena estabilidad térmica manteniendo tamaños de dominio cristalino por debajo de 100 nm después de un recocido isotérmico a altas temperaturas durante 4 horas.

Mediante prensado en caliente por paso de corriente “field-assisted hot pressing” (FAHP) se obtuvieron productos totalmente densificados por consolidación directa. La temperatura de procesamiento se mostró como una variable fundamental en su efecto sobre la microestructura y dureza de las muestras procesadas. Gracias a las bajas temperaturas de procesamiento y los tiempos cortos, las aleaciones consolidadas a partir de polvos nanoestructurados de 7075 Al y AZ91 Mg presentaron estructuras de grano ultra-fino y valores muy altos de dureza.

Compactos prensados uniaxialmente en frío se utilizaron para analizar la respuesta de los polvos en estado de suministro y aleados mecánicamente. En base a los resultados obtenidos se optimiza, para cada material, el tiempo y temperatura óptimos de sinterización. Además se estudió el efecto de la atmósfera de sinterización, siendo más eficiente en el caso de los compactos de AZ91 la respuesta a la sinterización en atmósfera de nitrógeno que en atmósfera de argón.

Se desarrollaron ensayos de compresión en caliente para analizar el comportamiento de los materiales así como sus propiedades de “conformabilidad” tanto de los polvos en estado de suministro como los polvos aleados mecánicamente. Con los datos obtenidos de los ensayos de compresión en caliente se desarrollaron mapas de procesado de todos los polvos. Se confirmó que la deformación juega un papel esencial en las condiciones de procesado de todos los materiales. Mediante los mapas de procesado se determinaron las condiciones óptimas para la deformación en caliente de cada material, condiciones que se pueden extrapolar en la producción de productos por extrusión en caliente.

Se utilizó extrusión en caliente (sin enlatado ni desgasificado) para fabricar aleaciones totalmente densas a partir de los polvos en estado de suministro y aleados mecánicamente. Se estudió en profundidad su microestructura y propiedades mecánicas. Los resultados obtenidos confirmaron que este método de procesado es una técnica de consolidación muy adecuada para estas familias de materiales.

PREFACE

This Ph.D. thesis is based on the work carried out at the Department of Materials Science and Engineering of Universidad Carlos III De Madrid (Leganés, Spain) and IMDEA Materials Institute (Getafe, Spain).under the supervision of Professor Jose Manuel Torralba. The project was mutually funded by IMDEA Materials Institute and the Comunidad de Madrid through the ESTRUMAT Grant #S2009/MAT-1585.

This thesis is divided into six chapters. Chapter 1 includes an introduction to this doctoral thesis and its motivation and research objectives. In chapter 2, a literature review that is related to the objectives and research background of this research work is presented. Chapter 2 basically covers three major topics: the current status of Al and Mg PM, the PM techniques and routes generally used for the production and consolidation of Al and Mg powders, and the hot deformation of Al and Mg powder metallurgy (PM) alloys. Chapter 3 introduces the materials and experimental procedures employed during this research, which includes the preparation of specimens and their characterization. In chapter 4 and 5, the main results of this Ph.D. thesis, which were already reported in detail in the following appended papers, are reviewed and discussed. Chapter 6 presents the main conclusions derived from this research work. Finally, suggestions for future work regarding the subject of this project are also made in chapter 6.

This thesis is complemented by the following papers published based on the results of this Ph.D. work. From these papers, six belong to the journals indexed by Journal Citation Report (JCR) and the rest to the international conference proceedings. For this reason, the results already presented and discussed in these papers are not fully included in chapters 4 and 5 to avoid repetition of the information appearing in the text and to take full advantage of the published papers which are attached as an appendix at the end of the thesis. The following are the published papers included in the appendix:

Papers on Al PM

Al I. Optimisation of mechanical milling process for production of AA 7075/(SiC or TiB₂) composite powders

M. A. Jabbari Taleghani, E. M. Ruiz Navas, M. Salehi, J. M. Torralba
Powder Metallurgy, 55(4) (2012) 280-286

Al II. The microstructural evolution of a premixed Al-Zn-Mg-Cu powder through high-energy milling and subsequent isothermal annealing

M. A. Jabbari Taleghani, J. M. Torralba
Proceedings of Euro PM2013 Congress, Gothenburg, Sweden, 15-18 Sept., 2013
Published in CD ROM format, ISBN: 978-1-1899072-31-1

Al III. Compressibility characteristics of a nanostructured 7075 Al alloy powder produced by high-energy milling

M. A. Jabbari Taleghani, J. M. Torralba

Proceedings of Euro PM2013 Congress, Gothenburg, Sweden, 15-18 Sept., 2013

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Al IV. Hot deformation behaviour and flow stress prediction of 7075 aluminium alloy powder compacts during compression at elevated temperatures

M. A. Jabbari Taleghani, E. M. Ruiz Navas, M. Salehi, J. M. Torralba

Materials Science and Engineering: A, 534 (2012) 624-631

Al V. Microstructural and mechanical characterisation of 7075 aluminium alloy consolidated from a premixed powder by cold compaction and hot extrusion

M. A. Jabbari Taleghani, E. M. Ruiz Navas, J. M. Torralba

Materials and Design, 55 (2014) 674-682

Papers on Mg PM

Mg I. The microstructural evolution of a pre-alloyed AZ91 magnesium alloy powder through high-energy milling and subsequent isothermal annealing

M. A. Jabbari Taleghani, J. M. Torralba

Materials Letters, 98 (2013) 182-185

Mg II. An Investigation on the compressibility of a pre-alloyed Mg-Al-Zn powder

M. A. Jabbari Taleghani, J. M. Torralba

Proceedings of Euro PM2012 Congress, Basel, Switzerland, 16-19 Sept., 2012

Published in CD ROM format, ISBN: 978-1-1899072-31-1

Mg III. The effect of mechanical milling on the compressibility of a pre-alloyed Mg-Al-Zn powder

M. A. Jabbari Taleghani, J. M. Torralba

Proceedings of Euro PM2013 Congress, Gothenburg, Sweden, 15-18 Sept., 2013

Published in CD ROM format, ISBN: 978-1-1899072-31-1

Mg IV. Hot deformation behavior and workability characteristics of AZ91 magnesium alloy powder compacts – A study using processing map

M. A. Jabbari Taleghani, J. M. Torralba

Materials Science and Engineering: A, 580 (2013) 142-149

Mg V. Hot workability of nanocrystalline AZ91 magnesium alloy

M. A. Jabbari Taleghani, J. M. Torralba

Journal of Alloys and Compounds, 595 (2014) 1-7

Contribution to the appended papers

In this research work presented in the appended papers, the Ph.D. candidate, in close co-operation with Professor Jose Manuel Torralba and under his supervision, designed and performed all the experimental work, assessed and analyzed the obtained results, and wrote all of the manuscripts of the appended papers.

MOTIVATION AND OBJECTIVES

1

CHAPTER 1 MOTIVATION AND OBJECTIVES

1.1 Introduction

Recent efforts by the transportation industry to increase the fuel efficiency and to reduce the fuel consumption and exhaust emissions of vehicles and aircrafts, while maintaining their performance, have resulted in a great research interest in light weight structural materials. As a result, Aluminum (Al) and magnesium (Mg) alloys have received considerable attention over the past decades as a potential material of choice to achieve significant weight savings.

Although the market for Al and Mg products continues to grow, many opportunities remain untapped because of the low stiffness and strength of Al and Mg alloys in comparison with ferrous alloys and some other structural materials.

Al and Mg PM combines the superior properties of these light metals with the advantages of PM to produce high-performance, net- or near-net-shaped parts, thus reducing or eliminating the capital and operating costs associated with intricate machining operations. Light metals PM has traditionally been a small part of the total PM market, and indeed, a small part of the total light metals market as well. However, recently the automotive and aerospace markets have given light metals PM a large boost, and Al and Mg PM is expected to experience a large growth in the next decade [1].

On the other hand, grain refinement is considered an effective way to increase the strength of materials as expressed by the Hall–Petch relation [2]. The powders produced by powder metallurgy (PM) techniques, such as atomization and high-energy milling, possess a very fine grain structure, which can result in superior mechanical properties for the bulk alloys consolidated from fine-grained PM powders. Therefore, fabrication by PM has considerable potential for Al and Mg alloys, and the manufacturing of diverse light weight products by PM techniques can increase the consumption of Al and Mg considerably.

In the 1960s, high-energy milling was first developed by Benjamin and his co-workers to fabricate oxide-dispersion-strengthened (ODS) nickel-based superalloys [3]. In recent years, this technique has been widely exploited for the production of nanostructured materials, and grain sizes with nanometer dimensions have been observed in almost all high-energy milled pure metals, metallic alloys, and intermetallic compounds [4]. Thanks to an ultra-fine grain structure and significantly large volume fraction of grain boundaries, nanocrystalline metals and alloys (with grain sizes less than 100 nm) processed by high-energy milling exhibit significantly improved mechanical properties over their microcrystalline counterparts.

The Al and Mg powders processed by PM techniques, such as mechanical grinding, atomization, and high-energy milling, are then consolidated by different PM routes. Sintering is widely regarded as the most convenient PM route for the consolidation of metallic powders. However, the presence of residual porosity in the microstructure of sintered products remains as an obstacle to overcome for many applications [5]. Powder extrusion,

powder forging, and powder rolling are the PM processing techniques that have been developed for the production of fully dense, high-performance materials from powders. Compared with other PM routes such as sintering and hot pressing, the shear stresses involved in the aforementioned techniques make them an ideal process for the production of bulk Al and Mg alloys from powder mixtures. These shear stresses lead to the breakage of the stable oxide layer covering the powder particles [6]. Field-assisted sintering techniques (FAST) combine simultaneously the application of pressure and electric current directly on the sample. Joule heating provides high heating rates, allowing dense compacts to be obtained under uniform heating at relatively low temperatures and in short processing times (typically a few minutes). Another advantage of FAST is that the plasma formation between powder particles to facilitate the sintering process also aids in the elimination of surface impurities, leading to enhanced sintering and consolidation. Considering all above, FAST is considered an effective sintering technique for the materials widely regarded as hard-to-sinter. FAST takes only a few minutes to complete a sintering process compared to conventional sintering processes which may take hours for the same. Therefore, coarsening of nano-sized grains and/or fine particles during the sintering process can be avoided, suggesting that FAST is ideal for consolidating the nanostructured powders processed by high-energy milling while maintaining their nano features [7, 8].

1.2 Research objectives

Current research initiatives of the Al and Mg PM industry are looking at developing improved PM alloys and reducing the cost and complexity of fabrication. In other words, the Al and Mg PM industry today is aiming to improve the mechanical properties of the produced structural parts in a cost-effective manner. This can be achieved through:

- Development of new or ultrafine-grained PM alloys
- Minimizing the residual porosity present in the microstructure of the consolidated materials
- Studying the effects of different consolidation routes and related process variables on the microstructure and mechanical properties of the consolidated materials
- Development of new PM techniques and optimizing the conventional PM routes for the consolidation of Al and Mg PM alloys

The surface layer formed on Al and Mg powders during powder production and processing acts as a barrier to diffusion in sintering, leading to a weak interparticle bonding and a large amount of residual porosity for the sintered products. Consequently, solid state sintering of the mentioned powders is considered unfeasible. The sintering response of Al and Mg powders can be improved through liquid phase sintering. Development of commercial Al premixes in the past decade which can be sintered to high densities through liquid phase sintering is considered a great breakthrough for the Al PM industry. Nevertheless, the

presence of some amount of residual porosity in the Al sintered parts is inevitable. The residual porosity generally has a very detrimental effect on the mechanical properties of PM products.

The major issue in the development of the Mg PM is the availability of commercial Mg powders and premixes [9]. To date, very limited research has been carried out on the sintering behavior of Mg-based powders.

The **motivation** of this thesis is to improve the attractiveness of Al and Mg PM for industrial applications. Using a 7075 Al alloy and an AZ91 Mg alloy, which show relatively high strengths when compared with all other commercial Al and Mg alloys, as the starting materials, the **main objective** of this work is to produce high-performance Al and Mg alloys via PM using different powder processing techniques and consolidation routes and to understand the effects of consolidation route and its process variables through undertaking a comprehensive study of the microstructural and mechanical characteristics of consolidated alloys. The following are the sub objectives to be achieved for the fulfillment of the main objective of this research work:

- Optimization of the mechanical alloying process to produce nanostructured 7075 Al and AZ91 Mg alloy powders with favorable microstructural, morphological, and particle size characteristics.
- Evaluation of the thermal stability of the nanostructured powders processed by mechanical alloying.
- Evaluation of the compressibility and sintering response of the as-received and as-milled 7075 Al and AZ91 Mg powders.
- Studying the hot deformation behavior and workability characteristics of the as-received and as-milled 7075 and AZ91 powders to determine the optimum hot deformation conditions for each powder.
- Consolidation of the as-received and as-milled 7075 Al and AZ91 Mg powders by different PM routes, including conventional sintering, spark plasma sintering, hot compression, and powder extrusion, to study the effects of consolidation route on the microstructure and mechanical properties of the processed bulk alloys.

References

- [1] G.E. Totten, D.S. MacKenzie, Handbook of aluminum: Vol. 1: physical metallurgy and processes, Marcel Dekker, New York, United States of America, 2003.
- [2] W.F. Hosford, Mechanical behavior of materials, 2nd ed., Cambridge University Press, New York, United States of America, 2009.
- [3] J. Benjamin, Metallurgical and Materials Transactions B, 1 (1970) 2943-2951.
- [4] C. Suryanarayana, Progress in Materials Science, 46 (2001) 1-184.
- [5] R.E.D. Mann, R.L. Hexemer Jr, I.W. Donaldson, D.P. Bishop, Materials Science and Engineering: A, 528 (2011) 5476-5483.

- [6] C. Zubizarreta, S. Giménez, J.M. Martín, I. Iturriza, *Journal of Alloys and Compounds*, 467 (2009) 191-201.
- [7] M. Kubota, J. Kaneko, M. Sugamata, *Materials Science and Engineering: A*, 475 (2008) 96-100.
- [8] M. Kubota, *Journal of Alloys and Compounds*, 504, Supplement 1 (2010) S319-S322.
- [9] P. Burke, C. Petit, S. Yakoubi, G.J. Kipouros, Thermal Effects of Calcium and Yttrium Additions on the Sintering of Magnesium Powder, in: *Magnesium Technology 2011*, John Wiley & Sons, Inc., 2011, pp. 481-484.

LITERATURE REVIEW

2

CHAPTER 2 LITERATURE REVIEW

2.1 Al and Al Alloys

With an annual consumption of about 24 million tons, Al is the most heavily consumed non-ferrous metal in the world. Al is especially well-known for its low density (2.7 g/cm^3), high specific strength, high electrical and thermal conductivity, and its resistance to atmospheric corrosion. Al's unique combination of properties makes it an ideal candidate for conventional and novel applications in the transportation, defense, construction, food, and electrical industries. Opportunities for Al are expected to grow significantly in the near future as the demand for technologically complex and ecologically sustainable products continues to increase.

The elastic properties for pure Al are presented in Table 2.1. Pure Al, almost like all pure metals, has a low strength and is rarely used in applications where resistance to deformation and fracture is necessary. Therefore, alloying elements are added to Al mainly to improve its strength. The low density combined with high strength has made Al alloys attractive in applications where specific strength (strength-to-density ratio) is a major design consideration. For structural applications, the strongest Al alloy which is cost-effective and satisfies other required properties, such as ductility and toughness, is normally selected [1]. Al products can be manufactured by diverse processing routes such as casting, plastic deformation, and powder metallurgy. Besides, the heat treatment including quenching and aging is the most widely used way to improve strength properties of Al alloys.

Table 2.1. The elastic properties of pure Al and Mg [1, 2].

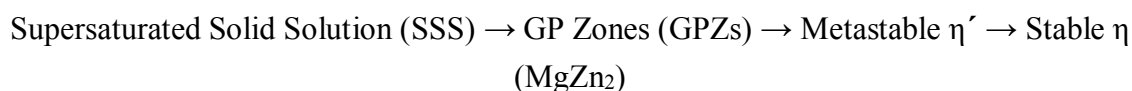
Element	Young's Modulus (E) (GPa)	Specific Young's Modulus (GPa.cm ³ /g)	Shear Modulus (G) (GPa)	Specific Shear Modulus (GPa.cm ³ /g)	Poisson's Ratio (ν)
Al	69-72	26-27	25-26.5	9-10	0.31
Mg	45	26	17	10	0.29

2.1.1 7xxx series Al Alloys

Having a superior combination of properties, such as high strength and fracture toughness, low density, good workability and weldability, and remarkable stress corrosion cracking resistance, 7xxx series Al alloys based on the ternary Al-Zn-Mg or the quaternary Al-Zn-Mg-Cu alloying systems have long been regarded as some of the best candidates for the demanding structural applications in the aerospace and automotive industries [3-6]. In

fact, 7xxx series Al alloys represent some of the highest strength Al alloys in commercial use among the Al alloys [7].

The good strength of the 7xxx series Al alloys is due to the fact they are precipitation hardening alloys. The usual precipitation sequence of 7xxx series Al alloys during the aging treatment can be summarized as [8-10]:



Metastable η' , instead of stable η , is believed to be responsible for peak hardening of these alloys. GPZs and η' often form during the early stages of precipitation. η phase is the stable phase which forms during solidification and cooling of Al-Zn-Mg-(Cu) alloys. T phase ($\text{Al}_2\text{Mg}_3\text{Zn}_3$, also known as $\text{Mg}_{32}(\text{Al}, \text{Zn})_{49}$) is a metastable phase of Al-Zn-Mg-(Cu) alloying system that can be produced through rapid solidification and cooling [9]. Considering the high cooling rate in atomisation, the presence of T phase in atomised Al-Zn-Mg-(Cu) alloy powders is highly probable.

2.2 Mg and Mg Alloys

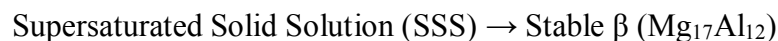
Mg is virtually the lightest of all structural metals (Be is even lighter, but its use is negligible). It has a density of 1.74 g/cm³, which is approximately one-fourth the density of steel and two-thirds that of Al. Because of its low density and high specific mechanical properties, Mg-based materials are actively pursued by companies for weight-critical applications [11]. Besides, Mg is a very promising candidate for biocompatible and biodegradable applications in modern medicine [12]. In 2010, worldwide Mg production was estimated to reach 810,000 tons per year.

The elastic properties for pure Mg are presented in Table 2.1 [2]. If we analyze the specific elastic properties, both pure Al and Mg possess similar values. In most structural applications, pure Mg is alloyed with other elements. Mg alloys have received considerable attention as a structural material in recent years due to their interesting properties, such as low density, high strength-to-weight ratio, good damping characteristics, superior machinability, and excellent castability [13-15]. Most of the research and development on these alloys has been performed by the automotive industry; and die casting has been the main manufacturing route for Mg products because of the poor workability of Mg at room temperature, which is a result of its HCP crystal structure [16, 17]. Fabrication by plastic forming at elevated temperatures has also considerable potential for Mg alloys because the worked alloys have greater strength and ductility than the castings [18, 19]. Many Mg alloys are heat-treatable, and the strength of these Mg alloys can be increased through solid solution strengthening and precipitation hardening.

2.2.1 AZ Mg Alloys

AZ indicates that Al and zinc (Zn) are the main two alloying elements in AZ series Mg alloys. Al is one of the most commonly used alloying elements in Mg, as it has the most favorable influence on Mg. Addition of Al results in the enhancement of hardness and strength. It also improves castability. The alloy in excess of 6 wt% of Al can also be heat treated. Zn is usually used in conjunction with Al to increase the strength without reducing ductility. The increase in strength to comparable levels is not achievable if only Al content is increased [11]. Due to the fact that Al can result in high strengths of the alloys, the group AZ can produce high (to very high) strengths. Mg-Al-Zn alloys have become one of the most important Mg alloys with a wide range of applications in the automotive industry. In fact, among all of the existing Mg alloys, AZ91 (Mg-9Al-1Zn) is the most common commercial Mg alloy. This is attributed to the best combination of castability, mechanical strength and ductility [20, 21].

According to the equilibrium Mg-Al alloy phase diagram, the equilibrium phases are the HCP Mg-rich α phase and $\text{Mg}_{17}\text{Al}_{12}$ - β phase with a complex BCC structure. The maximum solid solubility of Al in Mg is 12.7 wt% at 437 °C and decreases to about 2 wt% at room temperature [22, 23]. As a result, coarse β precipitates appear in the cast microstructure when Mg-Al-Zn alloys contain more than 2% Al. Mg-Al binary alloys with a high content of Al are precipitation hardening alloys. The addition of Zn to the Mg-Al alloying system reduces the solid solubility of Al in Mg, increasing the amount of precipitate phase formed upon aging and, thus, causing a moderate increase in strength [24]. The usual precipitation sequence of AZ series Mg alloys during the aging treatment can be summarized as [25]:



The precipitation of the β -phase through the aging process in Mg-Al-Zn alloys has a relatively poor strengthening effect due to the direct formation of equilibrium β precipitates without any GP zones or intermediate phase precipitation.

2.3 Fine-Grained and Nanocrystalline Materials

Nanocrystalline materials are single or multi-phase polycrystals with nano scale (1-250 nm) grain size. At the upper limit (grain sizes of 250-1000 nm), the term ultra-fine grain size is often used. Nanocrystalline materials contain a large volume fraction of grain boundaries, which may significantly change their physical, mechanical, and chemical properties in comparison with conventional coarse-grained polycrystalline materials, which have grain sizes usually in the range 10–300 μm [26].

Grain size is known to have a significant effect on the mechanical behavior of materials, in particular, on the yield stress. The dependence of yield stress on grain size in metals is well established in the conventional polycrystalline range (micrometer and larger sized grains).

Yield stress, σ_y , for materials with grain size d , is found to follow the Hall-Petch (H-P) relation [27, 28]:

$$\sigma_y = \sigma_0 + k_{HP} d^{1/2} \quad (2.1)$$

where σ_y is the yield strength, σ_0 is a constant often associated with the friction stress felt by a dislocation in the pile-up, d is the grain diameter, and k_{HP} is a constant.

As suggested by the H-P relation (Equation 2.1), the yield strength of metallic materials is enhanced with grain size reduction. However, as the grain size is reduced to the submicron range, the k_{HP} value tends to decrease. Consequently, the extrapolation of H-P relation for a microcrystalline material cannot always be used to predict the yield strength of its ultrafine-grained and nanocrystalline counterpart. The deviation from H-P relation with grain size reduction can be attributed to the change in deformation mechanisms. In coarse-grained materials, dislocation slip is believed to be the dominant deformation mechanism, whereas in nanocrystalline materials, the deformation mechanism has been proposed as combined dislocation and grain boundary activities [29].

Ultrafine-grained and nanocrystalline metallic alloys exhibit significantly improved mechanical properties over their microcrystalline counterparts [26]. As a result, the synthesis of nanocrystalline materials has been the subject of widespread research over the past couple of decades. Nanocrystalline materials can be synthesized either by consolidating small clusters or breaking down the polycrystalline bulk material into crystalline units with dimensions of nanometers. These approaches have been classified into bottom-up and top-down. In the bottom-up approach we have to arrange the nanostructure atom-by-atom, layer-by-layer. In the top-down approach we start with the bulk material and break down the microstructure into a nanostructure. The five most common methods of producing nanocrystalline materials are: (1) inert gas condensation, (2) mechanical alloying, (3) electrodeposition, (4) crystallization of amorphous materials, and (5) severe plastic deformation. Mechanical alloying has proven to be an effective technique for processing nanocrystalline metallic materials. Therefore, the synthesis of nanocrystalline Al and Mg alloys by mechanical alloying has been a topic of great interest in recent years [30-33].

So far, most of the research work on nanocrystalline alloys has been carried out on body-centered cubic (BCC) and face-centered cubic (FCC) metals, and studies on nanocrystalline Mg alloys are relatively scarce. However, grain refinement has considerable potential for Mg alloys as fine-grained Mg alloys exhibit an interesting combination of high strength and high ductility at room temperature and superplasticity at elevated temperatures [14, 34]. The k_{HP} constant in H-P relation (Equation 2.1) increases with increasing Taylor factor, which is mainly dependent on the number of slip planes available for deformation. In HCP metals such as Mg, the slip systems are more limited than for BCC and FCC materials which increases the Taylor factor. The high Taylor factor and therefore k_{HP} value for HCP metals results in a strong relation between grain size and strength. To maximize the strength of Mg and its alloys, a very small grain size is required. As can be seen in Fig. 2.1, the slope of the

HCP Mg alloy is steeper than that of the FCC Al alloy. The strength of the Mg alloy is lower than the Al alloy at grain sizes larger than 2.2 μm , but increases sharply as grain size is reduced.

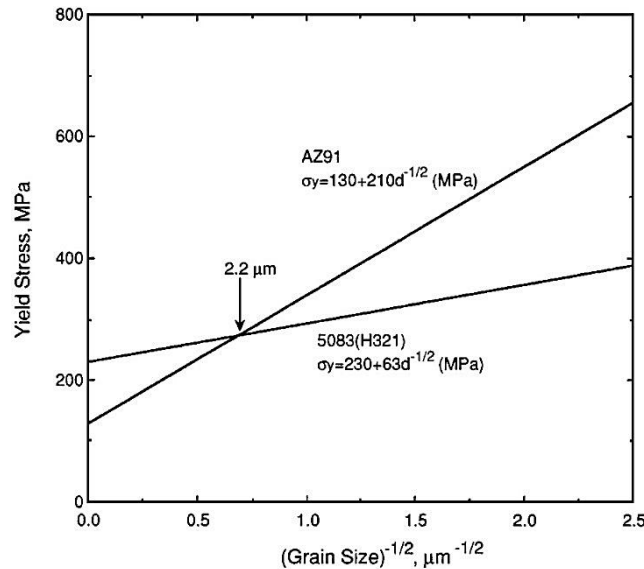


Fig. 2.1. Yield strength as a function of grain size, AZ91 Mg alloy and 5083 Al alloy [14].

2.4 Powder Metallurgy (PM) of Al and Mg.

Powder metallurgy (PM) covers a broad subject of powder production, powder consolidation, and characterization of both powder and bulk samples. Consolidation into net-shaped forms is achieved by the application of pressure and heat at a temperature below the melting point of the major constituent. The available literature on PM presents extensive information about PM technology and relevant processing routes and techniques [35-40].

Although PM is just small fraction of the global metal industry, it plays an important role in many sectors because it has many advantages compared to other conventional technologies, being the main one the ability to produce net- or near-net-shaped parts that require little or no post processing steps before being put into service. Unlike cast and wrought production, PM components can be made to any geometry for which a die can be designed and produced. PM has a high volume of production and a low processing temperature, suggesting that it can also be economical. Conventional PM, that is, when the sequence of production is uniaxial pressing and sintering, offers unique capabilities in alloy compositions and microstructural development that are extremely difficult (if not possible) and costly to obtain by any other traditional processing technique. Therefore, PM is a particularly suitable process for the development of novel materials with tailored alloy compositions.

PM is not without fault though. The main concern is porosity and how it affects mechanical properties of PM products. Moreover, production in PM is limited to high

volumes because of the expense of producing compaction dies. The cost of the raw powder materials can also be prohibitive. In the most common pressing process, i.e. uniaxial, the area limit for a part is about 200 cm². Lastly, the PM parts produced by uniaxial cold pressing show a degree of anisotropic properties due to the density gradient.

2.4.1 Powder Metallurgy of Al

While PM materials are dominated by ferrous alloys (which are close to 80 % of global metal powder production), there is a growing interest in Al PM. Al PM alloys are an attractive material for the automotive industry, given the low density and high strength-to-weight ratio of Al itself as well as fabrication advantages associated with the PM process. For example, Al PM is often used to produce the camshaft main bearing caps found in combustion engines. Such components, historically produced by die casting, are precision parts as they ensure proper alignment of a camshaft when bolted to the block. Die cast camshafts do not meet the required dimensional tolerances and must be heavily machined prior to use. Conversely, PM production methods offer tighter dimensional tolerances to avoid the majority of expensive machining operations.

In an effort to expand the scope of application for Al PM products, considerable research has emphasized the development of new alloys. Most of the Al PM alloys used today are those based on the 2xxx (Al-Cu-Mg-Si) and 7xxx (Al-Zn-Mg-Cu) wrought and cast alloy compositions. PM alloys generally differ slightly in chemistry from the wrought and cast counterparts to optimize the press and sinter abilities of the alloy.

In the past decade, premixed Al-based powders have attracted great attention. These powders are ready-to-press and can be sintered to high densities through liquid phase sintering. A number of leading powder producers have addressed this interest and developed commercial premixes mainly based on high strength Al alloys. We can include here the Alumix 13 and 123 (2xxx series), Alumix 321 (6xxx series), and Alumix 431D (7xxx series) produced by Ecka Granules, Germany. Martin et al. [41] studied the sintering behavior of the mentioned premixes and reached a maximum sintered density of 97 % of the theoretical value. Min et al. [42] examined the sintering characteristics of AMB 2712 (2xxx series), a commercial premixed powder produced by Ampal, USA. Their sintering processes yielded PM parts with a maximum relative density of 93 %.

Porosity has a very detrimental effect on the mechanical properties of PM alloys. Although the newer Al PM alloys offer major strength improvements, the presence of a small amount of residual porosity in the sintered product remains as a hurdle to overcome [43]. In ferrous products, this feature can be eliminated by forging the as-sintered materials [44]. This is known to increase all mechanical properties significantly with the most prominent gains realized in yield strength, ductility, and fatigue life. PM forging is now a widely used method of producing steel parts of high density for the automotive industry [37]. It is now known that hot deformation of sintered Al preforms can also impart significant mechanical gains [45,

46]. However, it remains an unexploited technology in the production of Al PM components. The continued growth of Al PM in automotive applications is dependent on the improvement of dynamic properties through development of higher densities. In this regard, development of full density, net-shaped processes and optimisation of processing parameters for the consolidation of commercial Al PM premixes is of great significance.

2.4.2 Powder Metallurgy of Mg

Mg is an ideal candidate for PM processing. Because of its HCP crystal structure, traditional forming methods are difficult to be used for the production of Mg products, and the PM ability to produce net- and near-net-shape parts would be a great advantage. The unique alloy chemistries that are possible through rapid solidification and mechanical alloying may also lead to the development of new Mg alloys with improved mechanical properties and high temperature or corrosion resistance. With net shape processing and new novel alloys, PM will help Mg to reach its full potential as a structural metal [47]. The major issue in the development of the Mg PM is the availability of commercial Mg powders.

To date, little research has been done on the use of PM routes for the production of Mg products. The previous studies on Mg PM mainly concern the production of Mg matrix composites [48-50], where PM can prevent some of the matrix-reinforcement interface issues when the matrix metal is in the molten state [51]. The processing of Mg matrix composites by PM routes also allows a highly homogenous mixture of the reinforcement particles within the matrix, resulting in consistent mechanical properties in all directions.

The other major research focus in the Mg PM is the use of rapidly solidified powders to produce a very fine grain structure in the final bulk product. With the greatly reduced grain size as compared to parts produced through ingot metallurgy, the strength and superplastic properties of the Mg alloys are proportionally increased [14, 52]. Moreover, powders of alloys that contain rare earth elements and other additions are produced by atomization, where rapid solidification allows extended solubility not possible with ingot metallurgy. Alloying additions are chosen to improve strength, creep resistance and superplasticity [53, 54].

Hot pressing and hot extrusion (with canned powders or without canning and degassing) have been used to consolidate Mg-based powders in most of the previous works on Mg PM.

Recently, new sintering and consolidation techniques have been identified that may better address issues unique to Mg. Equal channel angular pressing (ECAP) [55] is a method to provide extremely high strain value, equivalent to extruding at a 30:1 ratio, without a change in cross sectional dimensions. The high strain involved breaks any surface layer on the particles and plastically deforms the powders to ensure good interparticle bonding, and provides adequate pathways for diffusion. While cross sectional dimensions are retained, it is still only possible to produce rods of material, and not near-net-shape parts. Spray forming has been used to produce Mg alloy billets [25, 56-60]. Spray forming allows the rapid

solidification and deposition of high-density materials from a liquid alloy. Contamination in spray forming is minimized because powder production, compaction and consolidation are completed in one step (and under a well-controlled atmosphere). The process could be tailored to be near-net-shaped, as the spray can be prepared for the production of simple, two dimensional parts. However, to realize full strength and density, the parts produced by spray forming are then hot deformed. Spark plasma sintering (SPS) has been used by a few researchers to produce Mg alloys [61] and composites [62, 63]. SPS employs very short sintering times, and the high energy pulse has been attributed to cleaning contaminants from powder surfaces in-situ. Therefore, SPS seems to be specially suitable for sintering of the nanocrystalline Mg powders produced by mechanical alloying [64]. Dies for the process are either graphite or metal and allow for near-net-shape processing.

2.4.3 The PM Processing Routes

The four main steps reported in the literature for the production of a PM part are: (1) powder production and processing, (2) powder mixing, (3) powder consolidation, (4) post consolidation operations such as sizing, machining, and heat treatment. There are several PM processing routes available, depending on the powder(s) being used and the properties and objectives being perused. The most common PM processing routes for Al and Mg PM are illustrates in Fig. 2.2. In this review we will focus on the PM of Al and Mg, and the PM processing routes of interest to the subject and objectives of this thesis will be discussed in detail in the following sections.

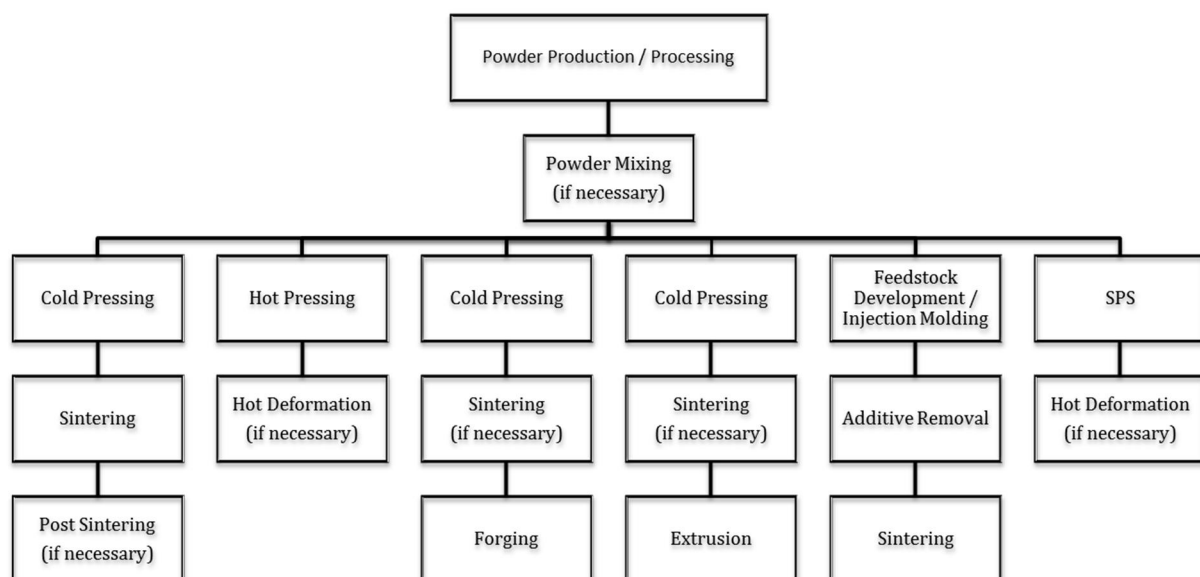


Fig. 2.2. Chart of the most common PM processing routes for Al and Mg PM.

2.5 Powder Production

At present, it is possible to produce powder from more than 50 % of all metals within the periodic table. The required physical and chemical characteristics of the powder may be produced by a variety of methods. Generally, these processing methods can be categorized into three main groups [65]:

- Physical: e.g. atomization of a liquid metal by high-pressure air or water jets.
- Chemical: includes electrolysis of solutions or fused salts, thermal decomposition, and chemical displacement.
- Mechanical: machining, crushing, grinding, or milling of metallic stock to powder.

The choice of method depends on many factors including the needed physical-chemical characteristics and the economic factors.

2.5.1 Atomization

Atomization is widely used for production of elemental and alloyed powders. They include powders from: Al, Fe, Cu, Sn, Co, Ti and Ni systems. The basic principle of atomization involves three steps: (1) melting of initial material to form of a stream of molten metal, (2) disintegration of molten metal into droplets and (3) solidification of droplets to solid particles.

Nearly all Al powder used for the production of light-weight parts is produced by inert gas (N₂, He, Ar) atomization. This technique uses a high-velocity inert gas stream to break molten Al into very fine particles. The molten particles solidify during free fall, typically giving them a spherical shape. The small size of the molten droplets combines with the cooling ability of the inert gas to create a very high solidification rate. The resultant powders have a high degree of homogenization and a fine microstructure [1].

Air atomization is a technique for producing low cost Al powders that are passivated. As implied by the name, air is used as the carrier gas. The exposure of the molten Al droplets to air results in significant oxygen pickup and oxide formation. However, one study has determined that the resulting oxide is almost similar to that produced by inert gas atomization. Air atomization produces a shape that is more irregular than the nearly spherical shape of the inert gas atomized powders [1].

Water atomization is receiving some attention as a method for producing Al alloy powders [66]. In water atomization the impinging water stream cools the molten Al and breaks it into small pieces. The result is a rapidly solidified and cooled (faster than gas atomization) powder of irregular shape. One of the concerns with water atomization is oxygen contamination of the powder and the formation of hydrated layers by reaction with water. Therefore degassing and drying procedures will be necessary to utilize this powder for PM.

Recently Mg powders have also been produced commercially by inert gas atomization by a number of companies, such as Tangshan Weihao Magnesium Powder Co and ESM Special Metals & Technology. The atomized Mg powders have very little surface oxide. However, due to their spherical morphology, the compacts cold pressed from atomized Mg powders show poor green strength.

2.5.2 Mechanical Grinding

Unlike Al most commercial Mg powders are produced by mechanical grinding. The low cost and less restrictive requirements for the main intended use of Mg as a granular reactant make grinding attractive. For PM applications the angular morphology of the powder gives good green strength because of mechanical interlocking, but the powder particles are typically covered by a thick surface layer. The layer is hypothesized to contain primarily oxides, but hydroxides, carbonates and hydrates are possible due to long exposure to atmospheric conditions during the grinding process.

2.5.3 Mechanical Alloying

Mechanical alloying is a solid-state powder processing technique involving repeated welding, fracturing, and re-welding of powder particles in a high-energy ball mill. The central event is that the powder particles are trapped between the colliding balls during milling and undergo excessive deformation and/or fracture (Fig. 2.3). Two different terms are commonly used in the literature to denote the processing of powder particles in high-energy ball mills. Mechanical alloying describes the process when mixtures of powders (of different metals or alloys/compounds) are milled together. Material transfer is involved in this process to obtain a homogeneous alloy. On the other hand, milling of uniform composition powders, such as pure metals, intermetallics, or pre-alloyed powders, where material transfer is not required for homogenization, has been termed mechanical milling [67].

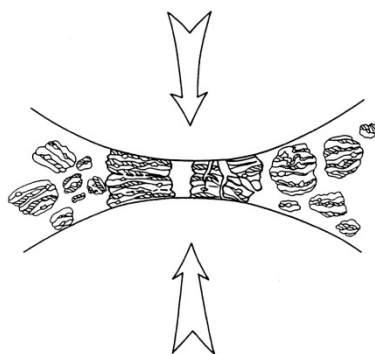


Fig. 2.3. Ball-powder-ball collision of powder mixture during mechanical alloying [68].

In the 1960s, mechanical alloying was first developed by Benjamin and his co-workers to fabricate oxide-dispersion-strengthened (ODS) nickel-based superalloys [69]. High-energy milling has now been shown to be capable of synthesizing a variety of equilibrium and non-equilibrium alloy phases starting from blended elemental or pre-alloyed powders. The non-equilibrium phases synthesized include supersaturated solid solutions, metastable crystalline and quasicrystalline phases, nanostructures, and amorphous alloys.

In recent years, mechanical alloying has been widely exploited for the production of nanocrystalline materials. Grain sizes with nanometer dimensions have been observed in almost all mechanically milled pure metals, alloys, and intermetallics. Since an oxide layer is always present on the surface of the Al and Mg powder particles either at the start of processing or during milling, its incorporation into microstructure contributes to significant improvements in the mechanical properties of the powders processed by mechanical alloying. Furthermore, process control agents (PCAs) are normally added to assist in minimizing cold welding during the milling process. Carbides are formed during mechanical alloying by the decomposition of the PCA. Both the oxide or carbide type dispersions are about 30-50 nm in size and stabilize the nano scale grain size [68].

Mechanical alloying is a complicated process. Hence, the processing of a product with the desired microstructure and properties entails the optimization of many process variables including, but not limited to, the type of mill, ball to powder weight ratio (BPR), milling speed, milling time, and the type and quantity of the process control agent (PCA). Some of these process variables are interrelated.

Although the processing and characterization of nanostructured Al alloys and composites by mechanical alloying has been the subject of many studies, studies on the high-energy milling of Mg and its alloys are scarce. Most of the previous works on the high-energy milling of Mg alloys concern either the processing of Mg matrix composites [70-73] or high performance Mg-based hydrogen storage alloys [74-76]. A handful of studies have also examined the microstructural characteristics, thermal stability, and mechanical properties of nanocrystalline Mg alloys processed by high-energy milling. It has been reported that the grain sizes of Mg and its alloys can be refined to 30-50 nm through high-energy milling, and nanocrystalline Mg alloys produced by this technique show excellent resistance to grain growth during isothermal annealing and/or subsequent consolidation processes at high temperatures, leading to superior mechanical properties for the bulk alloys consolidated from mechanically milled Mg-based powders [32, 33, 64, 77].

To be suitable for structural applications, the nanocrystalline Al and Mg powders produced by mechanical alloying should be consolidated to bulk materials. Field-assisted sintering techniques and/or extrusion have been used in most of the previous works on the consolidation of nanocrystalline Al and Mg powders, and studies on the conventional sintering of milled powders are very scarce. The employed consolidation route can have significant effects on the microstructure and mechanical properties of the processed bulk alloy. However, there are no systematic studies concerning the effects of different

consolidation routes on the microstructure and mechanical properties of the bulk alloys processed from nanocrystalline Al and Mg powders. Due to the lack of knowledge in this regard and the importance of nanocrystalline Al and Mg alloys to light metals PM industry, the consolidation of nanocrystalline Al and Mg powders by different PM techniques were examined in the present study.

2.6 Powder Compaction.

In PM processing of materials, raw powders are generally compacted in order to increase density and strength, control porosity, and create a “green” body with the desired dimensions of a final part. There are several methods of powder compaction used in PM processing, ranging from uniaxial cold compaction to cold or hot isostatic pressing to direct powder forging.

Uniaxial cold compaction, also known as die compaction, is widely regarded as the most convenient PM technique for compacting metallic powders, especially in high volume production scenarios. It starts with bulk powders containing small amounts of lubricant to eliminate friction between particles and particles and die wall. The powder is compacted inside a die between upper and lower punches. There are three main types of uniaxial compaction; single action, double action, and floating die. These three types of compaction types, combined with the possibility of using multilevel punches and dies, gives the opportunity of manufacturing thousands of different complex parts. Single action pressing is when pressure is transmitted from one punch (i.e. one direction only). Double action pressing is when pressure is simultaneously transmitted from both bottom and top punches. Floating die is one where the relative punch and die motions are such that both punches work against the die center simultaneously. A typical uniaxial cold compaction cycle is shown in Fig. 2.4.

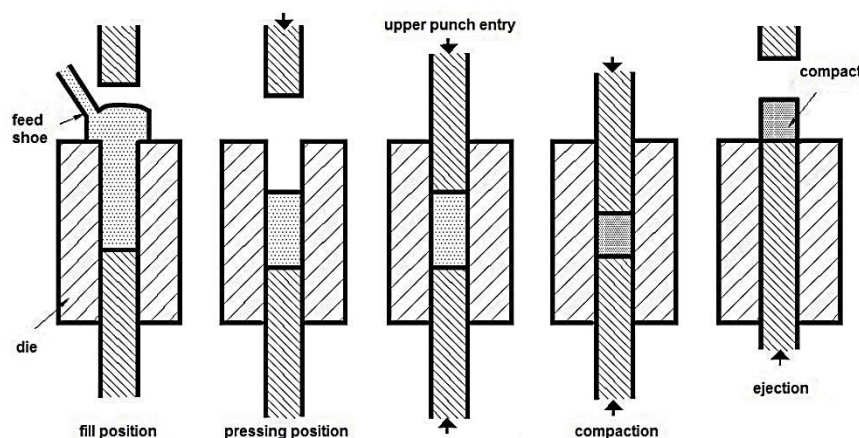


Fig. 2.4. Industrial pressing sequence for uniaxial cold compaction [38].

The uniaxial cold compaction of a Metal powder is generally divided into four key stages: (1) rearrangement, (2) localized deformation, (3) homogeneous deformation, and (4) bulk compression. The rearrangement phase refers to the movement of powder particles to fill the larger voids. This is then followed by localized deformation wherein simple point contacts between particles deform into flattened surfaces. Homogeneous deformation is where the pores begin to collapse and the powders are work hardened. The final stage is bulk compression. Here, powders are heavily work hardened and effectively act as a solid, incompressible body. Fig. 2.5 illustrates the different stages of a compaction sequence as related to compaction pressure and the green density attained.

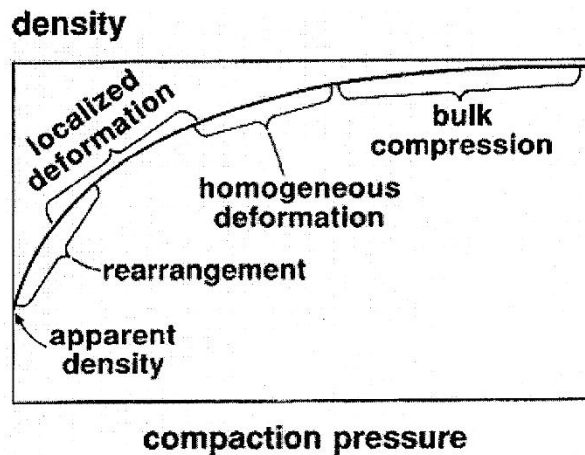


Fig. 2.5. Typical sequence of events during powder compaction [35].

As the green compact (the compacted powder) is then consolidated by PM processes such as sintering or extrusion, the compaction process is considered very important. It has been reported that the green density has significant effects on both the consolidation behavior of a green compact and the microstructure and mechanical properties of the consolidated material [78]. Therefore, several empirical and theoretical equations have been proposed to model the densification behavior of metallic powders. Since the first compaction equation published by Walker in 1923, more than 20 different compaction equations have been proposed, of which the most widely quoted equations are Balshin [79], Kawakita [80], Heckel [81], Ge [82], and Panelli and Ambrosio [83]. These equations relate the main macroscopic parameters like relative density (D) to compaction pressure (P).

Panelli and Ambrosio equation has widely been used to study the compressibility of Al powders. Some researchers have also used this equation to examine the effect of mechanical alloying on the compressibility of pure Al [84] and Al alloy powders [85, 86]. In 1998, Panelli and Ambrosio developed the following equation [83]:

$$\ln(1/(1-D)) = K_{\text{pan}} P^{(1/2)} + B_{\text{pan}} \quad (2.2)$$

where D is the relative density of powder compact, P is the compaction pressure, and K_{pan} and B_{pan} are the constants of the equation. The K_{pan} constant of a powder depends on its plastic deformation capacity during the compaction process. High K_{pan} values are obtained when soft metals such as aluminum and copper are compacted.

The commercial Al PM premixes, which were previously discussed in the section “2.4.1 Al Powder Metallurgy”, show excellent compressibility and reach a relative green density of about 95 % at a compaction pressure of 600 MPa [87, 88]. However, the process of nanocrystalline Al powders from Al PM premixes by mechanical alloying can significantly change their compressibility. To date, no information is available on the effects of mechanical alloying on the compressibility of commercial Al PM premixes. There are also no studies available investigating the compressibility of Mg powders produced by different PM techniques.

2.7 Sintering.

Once powders are compacted, they are then sintered to enhance mechanical properties. Sintering involves the heating of green compacts to temperatures that are typically at or above two-third the melting point of the material. Green compacts have a high energy state given the massive amount of surface area. As such, the system will attempt to lower its surface energy by mass transport on the atomic level when sintered. Sintering itself is defined as a thermal treatment for bonding particles into a coherent, mostly solid structure via mass transport events that occur at the atomic level. Such bonding leads to improved strength and lower system energy [35]. The most important parameters in the sintering process are temperature, time and protective atmosphere. These variables are specific for each material system and have to be controlled during sintering. Other factors influencing the sintering process (and specially the final microstructure) are heating and cooling rate. The two main types of pressure-less sintering processes are solid state and liquid phase sintering.

2.7.1 Solid State Sintering.

Solid state sintering is a diffusion process by which the particles form bonds (necks) between each other. To accomplish this, mass transport within the sintering compact is inevitably required. Mass transfer in solid state sintering can be realized by surface diffusion, viscous flow, lattice or volume diffusion, grain boundary diffusion and evaporation and condensation. Lattice volume diffusion, viscous flow and grain boundary diffusion are mechanisms which contribute to densification and shrinkage. Shrinkage occurs because material is removed from the contact area of the particles. On the other hand, in surface diffusion and vapor mechanisms, there is no shrinkage even though the neck growth occurs.

2.7.2 Liquid Phase Sintering.

Liquid phase sintering (LPS) is sintering in the presence of a small amount of a liquid phase. The quantity is controlled by temperature and alloy composition. Diffusion rates (mass transport) are much faster in a liquid than a solid, therefore LPS is used to produce dense materials from powders with desirable mechanical properties in a much shorter amount of time than solid state sintering.

During LPS, the material is consolidated through four stages as illustrated in Fig. 2.6. The first stage is the heating of the initially mixed and compacted powders. This is when the grains bond slightly by solid-state sintering at the contact points between the powders. Next is the rearrangement stage where the liquid first forms. The liquid is drawn into the inter-particle regions through capillary action. This allows the particles to rearrange by slipping past each other, resulting in rapid densification. The next stage is solution re-precipitation, where small grains dissolve in the liquid and re-precipitate on larger grains. This stage results in grain growth through the mass transport in the liquid phase. The material then experiences final stage sintering, where the compact attains a condition of solid contacting grains. This final stage is essentially a solid-state sintering situation [89].

An important factor in LPS is the wetting of the liquid on the solid grains. Wetting is the ability of a liquid to spread over a solid. With good wetting, a capillary force is applied on the solid grains pulling them together so as to invoke rapid densification of the material [89]. Reactive wetting (between the liquid and the solid) or non-reactive wetting character plays an important role in the system and the final densification after the sintering process [90].

Different types of LPS include supersolidus and transient LPS. Supersolidus LPS relies on pre-alloyed powders instead of mixed powders. The type of sintering involves the heating of the alloyed powders to a temperature between the solidus and liquidus to nucleate a liquid within each particle. The semisolid particles become soft and densify rapidly by capillary induced rearrangement. Transient LPS is where the liquid is totally soluble in the solid at the sintering temperature. During heating, a liquid forms and then disappears over time as it forms an alloy. This type of sintering is sensitive to process conditions as swelling can occur due to the liquid alloying with the solid before rearrangement of the solid particles transpires [36].

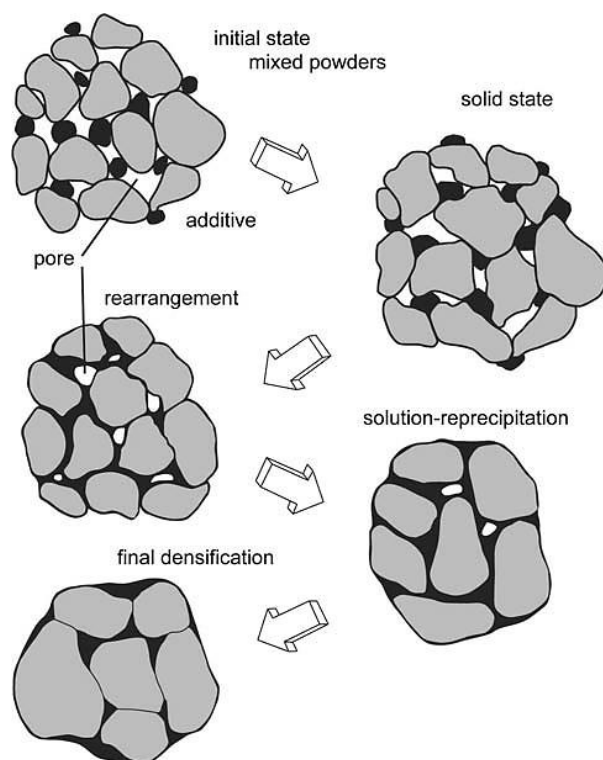


Fig. 2.6. Schematic demonstrating the mechanisms of liquid phase sintering [89].

2.7.3 Sintering of Al PM Alloys.

Sintering is considered the most critical step in Al PM processing. Al reacts readily with oxygen and moisture to form oxides and hydroxides. These compounds are thermodynamically stable and cannot be reduced by hydrogen at practical operating temperatures. An inert atmosphere of dry nitrogen is normally employed to keep these compounds from forming and to improve the sintering response of Al PM alloys. Al PM alloys also contain Mg to break up the oxide layer present on the Al-based powders to facilitate sintering [91-93]. To reach high densities through the sintering process, Al PM alloys are usually sintered at a composition and temperature where liquid phase sintering can occur. An amount of 10 to 20 wt% of liquid is generally employed to maximize the sintered density. However, the liquid phase sintering of Al alloys can cause distortion, which is problematical to accommodate during design and to modify after sintering [94].

Ecka Granules (Germany) produces several Al PM premixes (under the designation ECKA Alumix) which are sold commercially. Table 2.2 contains the chemical compositions of the most commonly used Alumix premixes.

Previous studies on the sintering of Alumix premixes confirm that these powders can reach a maximum sintered density of 97 % of the theoretical value [10, 41]. Both transient and supersolidus LPS have been reported to be responsible for the excellent sinterability of Alumix premixes.

Table 2.2. Chemical composition of the most commonly used Alumix premixes

Premix	Cu (wt%)	Mg (wt%)	Si (wt%)	Zn (wt%)	Al (wt%)	Wax (wt%)
Alumix 13	4.5	0.5	0.2	-	Balance	1.5
Alumix 123	4.4	0.5	0.7	-	Balance	1.5
Alumix 321	0.2	1	0.5		Balance	1.5
Alumix 431	1.6	2.5	5.5		Balance	1.5

Alumix 431D is a ready-to-press PM premix based on the 7xxx series Al alloys. Alumix 431D shows signs of being highly responsive to a typical industrial sintering process while maintaining the high-strength characteristic of a 7XXX series Al alloy. Table 2.3 summarizes the ambient tensile testing properties measured for sintered Alumix 431D in the T1 and T6 conditions. Data on wrought 7075 are also included for comparison purposes.

Table 2.3. A summary of the tensile testing properties measured for Alumix 431D [10].

System	Yield Strength (MPa)	UTS (MPa)	Elongation (%)	E (GPa)
Alumix 431D - T1	279	323	1.4	66
Alumix 431D - T6	444	448	0.9	65
Wrought 7075 - T6	485	550	14	71

The mechanical alloying of Al PM premixes to produce a nanocrystalline alloy powder can significantly affect their sintering behavior. In an effort to understand the effects of mechanical alloying on the sintering behavior of Al PM premixes, current work examines the sinterability of the mechanically milled Alumix 431D powder.

2.7.4 Sintering of Mg powders.

It has been claimed that Mg is unsuitable for PM production without the use of a high-shear-stress process to break the stable oxide layer on the surface of the Mg-based powders. The oxide is very stable and is an effective barrier to diffusion. Cold isostatic pressing, hot isostatic pressing, hot pressing, and conventional sintering are believed not to be capable of doing much damage to this oxide layer. To date, a small number of studies on the sintering behavior of pure Mg powder have only been completed [12, 50, 95].

Wolff et al. [12] used the traditional cold pressing and sintering PM route to produce pure Mg as well as Mg-Ca alloys. The presented process required a complex sintering apparatus to protect the samples from further oxidation during the long 64 hour time at temperature. The study concludes that the oxygen getter is essential for sintering Mg powders, and that calcium additions enhance sinterability through the formation of a transient liquid phase.

Traditionally sintering of Mg PM alloys has been carried out in inert Ar atmosphere to provide the best protection from oxidation during heating at high temperature [95]. Burke [96] has studied the effects of sintering atmosphere on the sintering behavior of pure Mg powders. In this work is reported that changing the sintering atmosphere from Ar to N₂ produces samples with improved properties. Also it was found that Calcium diffuses readily through the Mg matrix and greatly improves density and hardness due to reduction of MgO and disruption of the surface layer found on Mg particles.

While the obtained results were promising, for Mg PM to compete on a level with Al PM, industrial processing technologies using existing PM equipment are necessary to be developed. Until now, the sintering behavior of pre-alloyed Mg powders has not been studied. In this study, we aim to study the sintering behavior of pre-alloyed AZ91 Mg alloy powder produced by both grinding and atomization techniques. In addition, the effects of high-energy milling on the sinterability of pre-alloyed AZ91 powder will also be examined.

2.8 Field-Assisted Sintering Technique.

Field-assisted sintering technique (FAST) takes only a few minutes to complete a sintering process compared to conventional sintering which may take hours or even days for the same. FAST is a pressure-assisted high temperature sintering method in which a high-temperature plasma (spark plasma) is generally generated in the gaps between powder particles as a consequence of an electrical discharge. This plasma might play a fundamental role in the cleaning of the powder surface from contaminants and breaking the oxide layer that is inevitable formed after milling. Particularly, for pure Al it has been demonstrated that FAST really breaks the oxide layer, resulting in a sintering time of a few minutes at a temperature around 525-550 °C [5, 6].

A FAST unit is schematically shown in Fig. 2.7. It consists of a uniaxial pressure device, in which the water-cooled punches also serve as electrodes, a reaction chamber that can be evacuated, a direct current (dc) generator and pressure-, position- and temperature-regulating systems. In an FAST experiment, a weighed amount of powder is introduced in a die. The die may be built up with various materials, such as graphite, WC, refractory alloys, etc.

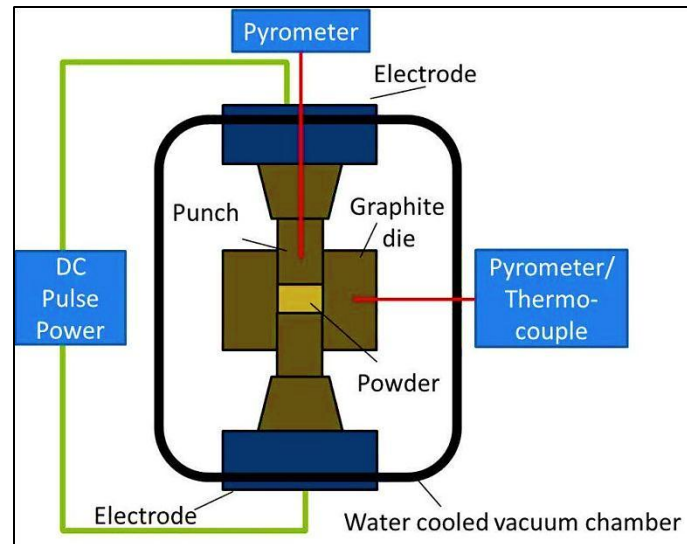


Fig. 2.7. Schematic drawing of an FAST system.

FAST processes offer many advantages over conventional consolidation techniques such as conventional sintering, hot pressing (HP), or even hot isostatic pressing (HIP). These advantages can be summarized as follows: better control of sintering energy, shorter sintering times, lower sintering temperatures and higher reproducibility. Particularly, FAST was designed to process materials that could not be sintered using conventional sintering techniques. These materials include nanostructured metal powders, intermetallic powders, and metal matrix composites (MMC). The mentioned powders are generally very hard and a first step of cold pressing (like in a conventional sintering process) becomes impracticable. Furthermore, the FAST mechanism suggests very short sintering times at lower temperatures. These advantages are especially decisive when the starting material is a nanostructured metal powder. Therefore, coarsening of fine grains and nano-sized dispersed particles can be avoided.

In the last decade some researchers have employed the FAST to produce bulk samples from nanostructured pure Al or Al alloy powders [97-100] and Al composite powders [101-103] processed by mechanical alloying. The obtained results by these researchers clearly suggest that the combination of mechanical alloying and FAST processes can produce highly dense, nanostructured materials with enhanced mechanical properties compared to those produced by conventional powder metallurgy routes. Recently, the technique has also been applied to prepare coarse grained Al samples [104-106]. However, limited microstructural characterization of FAST consolidated materials has been undertaken.

As mentioned before, the plasma generated between powder particles in FAST to facilitate the sintering process also aids in the elimination of surface impurities and so results in enhanced sintering and consolidation. This special feature makes FAST an ideal processing technique for the consolidation of Mg-based powders. However, studies on the processing of bulk samples from Mg-based powders by FAST are very scarce. Due to the lack of knowledge in the field and considering the mentioned advantages for FAST, one type

of FAST technique, i.e. field assisted hot pressing (FAHP) has been chosen as one of consolidation techniques for this study.

2.9 Hot Deformation.

Deformation operations such as extrusion, forging, and rolling induce large amounts of plastic deformation into a material. If the temperature at which the material is worked is below 30% of its absolute melting temperature (T_M), it is termed cold working. During cold working, strain hardening occurs as grains are deformed and the dislocation density increases. Strain hardening increases strength and hardness, but decreases toughness by increasing brittleness. Materials can be annealed after cold working to restore ductility through the nucleation of strain free grains at the boundaries of the previous grains. Hot working takes place roughly above a homologous temperature of $0.6 T_M$, with typical hot-working temperatures being 70 to 80% of the absolute melting temperature. Strain hardening of the material is reduced or eliminated as the nucleation of new strain free grains occurs directly following deformation. Because strain hardening does not occur, the formability of the material increases and the induced stress required for plastic flow is reduced. Hot working can therefore be completed using higher strain rates than cold working. Grain refinement is possible through hot working, due to the high number of nucleation sites available to form the new strain free grains [107].

2.9.1 Hot deformation behavior and constitutive analysis.

A good understanding of the hot deformation behavior of a material is extremely important in hot deformation processes such as extrusion and forging. Processing parameters, such as the deformation temperature and strain rate, and material factors, such as chemical composition and microstructure of the starting material, are the main factors affecting the hot deformation flow stress. Thus, several studies have been performed to investigate the effect of processing parameters on the hot deformation behavior and flow stress of Al [3, 108-114] and Mg [19, 115-120] alloys. Furthermore, the flow stress behavior of these materials has been modeled, and constitutive equations that consider the effects of the deformation temperature and strain rate have been proposed to predict the hot deformation flow stress.

In the hot deformation of metallic materials, the relationship between the peak flow stress or steady-state flow stress of the material and deformation parameters, such as the deformation temperature and strain rate, can be expressed as [121]:

$$Z = \dot{\epsilon} \exp\left(\frac{Q}{RT}\right) = F(\sigma) \quad (2.3)$$

$$\dot{\epsilon} = Z \exp\left(-\frac{Q}{RT}\right) = F(\sigma) \exp\left(-\frac{Q}{RT}\right) \quad (2.4)$$

where Z (Zener-Hollomon parameter) is the temperature-corrected strain rate, $\dot{\epsilon}$ is the strain rate (s^{-1}), Q is the activation energy of hot deformation (J/mol), R is the gas constant ($8.31 \text{ J mol}^{-1} \text{ K}^{-1}$), and T is the absolute temperature (K). $F(\sigma)$ is called the stress function and corresponds to one of the following equations depending on the deformation conditions:

$$F(\sigma) = A_1 \sigma^m = Z \quad (2.5)$$

$$F(\sigma) = A_2 \exp(\beta\sigma) = Z \quad (2.6)$$

$$F(\sigma) = A_3 [\sinh(\alpha\sigma)]^n = Z \quad (2.7)$$

where A_1 , A_2 , A_3 , m , β , and n are constants of the material. α is the stress multiplier and is a constant that brings $\alpha\sigma$ into the correct range, forming parallel and linear plots of $(\ln \dot{\epsilon})$ versus $(\ln \sinh(\alpha\sigma))$.

Equation 2.5, i.e., the power law stress function, is commonly used for deformation processes that require low stress levels, such as creep, while Equation 2.6, i.e., the exponential law stress function, is used for higher levels of stress and strain rates. Alternatively, the hyperbolic sine law stress function (Equation 2.7) can be used for a wide range of stress levels.

In all of the aforementioned equations, the flow stress is a function of the deformation temperature and strain rate (i.e., deformation parameters). However, the effect of strain on the flow stress is not considered in these equations. Therefore, characteristic flow stresses, such as the peak flow stress or steady-state flow stress, are commonly used in the equations. When strain hardening or flow softening is remarkable, the effect of strain on the flow stress should also be included.

2.9.2 Hot deformation behavior of PM alloys.

The hot deformation behavior of bulk Al and Mg alloys has been the subject of many studies. Nevertheless, the deformation behavior of porous materials is different from that of bulk materials. Pores present in the microstructure act as stress concentration points, limiting the amount of deformation to fracture [122]. Moreover, the volume of voids is reduced during deformation, which results in an increase in density and densification. In addition to strain hardening, densification during deformation can enhance the flow stress of the material, which is known as densification hardening [123]. In the case of powder-based porous materials, such as powder compacts, due to friction between particles, redundant work is required to weld powder particles together, break welds between particles, and re-weld them together [124]. Thus, information on the deformation behavior of bulk Al and Mg alloys is not completely usable for the deformation of porous alloys with similar chemical compositions.

By hot deforming a PM alloy and allowing for some plastic flow, most of the voids present in the microstructure can be flattened and closed, yielding a material with properties similar to the equivalent wrought alloys. The goal in this process is to achieve tight dimensional tolerances and better mechanical properties through density increases. The hot deformation of sintered PM preforms is a relatively new method of hot working. A variation of this process is done using un-sintered but pre-heated green compacts. The powder is pressed, ejected from the die, moved to a furnace where it is quickly heated to deformation temperature.

Studies on the hot deformation behavior of Al PM alloys are scarce, and there are no systematic studies available on the hot deformation behavior of Mg PM alloys. Besides, there is no information available regarding the hot deformation behavior of nanocrystalline Al and Mg powders processed by mechanical alloying. In this study, the hot deformation behavior of 7075 Al and AZ91 Mg PM alloys is investigated. Moreover, the effect of mechanical alloying and corresponding structural changes on the deformation behavior of the mentioned PM alloys will be studied.

2.9.3 Workability and processing maps.

Workability is defined as the degree of deformation that can be achieved in a particular metalworking process without creating an undesirable condition. Generally, the undesirable condition is cracking or fracture, but it may be another condition, such as poor surface finish, buckling, or the formation of laps. In other words, workability refers to the relative ease with which a material can be shaped through plastic deformation. Workability is usually thought of as being limited by the onset of fracture. Greater workability of a material allows greater deformation and/or a more complex shape that can be produced before fracture occurs. Workability is a complex technological concept that is related to both material and process characteristics. Workability depends not only on the fracture resistance (ductility) of the material but also on the specific details (stress state) of the process as influenced by die geometry, workpiece geometry, and lubrication conditions. Ease of manufacture is aided when the material has a low flow stress (yield strength) so that the force that must be applied by the processing equipment and the stresses on the dies are lower [107].

Workability of a material can be evaluated by the use of processing maps that show the occurrence of damage as a function of processing variables such as temperature and strain-rate. Processing maps have been proven to be a useful tool for the optimization of hot working processes for a wide range of metals and their alloys or for the design of process parameters for new materials. It is helpful to identify different deformation mechanisms within different domains.

The processing map technique used in this study is based on the dynamic materials modeling (DMM), and the efficiency of the power dissipation (η) through microstructural changes during deformation is given by [125, 126]:

$$\eta = 2m/(m+1) \quad (2.8)$$

$$m = (\partial \log \sigma) / (\partial \log \dot{\epsilon}) \quad (2.9)$$

where m is the strain rate sensitivity of flow stress, σ is the flow stress, and $\dot{\epsilon}$ is the strain rate. The extremum principles of irreversible thermodynamics as applied to the continuum mechanics of large plastic flow were explored to define a criterion for the onset of flow instability, given by:

$$\xi = (\partial \ln[m/(m+1)] / \partial \ln \dot{\epsilon}) + m \leq 0 \quad (2.10)$$

In recent years, the processing-map technique has been widely used to study the workability of many bulk Al [127-130] and Mg alloys [125, 131-133] in terms of the various microstructural mechanisms operating at the different deformation conditions. However, studies on the workability of Al and Mg PM alloys are very scarce. Therefore, this study examines the workability characteristics of 7075 Al and AZ91 Mg PM alloys with a view to finding the optimum hot working parameters and evaluating the mechanisms of hot deformation. Furthermore, there are no systematic studies on the workability of nanocrystalline Al and Mg alloys processed by mechanical alloying. Consequently, the effects of mechanical alloying on the hot workability characteristics of the above-mentioned powders will also be investigated.

2.9.4 Hot compression.

The compression test is usually considered to be a standard bulk workability test. This is an ‘open forge’ test which is very severe with the material. The average stress state during testing is similar to that in many bulk deformation processes, without introducing the problems of necking (in tension) or material reorientation (in torsion). The absence of necking, as occurs in a tension test, means that a compression test can be conducted to large strains that are comparable to those found in deformation processes such as forging or extrusion. The stress state can be varied over wide limits by controlling the barreling of the specimen through variations in geometry and by reducing friction between the specimen ends and the anvil with lubricants.

The basic data obtained from the compression test are the load and displacement (stroke), which should then be converted to the true stress-true strain curves. The true stress is the load P divided by the instantaneous cross-sectional area with diameter (D). If the compression deformation is homogeneous, then this is given by [107]:

$$\sigma_a = \sigma_0 = 4P/\pi D^2 = 4Ph/\pi D_0^2 h_0 \quad (2.11)$$

where h is the height of the specimen, and σ_a is the average true axial stress, which is equal to the flow stress σ_0 or effective stress $\bar{\sigma}$ for homogeneous deformation. The true strain in the hot-compression test is found from Equation 2.12 [107]:

$$\varepsilon = \ln h/h_0 = \ln (1-\Delta h/h_0) \quad (2.12)$$

The true strain rate, $\dot{\varepsilon}$, in a compression test is [107]:

$$\dot{\varepsilon} = d\varepsilon/dt = - (dh/h)/dt = - dh/hdt = - v/h \quad (2.13)$$

where v is the velocity of the platen, and h is the height of the specimen at time, t . Because h decreases continuously with time, the velocity must decrease in proportion to $(-h)$ if $\dot{\varepsilon}$ is to be held constant.

The data attainable through the compression test can be analyzed by Dynamic Material Modeling technique to evaluate the workability of a material and to develop the processing maps at different strains. These maps can then be used to find the optimum hot working condition for the material under study.

2.9.5 Extrusion.

The hot extrusion process consists essentially of preheating the cylindrical billet of a metal, placing it in a container of slightly larger diameter, closed at one end by a ram, and at the other end by a die. The temperature to which the billet is pre-heated depends on the material to be extruded, the ram speed, and the extrusion ratio. The die has an opening with the cross section of the required product. As the ram is moved inward, the billet is forced under sufficiently large pressure to extrude through the opening in the die as illustrated in Fig. 2.8. The extrusion process is an industrial forming method for producing long profiles with a uniform cross section, allowing complex shapes.

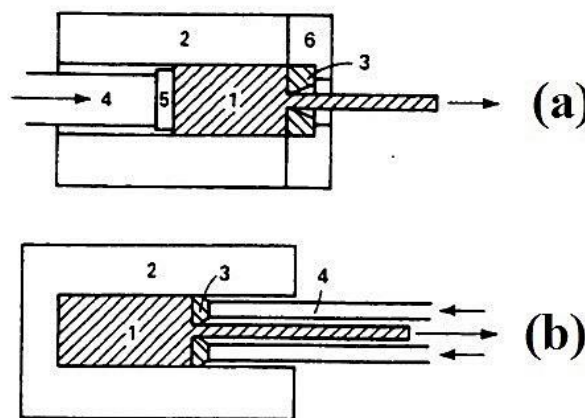


Fig. 2.8. Basic methods of extrusion: **a)** forward (direct), **b)** backward (indirect). Objects: 1) billet, 2) chamber, 3) die, 4) stem, 5) dummy block, 6) die holder.

Powder extrusion (PE) is a PM processing method that has been developed for the production of fully dense, high-performance materials from powders. Compared with other PM routes such as sintering and hot pressing, the shear stresses involved in PE make it an ideal process for the production of bulk Al and Mg alloys from powder mixtures. One of the main difficulties in sintering Al and Mg alloys is the presence of a surface oxide layer intrinsic to Al-based and Mg-based powders. In the case of PE, the shear stresses break the oxide layer covering the particle surfaces of these powders, leading to a well-bonded microstructure and superior after-extrusion mechanical properties [40].

According to Verlinden et al. [134], there are three methods for the extrusion of powder mixtures: loose powder extrusion, green billet extrusion, and powder extrusion using canning and degassing. The third method is mainly used for Al powders [135], but canning and degassing constitute a costly and inconvenient processing step. Consequently some researchers made efforts towards the extrusion of Al powder mixtures without canning and degassing [136, 137]. These researchers directly extruded the green billets cold compacted from Al powder mixtures using a mixture of graphite and oil serving as both a lubricant [138] and an oxidation barrier [139]. They studied the microstructures and mechanical properties of the extruded products. Their promising results imply that the employed method can replace powder extrusion using canning and degassing for Al-based powders [140].

In an attempt to consolidate atomized Mg-based powders, Zhang et al. produced bulk samples from Argon-gas atomized ZK60 [141] and AZ91 [142] powders by vacuum hot pressing at 200 °C followed by hot extrusion at temperatures ranging from 200-350 °C. These researchers have reported that the extrusion temperature has significant effects on the microstructure and mechanical properties of the extrusion products. Similarly, canning and vacuum hot pressing have been used in most of the previous works on the extrusion of nanocrystalline Mg powders processed by mechanical alloying [77, 143, 144]. To date, no effort has been made to produce bulk samples by direct hot extrusion of powder compacts cold pressed from microcrystalline or nanocrystalline Mg powders.

The present study examines the processing of bulk alloys by direct hot extrusion of powder compacts cold pressed from 7075 Al and AZ91 Mg powders processed by different powder processing techniques. The main objective is to produce bulk alloys with homogeneous microstructure and superior mechanical properties from the mentioned powders.

References

- [1] G.E. Totten, D.S. MacKenzie, Handbook of aluminum: Vol. 1: physical metallurgy and processes, Marcel Dekker, New York, United States of America, 2003.
- [2] M.M. Avedesian, H. Baker, ASM specialty handbook: magnesium and magnesium alloys, ASM International, Ohio, United States of America, 1999.
- [3] N. Jin, H. Zhang, Y. Han, W. Wu, J. Chen, Materials Characterization, 60 (2009) 530-536.

- [4] M.R. Rokni, A. Zarei-Hanzaki, A.A. Roostaei, H.R. Abedi, *Materials & Design*, 32 (2011) 2339-2344.
- [5] Y. Yang, Z. Zhang, X. Li, Q. Wang, Y. Zhang, *Materials & Design*, 51 (2013) 592-597.
- [6] M.R. Rokni, A. Zarei-Hanzaki, A.A. Roostaei, A. Abolhasani, *Materials & Design*, 32 (2011) 4955-4960.
- [7] I.A. MacAskill, A.D.P. LaDepha, J.H. Milligan, J.J. Fulton, D.P. Bishop, *Powder Metallurgy*, 52 (2009) 304-310.
- [8] G. Sha, A. Cerezo, *Acta Materialia*, 52 (2004) 4503-4516.
- [9] L. Hadjadj, R. Amira, D. Hamana, A. Mosbah, *Journal of Alloys and Compounds*, 462 (2008) 279-283.
- [10] A.D.P. LaDelpha, H. Neubing, D.P. Bishop, *Materials Science and Engineering: A*, 520 (2009) 105-113.
- [11] M. Gupta, N.M.L. Sharon, *Magnesium, magnesium alloys, and magnesium composites*, John Wiley & Sons, Hoboken, New Jersey, United States of America, 2011.
- [12] M. Wolff, T. Ebel, M. Dahms, *Advanced Engineering Materials*, 12 (2010) 829-836.
- [13] Y.H. Wei, Q.D. Wang, Y.P. Zhu, H.T. Zhou, W.J. Ding, Y. Chino, M. Mabuchi, *Materials Science and Engineering: A*, 360 (2003) 107-115.
- [14] K. Kubota, M. Mabuchi, K. Higashi, *Journal of Materials Science*, 34 (1999) 2255-2262.
- [15] E.F. Volkova, *Metal Science and Heat Treatment*, 48 (2006) 473-478.
- [16] M. Kulekci, *Int J Adv Manuf Technol*, 39 (2008) 851-865.
- [17] S.J. Liang, Z.Y. Liu, E.D. Wang, *Materials Letters*, 62 (2008) 3051-3054.
- [18] K. Ishikawa, H. Watanabe, T. Mukai, *Materials Letters*, 59 (2005) 1511-1515.
- [19] K. Ishikawa, H. Watanabe, T. Mukai, *Journal of Materials Science*, 40 (2005) 1577-1582.
- [20] D. Zhang, S. Wang, C. Qiu, W. Zhang, *Materials Science and Engineering: A*, 556 (2012) 100-106.
- [21] B. Amir Esgandari, H. Mehrjoo, B. Nami, S.M. Miresmaeili, *Materials Science and Engineering: A*, 528 (2011) 5018-5024.
- [22] A. Srinivasan, U.T.S. Pillai, B.C. Pai, *Materials Science and Engineering: A*, 527 (2010) 6543-6550.
- [23] E. Contreras-Piedras, R. Esquivel-Gonzalez, V.M. López-Hirata, M.L. Saucedo-Muñoz, A.M. Paniagua-Mercado, H.J. Dorantes-Rosales, *Materials Science and Engineering: A*, 527 (2010) 7775-7778.
- [24] S. Celotto, T.J. Bastow, *Acta Materialia*, 49 (2001) 41-51.
- [25] J.-f. Huang, H.-y. Yu, Y.-b. Li, H. Cui, J.-p. He, J.-s. Zhang, *Materials & Design*, 30 (2009) 440-444.
- [26] M.A. Meyers, A. Mishra, D.J. Benson, *Progress in Materials Science*, 51 (2006) 427-556.
- [27] E.O. Hall, *Proceedings of the Physical Society. Section B*, 64 (1951) 747-753.
- [28] N.J. Petch, *The Journal of the Iron and Steel Institute*, 174 (1953) 25-28.
- [29] S. Takeuchi, *Scripta Materialia*, 44 (2001) 1483-1487.
- [30] M. Mhadhbi, M. Khitouni, M. Azabou, A. Kolsi, *Materials Characterization*, 59 (2008) 944-950.
- [31] A.S. Khan, B. Farrokh, L. Takacs, *Materials Science and Engineering: A*, 489 (2008) 77-84.

- [32] P. Cao, L. Lu, M.O. Lai, *Materials Research Bulletin*, 36 (2001) 981-988.
- [33] S. Hwang, C. Nishimura, P.G. McCormick, *Materials Science and Engineering: A*, 318 (2001) 22-33.
- [34] Y. Chino, M. Kobata, H. Iwasaki, M. Mabuchi, *Acta Materialia*, 51 (2003) 3309-3318.
- [35] R.M. German, *Powder Metallurgy science*, 2nd ed., Metal Powder Industries Federation, Princeton, United States of America, 1994.
- [36] R.M. German, *Powder metallurgy & particulate materials processing*, Metal Powder Industries Federation (MPIF), New Jersey, United States of America, 2005.
- [37] L.F. Pease, W.G. West, *Fundamentals of powder metallurgy*, Metal Powder Industries Federation, Princeton, NJ, United States of America, 2002.
- [38] F. Thummler, R. Oberacker, *Introduction to powder metallurgy*, Institute of Materials, London, United Kingdom, 1993.
- [39] G.S. Upadhyaya, *Powder metallurgy technology*, Cambridge International Science Publishing, Cambridge, England, 2002.
- [40] W. Schatt, K.P. Wieters, *Powder Metallurgy: Processing and Materials*, European Powder Metallurgy Association, Shrewsbury, UK, 1997.
- [41] J.M. Martín, F. Castro, *Journal of Materials Processing Technology*, 143-144 (2003) 814-821.
- [42] K.H. Min, S.P. Kang, B.-H. Lee, J.-K. Lee, Y.D. Kim, *Journal of Alloys and Compounds*, 419 (2006) 290-293.
- [43] R.E.D. Mann, R.L. Hexemer Jr, I.W. Donaldson, D.P. Bishop, *Materials Science and Engineering: A*, 528 (2011) 5476-5483.
- [44] R. Narayanasamy, V. Senthilkumar, K.S. Pandey, *Mechanics of Materials*, 38 (2006) 367-386.
- [45] A.D.P. LaDelpha, M.P. Mosher, W.F. Caley, G.J. Kipouros, D.P. Bishop, *Materials Science and Engineering: A*, 479 (2008) 1-9.
- [46] W.G.E. Mosher, G.J. Kipouros, W.F. Caley, I.W. Donaldson, D.P. Bishop, *Powder Metallurgy*, 54 (2011) 366-375.
- [47] P. Burke, in: *Process Engineering and Applied Science* Dalhousie University, Halifax, Nova Scotia, Canada, 2007.
- [48] D.J. Lloyd, *International Materials Reviews*, 39 (1994) 1-23.
- [49] H. Ye, X. Liu, *Journal of Materials Science*, 39 (2004) 6153-6171.
- [50] W. Xie, Y. Liu, D.S. Li, J. Zhang, Z.W. Zhang, J. Bi, *Journal of Alloys and Compounds*, 431 (2007) 162-166.
- [51] H.E. Friedrich, Mordike, B.L., *Magnesium technology - metallurgy, design data, applications*, Springer, Verlag Berlin, Germany, 2006.
- [52] H. Watanabe, T. Mukai, M. Mabuchi, K. Higashi, *Acta Materialia*, 49 (2001) 2027-2037.
- [53] T.S. Srivatsan, L. Wei, C.F. Chang, *Journal of Materials Science*, 30 (1995) 1832-1838.
- [54] Y. Kawamura, A. Inoue, *Materials Science Forum*, 419-422 (2003) 709-714.
- [55] C.J. Bettles, M.H. Moss, R. Lapovok, *Materials Science and Engineering: A*, 515 (2009) 26-31.
- [56] C.Y. Chen, C.Y.A. Tsao, *Materials Science and Engineering: A*, 383 (2004) 21-29.
- [57] X.-f. Wang, J.-z. Zhao, J. He, Z.-q. Hu, *Transactions of Nonferrous Metals Society of China*, 17 (2007) 238-243.

- [58] Y. Li, J. Huang, H. Cui, K. Tao, K. Zhang, J. Zhang, *Journal of University of Science and Technology Beijing, Mineral, Metallurgy, Material*, 15 (2008) 740-746.
- [59] Y. Li, Y. Chen, H. Cui, B. Xiong, J. Zhang, *Materials Characterization*, 60 (2009) 240-245.
- [60] B. Pucun, D. Taishang, H. Xiaohu, Z. Chunwang, X. Yongming, *Materials Characterization*, 61 (2010) 756-760.
- [61] H.T. Son, J.M. Hong, I.H. Oh, J.S. Lee, T.S. Kim, K. Maruyama, *Solid State Phenomena*, 124-126 (2007) 1517-1520.
- [62] W.N.A.W. Muhammad, Z. Sajuri, Y. Mutoh, Y. Miyashita, *Journal of Alloys and Compounds*, 509 (2011) 6021-6029.
- [63] J. Umeda, K. Kondoh, H. Imai, *Materials Science and Engineering: A*, 504 (2009) 157-162.
- [64] B. Zheng, O. Ertorer, Y. Li, Y. Zhou, S.N. Mathaudhu, C.Y.A. Tsao, E.J. Lavernia, *Materials Science and Engineering: A*, 528 (2011) 2180-2191.
- [65] J.M. Capus, *Metal powders: a global survey of production, applications and markets to 2010*, 4th ed., Elsevier, Oxford, Great Britain, 2005.
- [66] O.D. Neikov, A.V. Krajnikov, *Materials Science Forum*, 217-222 (1996) 1649-1654.
- [67] C. Suryanarayana, *Mechanical alloying and milling*, Marcel Dekker, New York, United States of America, 2004.
- [68] C. Suryanarayana, *Progress in Materials Science*, 46 (2001) 1-184.
- [69] J. Benjamin, *Metallurgical and Materials Transactions B*, 1 (1970) 2943-2951.
- [70] L. Li, M.O. Lai, M. Gupta, B.W. Chua, A. Osman, *Journal of Materials Science*, 35 (2000) 5553-5561.
- [71] S. Hwang, C. Nishimura, P.G. McCormick, *Scripta Materialia*, 44 (2001) 2457-2462.
- [72] M.O. Lai, L. Lu, W. Laing, *Composite Structures*, 66 (2004) 301-304.
- [73] J. Liu, C. Suryanarayana, D. Ghosh, G. Subhash, L. An, *Journal of Alloys and Compounds*, 563 (2013) 165-170.
- [74] N. Cui, P. He, J.L. Luo, *Acta Materialia*, 47 (1999) 3737-3743.
- [75] H. Imamura, K. Masanari, M. Kusuhara, H. Katsumoto, T. Sumi, Y. Sakata, *Journal of Alloys and Compounds*, 386 (2005) 211-216.
- [76] M. Anik, F. Karanfil, N. Küçükdeveci, *International Journal of Hydrogen Energy*, 37 (2012) 299-308.
- [77] F. Wen-bin, F. Wa, S. Hong-fei, *Powder Technology*, 212 (2011) 161-165.
- [78] M. Song, Y.-h. He, *Materials & Design*, 31 (2010) 985-989.
- [79] M.Y. Balshin, *Vestnik Metalloprom*, 18 (1938) 124-137.
- [80] K. Kawakita, K.H. Ludde, *Powder Technology*, 4 (1970/71) 61-68.
- [81] R.W. Heckel, *Transactions of the Metallurgical Society of AIME*, 221 (1961) 671-675.
- [82] R.d. Ge, *International Journal of Powder Technology*, 27 (1991) 211-216.
- [83] R. Panelli, F. Ambrosio Filho, *Powder Metallurgy*, 41 (1998) 131-133.
- [84] Z. Razavi Hesabi, H.R. Hafizpour, A. Simchi, *Materials Science and Engineering: A*, 454-455 (2007) 89-98.
- [85] J.B. Fogagnolo, E.M. Ruiz-Navas, M.H. Robert, J.M. Torralba, *Materials Science and Engineering: A*, 355 (2003) 50-55.

- [86] S. Sivasankaran, K. Sivaprasad, R. Narayanasamy, V.K. Iyer, *Powder Technology*, 201 (2010) 70-82.
- [87] M.F. Moreno, C.J.R. González Oliver, *Powder Technology*, 206 (2011) 297-305.
- [88] J. Bidulská, R. Bidulský, M.A. Grande, in: *PM2010 World Congress*, Florence, Italy, 2010.
- [89] R. German, P. Suri, S. Park, *Journal of Materials Science*, 44 (2009) 1-39.
- [90] E. Bernardo, R. de Oro, M. Campos, J. Torralba, *Metall and Mat Trans A*, 45 (2014) 1748-1760.
- [91] R.N. Lumley, T.B. Sercombe, G.M. Schaffer, *Metall and Mat Trans A*, 30 (1999) 457-463.
- [92] G.B. Schaffer, B.J. Hall, S.J. Bonner, S.H. Huo, T.B. Sercombe, *Acta Materialia*, 54 (2006) 131-138.
- [93] I.A. MacAskill, R.L. Hexemer Jr, I.W. Donaldson, D.P. Bishop, *Journal of Materials Processing Technology*, 210 (2010) 2252-2260.
- [94] G.B. Schaffer, S.H. Huo, *Powder Metallurgy*, 43 (2000) 163-167.
- [95] P. Burke, C. Petit, S. Yakoubi, G.J. Kipouros, *Thermal Effects of Calcium and Yttrium Additions on the Sintering of Magnesium Powder*, in: *Magnesium Technology 2011*, John Wiley & Sons, Inc., 2011, pp. 481-484.
- [96] P. Burke, in: *Process Engineering and Applied Science* Dalhousie University, Halifax, Nova Scotia, Canada, 2011.
- [97] T.T. Sasaki, T. Mukai, K. Hono, *Scripta Materialia*, 57 (2007) 189-192.
- [98] M. Kubota, B.P. Wynne, *Scripta Materialia*, 57 (2007) 719-722.
- [99] M. Kubota, *Journal of Alloys and Compounds*, 434-435 (2007) 294-297.
- [100] T.T. Sasaki, T. Ohkubo, K. Hono, *Acta Materialia*, 57 (2009) 3529-3538.
- [101] M. Kubota, P. Cizek, W.M. Rainforth, *Composites Science and Technology*, 68 (2008) 888-895.
- [102] M. Kubota, J. Kaneko, M. Sugamata, *Materials Science and Engineering: A*, 475 (2008) 96-100.
- [103] M. Kubota, *Journal of Alloys and Compounds*, 504, Supplement 1 (2010) S319-S322.
- [104] C.Y. Xü, S.S. Jia, Z.Y. Cao, *Materials Characterization*, 54 (2005) 394-398.
- [105] H. Kwon, D. Park, Y. Park, J. Silvain, A. Kawasaki, Y. Park, *Met. Mater. Int.*, 16 (2010) 71-75.
- [106] G.M. Le, A. Godfrey, N. Hansen, *Materials & Design*, 49 (2013) 360-367.
- [107] G.E. Dieter, H.A. Kuhn, S.L. Semiatin, *Handbook of workability and process design*, ASM International, Materials Park, Ohio, United States of America, 2003.
- [108] Y. Deng, Z. Yin, J. Huang, *Materials Science and Engineering: A*, 528 (2011) 1780-1786.
- [109] H. Zhang, L. Li, D. Yuan, D. Peng, *Materials Characterization*, 58 (2007) 168-173.
- [110] X. Huang, H. Zhang, Y. Han, W. Wu, J. Chen, *Materials Science and Engineering: A*, 527 (2010) 485-490.
- [111] M. Rajamuthamilselvan, S. Ramanathan, *Journal of Alloys and Compounds*, 509 (2011) 948-952.
- [112] G.Y. Lin, Z.F. Zhang, H. Zhang, D.S. Peng, J. Zhou, *Acta Metallurgica Sinica (English Letters)*, 21 (2008) 109-115.
- [113] H. Li, Z. Li, M. Song, X. Liang, F. Guo, *Materials & Design*, 31 (2010) 2171-2176.

- [114] H.E. Hu, L. Zhen, L. Yang, W.Z. Shao, B.Y. Zhang, *Materials Science and Engineering: A*, 488 (2008) 64-71.
- [115] A.G. Beer, M.R. Barnett, *Metall and Mat Trans A*, 38 (2007) 1856-1867.
- [116] X. Fang, D. Yi, B. Wang, C. Wu, H. Zhang, *Rare Metals*, 27 (2008) 121-126.
- [117] Z. Chen, Z. Li, C. Yu, *Materials Science and Engineering: A*, 528 (2011) 961-966.
- [118] K.P. Rao, Y.V.R.K. Prasad, K. Suresh, N. Hort, K.U. Kainer, *Materials Science and Engineering: A*, 552 (2012) 444-450.
- [119] L. Gao, A.A. Luo, *Materials Science and Engineering: A*, 560 (2013) 492-499.
- [120] Q. Chen, X. Xia, B. Yuan, D. Shu, Z. Zhao, J. Han, *Materials Science and Engineering: A*, 593 (2014) 38-47.
- [121] C. Zener, J.H. Hollomon, *Journal of Applied Physics*, 15 (1944) 22-32.
- [122] M. yan Zhan, Z. Chen, H. Zhang, W. Xia, *Mechanics Research Communications*, 33 (2006) 508-514.
- [123] P.T. Wang, M.E. Karabin, *Powder Technology*, 78 (1994) 67-76.
- [124] C. Zubizarreta, S. Giménez, J.M. Martín, I. Iturriza, *Journal of Alloys and Compounds*, 467 (2009) 191-201.
- [125] N. Srinivasan, Y.V.R.K. Prasad, P. Rama Rao, *Materials Science and Engineering: A*, 476 (2008) 146-156.
- [126] Y.V.R.K. Prasad, K.P. Rao, N. Hort, K.U. Kainer, *Materials Letters*, 62 (2008) 4207-4209.
- [127] J.C. Malas, S. Venugopal, T. Seshacharyulu, *Materials Science and Engineering: A*, 368 (2004) 41-47.
- [128] H.Z. Li, H.J. Wang, X.P. Liang, H.T. Liu, Y. Liu, X.M. Zhang, *Materials Science and Engineering: A*, 528 (2011) 1548-1552.
- [129] G.-Z. Quan, B.-S. Kang, T.-W. Ku, W.-J. Song, *Int J Adv Manuf Technol*, 56 (2011) 1069-1078.
- [130] J. Luo, M.Q. Li, D.W. Ma, *Materials Science and Engineering: A*, 532 (2012) 548-557.
- [131] H.T. Zhou, Q.B. Li, Z.K. Zhao, Z.C. Liu, S.F. Wen, Q.D. Wang, *Materials Science and Engineering: A*, 527 (2010) 2022-2026.
- [132] S. Anbu Selvan, S. Ramanathan, *Transactions of Nonferrous Metals Society of China*, 21 (2011) 257-264.
- [133] Y. Xu, L. Hu, Y. Sun, *Materials Science and Engineering: A*, 578 (2013) 402-407.
- [134] B. Verlinden, L. Froyen, in, *European Aluminium Association*, Brussels, Belgium, 1994.
- [135] J.M. Torralba, V. Lancau, M.A. Martínez, F. Velasco, *Journal of Materials Science Letters*, 19 (2000) 1509-1512.
- [136] J.B. Fogagnolo, M.H. Robert, E.M. Ruiz-navas, J.M. Torralba, *Journal of Materials Science*, 37 (2002) 4603-4607.
- [137] J.B. Fogagnolo, M.H. Robert, E.M. Ruiz-Navas, J.M. Torralba, *Journal of Materials Science*, 39 (2004) 127-132.
- [138] M. Adamiak, J.B. Fogagnolo, E.M. Ruiz-Navas, L.A. Dobrzański, J.M. Torralba, *Journal of Materials Processing Technology*, 155-156 (2004) 2002-2006.
- [139] F. Velasco, C.E. Da Costa, N. Candela, J.M. Torralba, *Journal of Materials Science*, 38 (2003) 521-525.

- [140] J.B. Fogagnolo, E.M. Ruiz-Navas, M.H. Robert, J.M. Torralba, *Scripta Materialia*, 47 (2002) 243-248.
- [141] Z. Zhang, R. Yang, G. Chen, Y. Zhao, Y. Shao, *Materials Letters*, 89 (2012) 166-168.
- [142] Z. Zhang, H. Yu, G. Chen, H. Yu, C. Xu, *Materials Letters*, 65 (2011) 2686-2689.
- [143] W.-b. Fang, W. Fang, H.-f. Sun, *Transactions of Nonferrous Metals Society of China*, 21, Supplement 2 (2011) s247-s251.
- [144] F. Wa, F. Wen-bin, S. Hong-fei, *Journal of Alloys and Compounds*, 509 (2011) 4887-4890.

MATERIALS AND EXPERIMENTAL PROCEDURE

3

CHAPTER 3 MATERIALS AND EXPERIMENTAL PROCEDURE

The experimental procedure of this Ph.D. thesis covers two main activities: (1) powder processing and (2) materials consolidation.

The first activity includes the processing of nanocrystalline 7075 Al and AZ91 Mg alloy powders by mechanical alloying. To this end, the effects of the content of PCA and the milling time are studied and the mechanical alloying process is optimized for the production of the above-mentioned powders. Furthermore, the thermal stability of the nanocrystalline alloy powders produced by high-energy milling is also evaluated through isothermal annealing.

The second activity deals with the consolidation of the as-received and mechanically alloyed powders by different processing routes. In this stage, the effects of each consolidation route and its processing variables on the microstructural and mechanical characteristics of the processed bulk materials are closely studied.

In Fig. 3.1 is schematically represented the full experimental procedure including the main milestones and the characterization techniques used to fulfil each step.

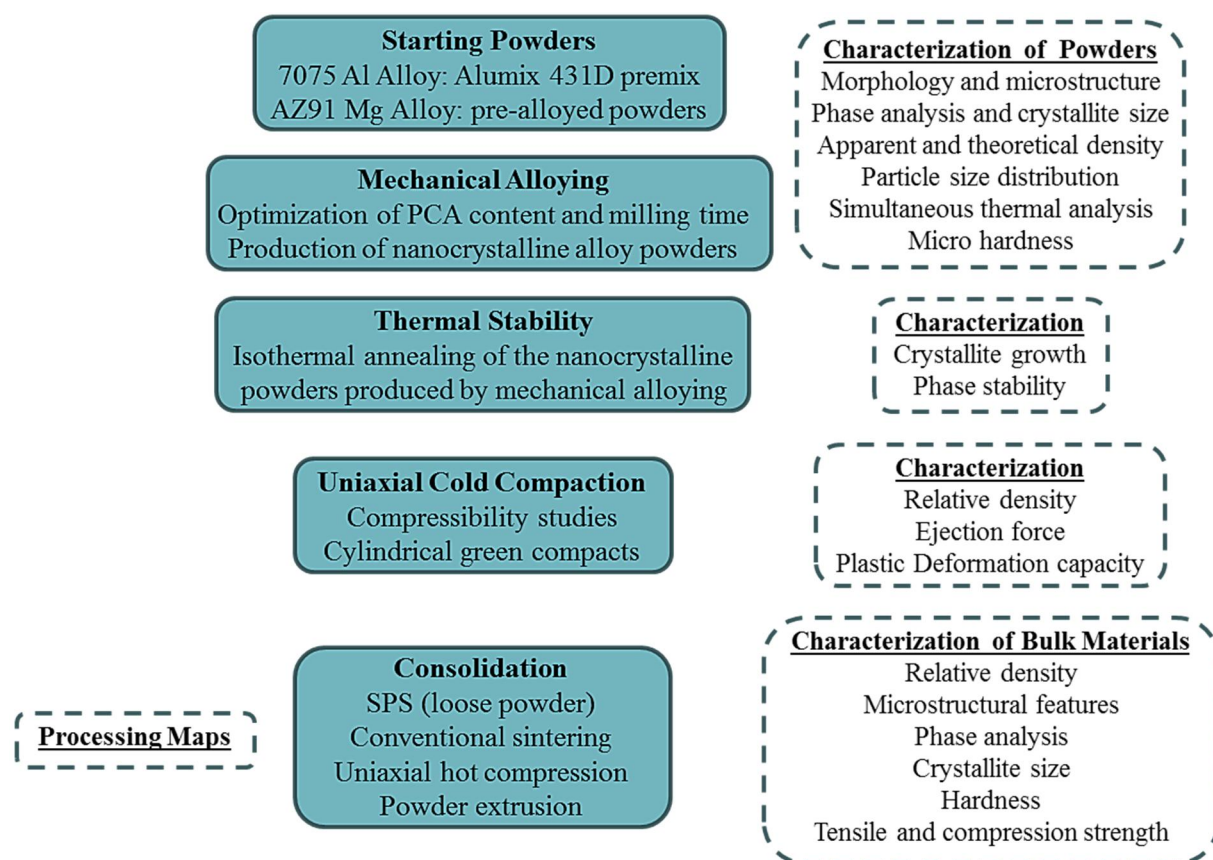


Fig. 3.1. Schematic diagram of the experimental procedure of this Ph.D. Thesis.

3.1 Starting Materials.

3.1.1 Alumix 431D Premix.

A commercially available premixed Al-Zn-Mg-Cu powder, Alumix 431D (Ecka Granules, Germany), with a chemical composition similar to AA 7075 alloy (5.6–6.4 wt% Zn, 2.4–3 wt% Mg, 1.5–2 wt% Cu, 0.1–0.3 wt% Sn, and the balance Al) was used in the current investigation. Because the premix was a ready-to-press blend, it contained approximately 1.5 wt% lubricant to facilitate the pressing step.

3.1.2 AZ91 Mg Alloy Powders.

The raw materials used for this study were two different kinds of pre-alloyed Mg-Al-Zn powder produced by mechanical grinding (Ecka Granules, Germany) and atomization (ESM Special Metals & Technology, USA), respectively, with a chemical composition equivalent to that of AZ91 D alloy (8.8 wt% Al, 0.6 wt% Zn, 0.2 wt% Mn, 0.03 wt% Si, and the balance Mg).

3.1.2 Pressing Lubricant.

Prilled or Beaded Acrawax C is an effective lubricant, processing aid, slip additive and pigment dispersant aid for most polymers including ABS, PVC, polypropylene, nylon, acetal, polyethylene and thermoplastic polyester. Powdered or Atomized Acrawax C (N,N' Ethylene Bisstearamide) is traditionally used as a lubricant and binder for cold compaction of powdered metal parts. For this study, Atomized Acrawax C (Lonza, Switzerland) with an average particle size of 6 μm was employed as the pressing lubricant whenever needed.

3.2 High-Energy Milling.

To produce nanocrystalline alloys, the starting powders were high-energy milled in a horizontal attritor (CM01 Simoloyer, ZOZ, Germany) using the following milling parameters: ball-to-powder weight ratio: 20/1; ball diameter: 5 mm; ball material: AISI 420 stainless steel; milling time up to 40 h, milling speed: 700 rpm; and milling atmosphere: Ar. Stearic acid (0–2 wt%) was also employed as the process control agent (PCA). These processing parameters were selected based on the previous experience in the research group on similar materials using the same attritor mill. To optimize the mechanical alloying process for the production of nanocrystalline alloys from the starting powders, the effects of PCA content and milling time on characteristics of the powders under milling were studied.

An attritor (a ball mill capable of generating higher energies) consists of a horizontal or vertical container with a series of impellers inside it. Set progressively at right angles to each

other, the impellers energize the ball charge, causing powder size reduction because of impact between balls, between balls and container wall, and between balls, agitator shaft, and impellers. A powerful motor rotates the impellers, which in turn agitate the steel balls in the milling container. The milling apparatus used for this study was equipped with a thermocouple to monitor and control the milling temperature. The temperature of the milling container during the milling process was kept below 35 °C using a continuous flow of water.

3.3 Powder Characterization.

A Malvern Mastersizer 2000 laser particle size analyzer, with a measurement range of 1 to 1000 microns, was used to determine the average particle size and particle size distribution of each powder. To this end, a small sample of the powder to be characterized was mixed with ethanol and added to the input pan of the machine where an impeller insured the powder was suspended. Some of the solution was drawn into the machine and passed by a helium neon laser. The particle size was calculated by diffraction and reported to the computer, which tabulated the result. The machine had been factory calibrated and the accuracy was checked by measuring the particle size of a known powder. The apparent density of each powder was measured in accordance with the MPIF 04 standard test method. A helium pycnometer AccuPyc 1330 (Micrometrics, USA) was used to measure the theoretical density of the as-received and mechanically alloyed Alumix 431D and AZ91 powders.

Morphology and cross-section microstructure of each powder was studied by scanning electron microscopy (SEM) using a Philips XL30 scanning electron microscope. Besides, the microstructural evolution and phase changes of the starting powders through high-energy milling and subsequent isothermal annealing were studied by X-ray diffractometry (XRD) using a Philips X'Pert X-ray diffraction system. The crystallite sizes of the powders processed by high-energy milling for different milling times were determined from the broadening of XRD peaks using the Williamson-Hall method. A Philips diffractometer with Cu K α radiation ($\lambda = 0.15406$ nm) generated at 40 kV and 40 mA was used for the XRD measurements. The XRD patterns were recorded in the 2θ range of 15–100 degrees (step size: 0.05 degree, time per step: 4 s). The hardness of the as-received and mechanically alloyed powders was determined by microhardness measurements using a Vickers indenter at a load of 10 gf.

As the nanocrystalline powders processed by high-energy milling are then consolidated by powder metallurgy (PM) routes, such as cold pressing and sintering, powder extrusion, powder forging, and powder rolling, the microstructural evolution of high-energy milled powders during subsequent consolidation processes at high temperatures was also studied by isothermal annealing. The isothermal annealing was performed at annealing temperatures of 200 °C, 300 °C, 400 °C, and 500 °C for annealing times of up to 4 h in an Ar atmosphere.

Differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) tests were conducted on the as-received and mechanically alloyed Alumix 431D and AZ91

powders using a simultaneous thermal analyzer (STA) 6000 manufactured by PerkinElmer. Each powder was heated in an alumina pan at a rate of 5 °C/min under flowing high-purity Ar or N₂ gas. For baseline subtraction, the empty alumina pan was initially tested in the same fashion.

3.4 Powder Compaction.

3.4.1 Compressibility Studies.

To study the compressibility characteristics of Alumix 431D and AZ91 powders (in the both as-received and mechanically alloyed states), 2 g and 1.3 g of the mentioned powders, respectively, were uniaxially cold pressed into cylindrical billets with diameters of 10 mm using compaction pressures ranging from 100 MPa to 600 MPa. At least two samples were compacted for each compaction pressure. The green densities of the compacts were calculated by measuring the weight and volume of the compacts using an accurate balance (± 0.01 g) and a micrometer (± 0.01 mm) (volumetric method). Furthermore, two different contents of atomized Acrawax C (average particle size: 6 μ m) (Lonza, USA), namely, 0.75 wt% and 1.5 wt%, were used to study the effect of this pressing lubricant on the compressibility of each powder except for the as-received Alumix 431D powder which already contained 1.5 wt.% pressing lubricant. The compressibility data obtained for each powder were then analyzed and fitted to the Panelli and Ambrosio compaction equation to quantify the compressibility of the powders.

3.4.2 Uniaxial Cold Compaction

The as-received and mechanically alloyed Alumix 431D and AZ91 powders were uniaxially cold pressed to produce cylindrical green compacts for conventional sintering, hot compression, and powder extrusion. Table 3.1 presents the dimensions of the cylindrical compacts employed for each consolidation route.

Table 3.1. Dimensions of the cylindrical green compacts employed for different consolidation routes.

Powder(s)	Consolidation Route	Diameter (mm)	Length (mm)
As-Received and Mechanically Alloyed	Conventional Sintering	10	5
As-Received	Hot Compression	10	15
Mechanically Alloyed	Hot Compression	10	12
As-Received and Mechanically Alloyed	Powder Extrusion	25	20

3.5 Conventional Sintering

The cylindrical green compacts uniaxially cold pressed at a pressure of 600 MPa from the as-received and mechanically alloyed Alumix 431D and AZ91 powders were sintered in a laboratory tube furnace manufactured by Carbolite (UK) under a controlled atmosphere using a heating and cooling rate of 5 °C/min.

The heating cycle for the compacts cold pressed from the as-received and mechanically alloyed Alumix 431D powders included a 20 min dwell at 400 °C for delubrication purposes followed by sintering at 590 °C, 605 °C, and 620 °C for 30 min and 60 min. After sintering, the samples were furnace cooled to ambient. A flowing atmosphere of ultra-high purity nitrogen (>99.999%) was maintained throughout the entire cycle. An example of a temperature profile used for the Al-based powders is depicted in Fig. 3.2 (a).

The powder compacts cold pressed from the as-received and mechanically alloyed AZ91 powders were directly heated to the required sintering temperature, ranging between 500 °C and 600 °C, and soaked at the sintering temperature for the required time, i.e. 1 h and 3 h. After sintering, the samples were furnace cooled to ambient. To study the effect of sintering atmosphere on the sintering response of AZ91-based powders, sintering was carried out in both ultra-high purity nitrogen and argon atmospheres (>99.999%). An example of a temperature profile used for the Mg-based powders is depicted in Fig. 3.2 (b).

The sintered specimens were sectioned in the center parallel to the pressing direction for the microstructural analysis. The sectioned samples were then mounted, ground, and polished.

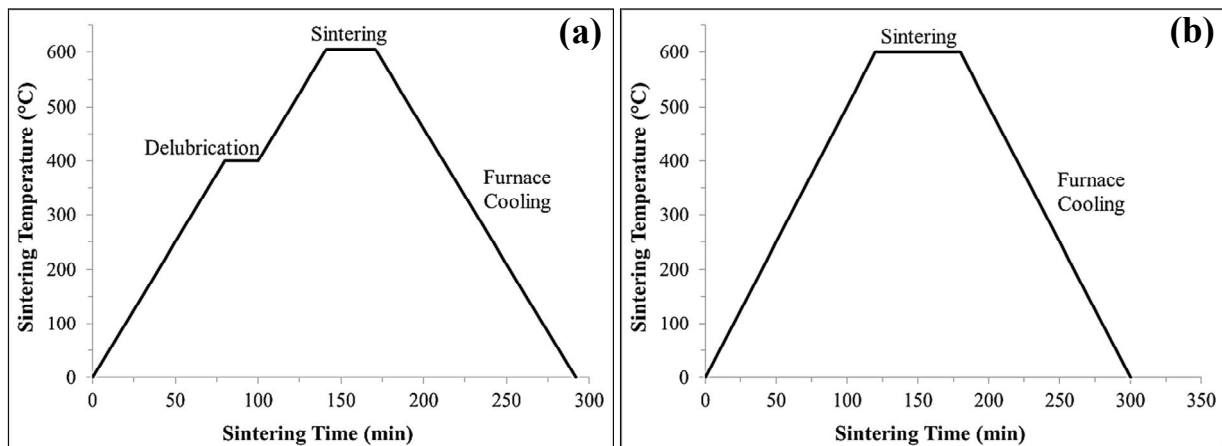


Fig. 3.2. Typical temperature profile used for the sintering of (a) Al-based and (b) Mg-based powders.

3.6 Field Assisted Hot Pressing (FAHP)

The mechanically alloyed Alumix 431D and AZ91 powders were consolidated by the FAHP process. For comparison purposes, the FAHP process was also used to consolidate the as-received powders. However, the as-received Alumix 431D powder contained 1.5 wt%

pressing lubricant, which made this powder unsuitable for the FAHP process. Consequently, the as-received Alumix 431D was not consolidated by the FAHP process.

FAHP was carried out in a Gleeble-3800 system (Dynamic Systems Inc, USA) using a graphite die. Cylindrical specimens measuring 10 mm in diameter and 5 mm in height were produced by FAHP. The temperature of the sample during the FAHP process was measured by a K type thermocouple inserted in a hole in the center of the graphite die (thermocouple 1 in Fig. 3.3). Another K type thermocouple attached to one of the punches of the graphite die was used for heating purposes (thermocouple 2 in Fig. 3.3). A vacuum of 10^{-5} Pa was maintained throughout the entire FAHP cycle.

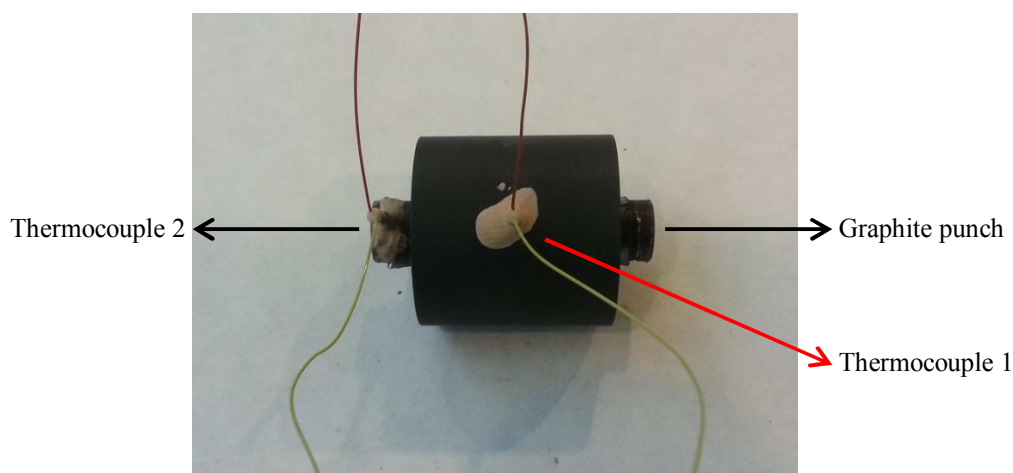


Fig. 3.3. The graphite die and K type thermocouples used for the FAHP process.

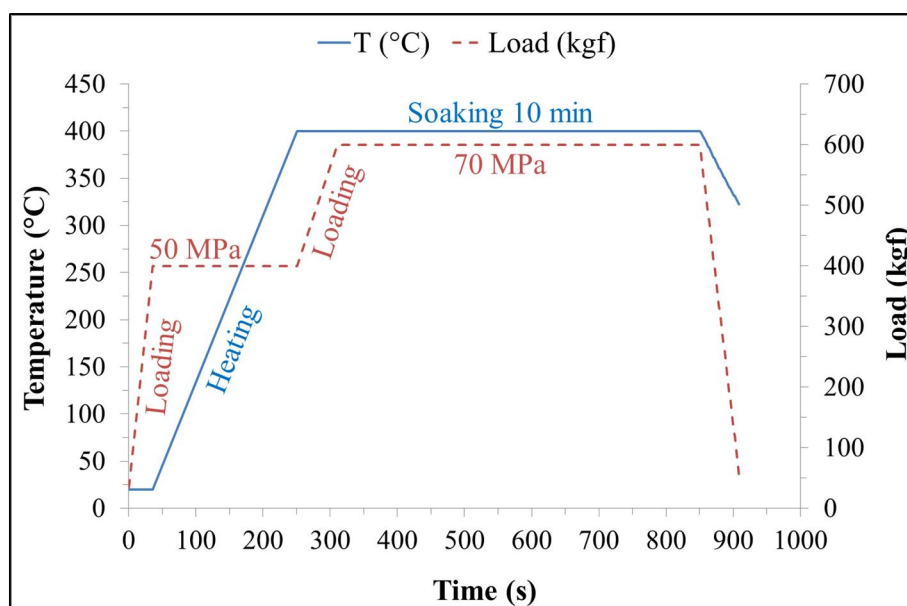


Fig. 3.4. The temperature-load profile used for the FAHP of samples at 400 °C.

Two different sintering temperatures were selected to produce bulk samples: 350 °C and 400 °C. The temperature-load profile used for the FAHP of samples at 400 °C is presented in Fig. 3.4. As seen, the load was first increased to 400 kgf (50 MPa) at room temperature. Then, the temperature was increased to 400 °C at a heating rate of about 100 °C/min while the load was maintained around 400 kgf. Next, the load was gradually increased from 400 kgf to 600 kgf (70 MPa) during the first minute of soaking at 400 °C and was maintained constant afterwards till the end of the soaking step at 400 °C. The total soaking time at 400 °C was 10 min. Upon completion of the process the load was removed and the die setup was cooled down to room temperature inside the chamber.

The bulk specimens produced by FAHP were sectioned in the center parallel to the FAHP direction for the microstructural analysis. The sectioned samples were then mounted, ground, and polished.

3.7 Uniaxial Hot Compression

3.7.1 The Effects of Relative Green Density

To study the effects of relative green density on the hot deformation behavior of powder compacts, the as-received Alumix 431D powder was uniaxially cold pressed into cylindrical billets with a diameter of 10 mm and a length of 15 mm. To produce powder compacts with dissimilar green densities, different compaction pressures were used. The pressures applied during pressing and the corresponding relative green densities are listed in Table 3.2.

Table 3.2. The effect of cold pressing pressure on the relative green density of Alumix 431D powder compacts.

Pressing Pressure (MPa)	Relative Green Density (%)
200	83
300	88.5
500	94
700	95

Different cold pressing pressures produce different green densities and levels of strain hardening, which both affect the deformation behaviour of powder compacts. Because the aim of the present study was to investigate the effect of the relative green density on the deformation behaviour, other factors that can affect the deformation behaviour of powder compacts were eliminated. Therefore, to minimise the effect of strain hardening due to cold compaction on the hot deformation behaviour, the powder compacts were subjected to a

stress relief heat treatment (the compacts were heated to 400°C at a rate of 5°Cs⁻¹, maintained at 400°C for 20 minutes, and furnace-cooled to room temperature) in a high-purity nitrogen atmosphere.

A K type thermocouple was inserted in a hole at the mid-height of the specimens for temperature measurement and control (Fig. 3.5). A graphite foil with a thickness of 0.05 mm was placed between the ends of the powder compacts and the anvils to minimise friction during the compression test. Prior to the compression tests, the samples were resistance-heated under vacuum to the required temperature at a heating rate of 3°Cs⁻¹ and were maintained at the test temperature for 1 min to minimise thermal gradients along the sample. Single-hit compression tests were carried out using a servo-controlled Gleeble-3800 system at strain rates of 0.01 s⁻¹, 0.1 s⁻¹, 1 s⁻¹, and 10 s⁻¹ and deformation temperatures of 350°C, 400°C, and 450°C. After the compression tests, the samples were cooled to room temperature at a cooling rate of approximately 10°Cs⁻¹. The load-stroke data were converted into true stress-true strain curves using the following equations:

$$\varepsilon = \ln ((H_0 + \Delta H) / H_0) \quad (3.1)$$

$$\sigma = \text{Load} / [(\pi R_0^2 H_0) / (H_0 + \Delta H)] \quad (3.2)$$

where H_0 and R_0 are the initial height and radius of the samples, respectively.

The true stress-true strain data obtained through the hot compression of Alumix 431D powder compacts were then analysed, and a constitutive equation that is capable of predicting the peak flow stress of Alumix 431D powder compacts and considers the relative green density, deformation temperature, and strain rate was proposed.

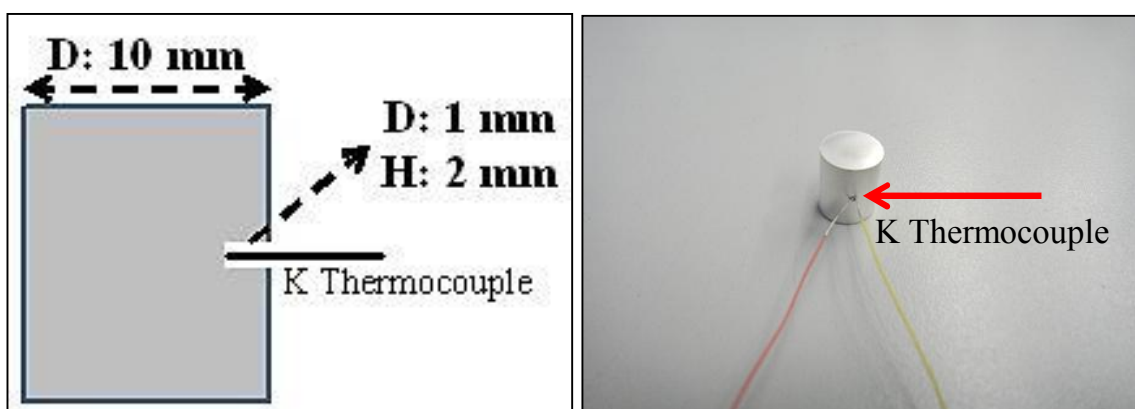


Fig. 3.5. K type thermocouple inserted in a hole at the mid-height of a specimen.

3.7.2 Hot Deformation Behavior

To study the hot deformation behavior and workability characteristics of the as-received and mechanically alloyed Alumix 431D and AZ91 powders, these powders were uniaxially cold pressed at a pressure of 600 MPa into cylindrical compacts measuring 10 mm in

diameter and 15 mm (for the as-received powders) or 12 mm (for the mechanically alloyed powders) in height.

The cylindrical compacts cold pressed from the as-received Alumix 431D powder were then subjected to a presintering (heating to 400 °C and holding at 400 °C for 20 min, followed by heating to 525 °C and soaking at this temperature for 45 min) heat treatment prior to hot compression. The goal of the presintering heat treatment was the homogenisation of microstructure with the help of a liquid phase that forms during presintering. In the case of mechanically alloyed Alumix 431D powder, the compacts were subjected to a delubrication (heating to 400 °C and holding at this temperature for 60 min) heat treatment. The aim of the delubrication heat treatment was elimination of the admixed pressing lubricant before hot compression. The compacts cold pressed from the as-received and mechanically alloyed AZ91 powder were directly used for hot compression without being subjected to any kinds of heat treatment.

A K type thermocouple was inserted in a whole at the mid-height of the specimens for temperature measurement and control (Fig. 3.5). A graphite foil with a thickness of 0.05 mm was placed between the ends of the powder compacts and the anvils to minimize friction during the hot compression test. Prior to the hot compression tests, the samples were resistance heated in an Ar atmosphere to the required temperature at a heating rate of 3 °Cs⁻¹, then maintained at the test temperature for 1 minute to minimize thermal gradients along the sample. Single-hit compression tests were performed using a servo-controlled Gleeble-3800 system (Dynamic Systems Inc, USA) at strain rates varied between 0.001 s⁻¹ to 10 s⁻¹ and deformation temperatures varied between 150 °C to 600 °C (depending on the starting powder), which cover the entire hot working range of Al and Mg alloys. The specimens were deformed to a true strain of 0.8. For microstructural and workability investigations, some specimens were also deformed to strains varied between 0.2 and 1.6. After hot compression, the samples were air-quenched to room temperature. The load-stroke data were converted into true stress-true strain curves using equations (3.1) and (3.2).

The hot-compressed specimens were sectioned in the center parallel to the hot compression direction for the microstructural analysis. The sectioned samples were then mounted, ground, polished.

The true stress-true strain data attainable through hot compression or the other workability tests can be analyzed by Dynamic Material Modeling technique to evaluate the workability of a material and to develop its processing maps.

3.7.3 Processing Maps

Coupling the processing conditions such as strain rate and deformation temperature to a desired microstructure is a valuable approach to deformation process optimization and this can be achieved by using processing maps. Processing maps have been proven to be a useful tool for the optimization of hot working processes for a wide range of metals and their alloys

[1], or for the design of process parameters for new materials. It is helpful in identifying different deformation mechanisms within different domains. As a product of the dynamic material modeling [2], it combines the efficiency of power dissipation and the instability of deformation. The dissipated power is related to the rate of internal entropy production due to the metallurgical processes involved and the partitioning of the total power between that due to the temperature rise and that due to microstructural changes. Strain rate sensitivity is considered a power partitioning factor [3]. The efficiency of power dissipation η is given by [4]:

$$\eta = 2m/(m+1) \quad (3.3)$$

$$m = (\partial \log \sigma) / (\partial \log \dot{\epsilon}) \quad (3.4)$$

where m is the strain rate sensitivity. Plotting the efficiency (in %) against temperature and strain rate at different strains results in the power dissipation maps, which can be seen as 2D or 3D surfaces. In a 3D power dissipation map, an increase of efficiency will result in the development of a *hill*. Above a threshold of efficiency, the area can be denoted as “safe” and such mechanisms as dynamic recrystallization, dynamic recovery or super plastic deformation may operate. On the other hand, the *valleys* represent “damaging” microstructural changes, such as void formation, wedge cracking, inter-crystalline cracking and other types of cracking.

The instability map is developed on the basis of an instability criterion and given by a dimensionless parameter ξ [2]:

$$\xi = (\partial \ln[m/(m+1)] / \partial \ln \dot{\epsilon}) + m \leq 0 \quad (3.5)$$

where ξ turns negative under specific temperature and strain rate conditions, flow instabilities like adiabatic shear bands or flow localization can be observed in the microstructure. The physical meaning of Equation 3.5 is that if the system is unable to generate entropy at a rate that at least matches with the imposed rate, it will localize the flow and cause flow instability.

Superimposing an instability map on a power dissipation efficiency map produces a processing map. The instability map shows the areas that will cause flow instability, whereas the power dissipation map shows the most efficient power dissipation areas.

3.8 Powder Extrusion

To produce fully-dense, high performance bulk materials from the as-received and mechanically alloyed Alumix 431D and AZ91 powders, the mentioned powders were uniaxially cold pressed at a pressure of 600 MPa into cylindrical compacts 25 mm in diameter and 15 mm thick.

Selected green compacts cold pressed from the as-received Alumix 431D powder were then subjected to either a delubrication (heating to 400 °C and holding at this temperature for 20 min) or presintering (heating to 400 °C and holding at 400 °C for 20 min, followed by heating to 525 °C and soaking at this temperature for 45 min) heat treatment prior to extrusion. In the case of mechanically alloyed Alumix 431D powder, the cylindrical compacts were subjected to a delubrication and stress relieving (heating to 400 °C and holding at this temperature for 60 min) heat treatment. The aim of the delubrication heat treatment was elimination of the admixed pressing lubricant before hot compression. The cylindrical compacts cold pressed from the as-received and mechanically alloyed AZ91 powder were directly used for extrusion without being subjected to any kinds of heat treatment.

Extrusion of the powder compacts was performed at a temperature varied between 300 °C to 500 °C (depending on the starting powder), without caning and degassing, using an extrusion ratio of 25:1 to ensure full density after extrusion. Before heating to the extrusion temperature, a thin layer of a mixture of graphite and oil was applied to the surfaces of the powder compacts, serving as both a lubricant and an oxidation barrier. The compacts were extruded to form rods 5 mm in diameter and approximately 300 mm long. After extrusion, the extruded rods were air cooled to room temperature.

For the characterization of the extruded materials, extrudates were sectioned parallel to the extrusion direction (i.e., longitudinal sections). To eliminate the possible effects of microstructural differences between different parts of the extrudates, all of the samples were cut from the middle of each extruded rod. The samples were then mounted and prepared using the conventional metallographic techniques.

3.9 Characterization of Consolidated Materials

The densities of consolidated samples were measured by Archimedes method following MPIF 42 standard test method. The bulk samples consolidated from the as-received and mechanically alloyed Alumix 431D and AZ91 powders by conventional sintering, FAHP, uniaxial hot compression, and extrusion were then sectioned in the center, mounted in conductive resin, and ground on SiC paper to a 2000 grit finish. The samples were finally polished using diamond suspensions of 1 and 0.25 µm.

Optical micrographs were recorded using an Olympus model GX71 optical microscope equipped with a ColorView digital camera. A Philips XL30 scanning electron microscope equipped with an EDAX EDS detector was used to study and examine the microstructures of consolidated samples. XRD was also employed for the qualitative analysis of the phases present in the microstructures of consolidated materials. A Philips X'Pert diffractometer with Cu K α radiation ($\lambda = 0.15406$ nm) generated at 40 kV and 40 mA was used for the XRD measurements. The XRD patterns were recorded in the 2θ range of 15–100 degrees (step size: 0.05 degree, time per step: 4 s).

Vickers hardness values were obtained to evaluate the success of different consolidation techniques employed to produce bulk samples from the as-received and mechanically alloyed Alumix 431D and AZ91 powders. A 136 ° pyramidal diamond indenter was forced into the surface of the samples using an applied load of 1 kgf and/or 5 kgf. The reported hardness value for each material is the average value of twelve measurements. Tension and compression testing, in accordance with the ASTM: E8M and ASTM: E9 standards, were only conducted on the bulk materials processed by powder extrusion. The number of specimens for tension and compression testing of each extruded alloy were three.

References

- [1] Y.V.R.K. Prasad, S. Sasidhara, Hot Working Guide – A Compendium of Processing Maps, ASM International, Materials Park, OH, U.S.A., 1997.
- [2] Y.V.R.K. Prasad, J. Mater. Eng. Perform., 12 (2003) 638-645.
- [3] Y.V.R.K. Prasad, T. Seshacharyulu, International Materials Reviews, 43 (1998) 243-258.
- [4] Y.V.R.K. Prasad, K.P. Rao, N. Hort, K.U. Kainer, Mater. Lett., 62 (2008) 4207-4209.

RESULTS AND
DISCUSSION FOR
7075 AL PM ALLOY

4

CHAPTER 4 SUMMARY OF RESULTS AND DISCUSSION FOR 7075 AL PM ALLOY

4.1 A 7075 Al PM Alloy: Alumix 431D Powder

The starting powder used for this study is Alumix 431D (Ecka Granules, Germany), which is commercially available as a premixed powder with a chemical composition equivalent to that of 7075 Al alloy (5.6–6.4 wt% Zn, 2.4–3 wt% Mg, 1.5–2 wt% Cu, 0.1–0.3 wt% Sn, and the balance Al). As this mixture is a ready-to-press blend, it typically contains 1.5 wt% lubricant to facilitate the pressing step.

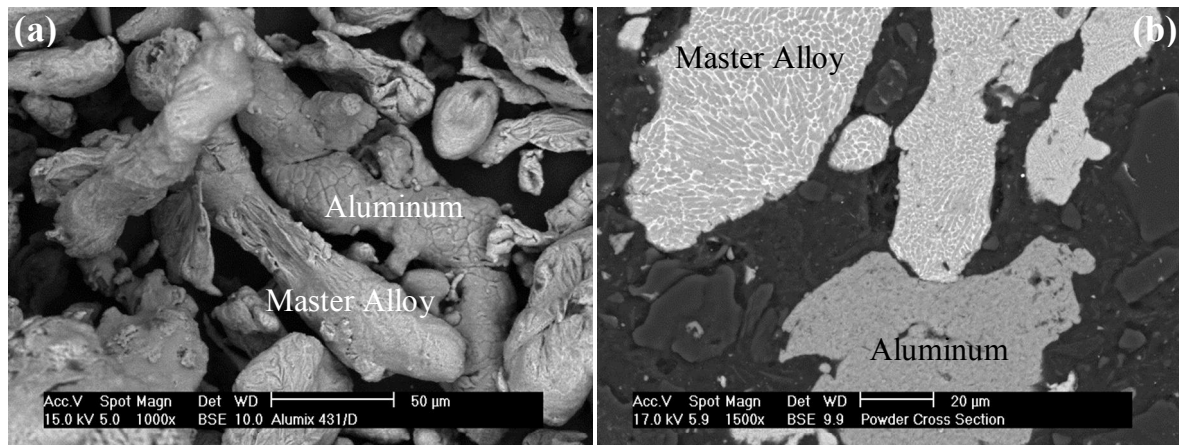


Fig. 4.1. (a) Morphology and (b) cross-section microstructure of the Alumix 431D premix.

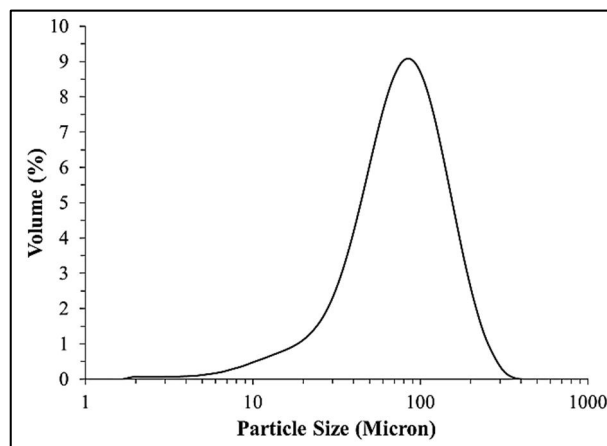


Fig. 4.2. Particle size distribution of the Alumix 431D premix.

Fig. 4.1 illustrates the morphology and cross-section microstructure of the Alumix 431D powder, showing that the powder particles of this premix have an irregular morphology, which is typical of atomized Al-based powders. The main component of Alumix 431D

premix is an atomized pure Al powder, which is mixed with a master alloy powder containing all of the alloying elements. The Al particles appear dark grey and show no specific features. The master alloy particles appear light grey and have a very fine cellular microstructure. A network of white phases is clearly visible in the microstructure of the master alloy powder particles. White phases are enriched with the alloying elements (Zn, Mg, and Cu) which results in a good contrast with the adjacent Al solid solution (Al (α)) matrix. The particle size distribution of Alumix 431D premix is presented in Fig. 4.2. The average particle size (D(0.5)) and particle size distribution (D(0.9) - D(0.1)) of the mixture were measured to be about 80 μm and 140 μm , respectively. The hardness of pure Al and master alloy particles were measured to be 30 ± 3 HV0.01 and 112 ± 12 HV0.01, respectively.

4.2 Mechanical Alloying

The **Paper Al I**, included in the appendix, mainly deals with the processing of nanostructured 7075 Al alloy by mechanical alloying of the Alumix 431D powder. The main objective of this study was to optimize the mechanical alloying process for the processing of a nanostructured alloy powder with the desired properties. To this end, the effects of the content of process control agent (PCA) and milling time on the evolution of powder particles during the milling process were carefully studied. In this section, the results presented in **Paper Al I** are briefly reviewed and discussed.

The effect of the content of PCA on various properties of the mechanically alloyed Alumix 431D powder is presented in Table 4.1. As suggested by Fogagnolo et al [1, 2], the correlation between the apparent density of a powder under milling and the milling time can be used to follow the morphological evolution of powder particles during the milling process and to determine the optimum milling time. The presented milling times in Table 4.1 correspond to the milling times necessary for the stabilization of the *apparent density* versus *milling time* plot for different contents of PCA (Fig. 4.3). These milling times were considered as the optimum milling time for each content of PCA.

Table 4.1. The effect of PCA content on various properties of the mechanically alloyed Alumix 431D powder [Paper Al I].

PCA Content (wt%)	Milling Time (h)	Powder Extraction Efficiency (%)	Average Particle Size (μm)	Crystalline Size (nm)
0	10	55	29	34
1	14	96	18	30
1.5	18	83	23	31
2	40	98	16	25

In agreement with the findings of other researchers [3-5], a higher content of PCA resulted in a lower average particle size for the milled Alumix 431D powder. It was also found out that, in addition to the content of PCA, the method of addition of PCA to Alumix 431D powder is also important. Compared to the Alumix 431D powder mixed with 1 wt% PCA, the powder mixture containing 1.5 wt% PCA showed a higher tendency for welding to the surfaces of grinding balls and the mill container, resulting in a lower powder extraction efficiency for the latter mixture. This can be related to the different method used for the addition of PCA to the latter mixture. In the case of latter mixture, 0.75 wt% of the PCA was added at the beginning of milling and the remaining 0.75 wt% was added after 6 h of milling.

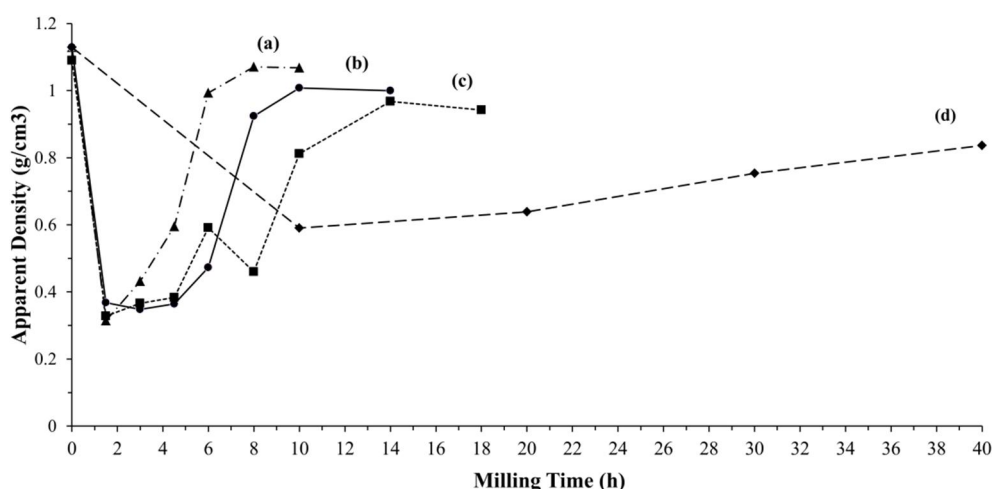


Fig. 4.3. Apparent density as a function of milling time for the Alumix 431D powder mixed with different contents of PCA [Paper Al I]. (a) 0 wt% PCA, (b) 1 wt% PCA, (c) 0.75 wt% PCA at milling time = 0 h and 0.75 wt% PCA at milling time = 6h, (d) 2 wt% PCA.

The evolution of the crystalline size of Alumix 431D powder with milling time did not show any dependence on the content and the method of addition of PCA. Only after 4.5 h of milling, the crystalline sizes of all powder mixtures reached a minimum of about 30 nm which remained constant afterwards (data not shown). This milling time approximately corresponds to the end of the first stage of milling in which plastic deformation is the dominant mechanism. It can be seen that through the addition of 1 wt% stearic acid to Alumix 431D powder at the beginning of the process, the processing of a nanostructured alloy powder can be reached after only 14 h of milling, with a powder extraction efficiency of 96 %. Although the optimum milling time for the Alumix 431D powder without using any PCA is only 10 h, the corresponding powder extraction efficiency is very low.

From the investigation carried out in **Paper Al I**, it can be concluded that the content of PCA has considerable effects on the milling of Alumix 431D powder. The employment of 1 wt% stearic acid as PCA results in an optimum balance among the milling time, apparent density, and powder extraction efficiency. Therefore, 1 wt% PCA was considered as the optimum content of PCA for mechanical alloying of the Alumix 431D powder in this study.

In addition to the content of PCA, the method of addition of PCA to Alumix 431D powder was also found to be important.

For detailed information on the above subject also see **Paper Al I**.

4.3 Mechanically Alloyed Alumix 431D Powder

The **Paper Al II** included in the appendix analyzes the effects of mechanical alloying and subsequent isothermal annealing on the microstructural characteristics of the Alumix 431D premix. To this end, the Alumix 431D powder was high-energy milled using the milling parameters optimized in **Paper Al I** (milling time: 14 h, 1 wt% PCA). Then, the mechanically alloyed powder was isothermally annealed. In this section, the results presented in **Paper Al II** are briefly reviewed and discussed.

The mechanically alloyed Alumix 431D (MA Alumix 431D) powder exhibited irregular, semi-equiaxed morphology (Fig. 4.4 (a)), implying that the employed milling time, i.e. 14 h, was sufficient for the milling process to reach its steady state, in which there is a balance between the cold welding and fracture of powder particles. After the milling process, no intermetallic phase was visible in the microstructures of the particles, and Al and master alloy particles were no longer distinguishable (Fig. 4.4 (b)). The microstructure of MA Alumix 431D powder appears dark grey and show no specific microstructural features. The average particle size ($D(0.5)$) and particle size distribution ($D(0.9) - D(0.1)$) of MA Alumix 431D powder were measured to be 18 μm and 50 μm , respectively, suggesting that the high-energy milling process had significant effects on the particle size characteristics of Alumix 431D powder. The hardness of MA Alumix 431D powder was measured to be 234 ± 10 HV0.01.

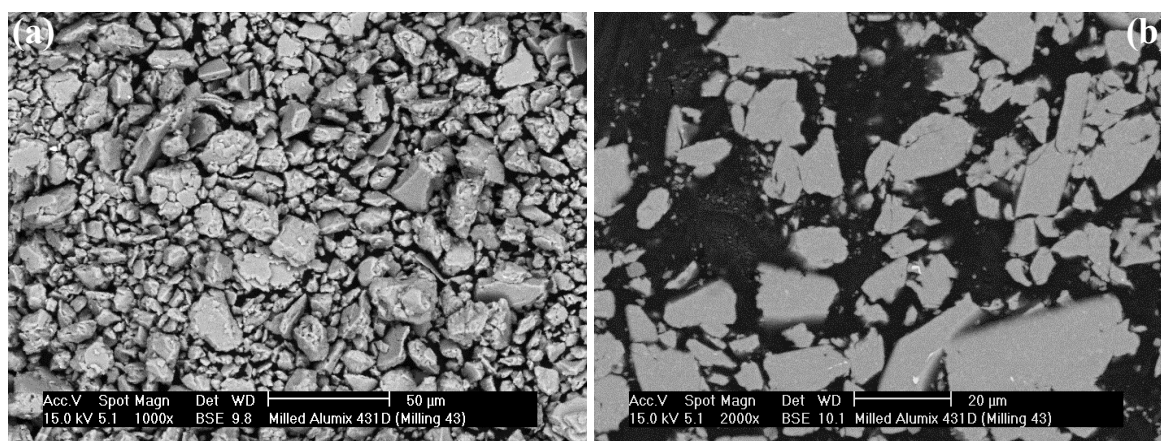


Fig. 4.4. (a) Morphology and (b) cross-section microstructure of the MA Alumix 431D powder (Paper Al II).

The XRD patterns of Alumix 431D and MA Alumix 431D powders are presented in Fig. 4.5. Analysis of the XRD patterns determined that the white phases present in the microstructure of the Alumix 431D powder (Fig. 4.1 (b)) are mainly $\text{Mg}_{32}(\text{Al}, \text{Zn})_{49}$ (the T phase). This phase is a metastable phase of Al-Zn-Mg and Al-Zn-Mg-Cu alloying systems

that can be produced through rapid solidification. The XRD peaks related to the α -Al phase became weaker and wider through high-energy milling (HEM) (Fig. 4.5). This phenomenon can be attributed to the reduction in particle size, the refinement of crystallite size, and the enhancement of lattice strain, all promoted by the severe plastic deformation of the Alumix 431D powder particles during HEM. Moreover, the diffraction peaks of the T- $\text{Mg}_{32}(\text{Al}, \text{Zn})_{49}$ phase are no longer detectable in the XRD pattern of MA Alumix 431D powder.

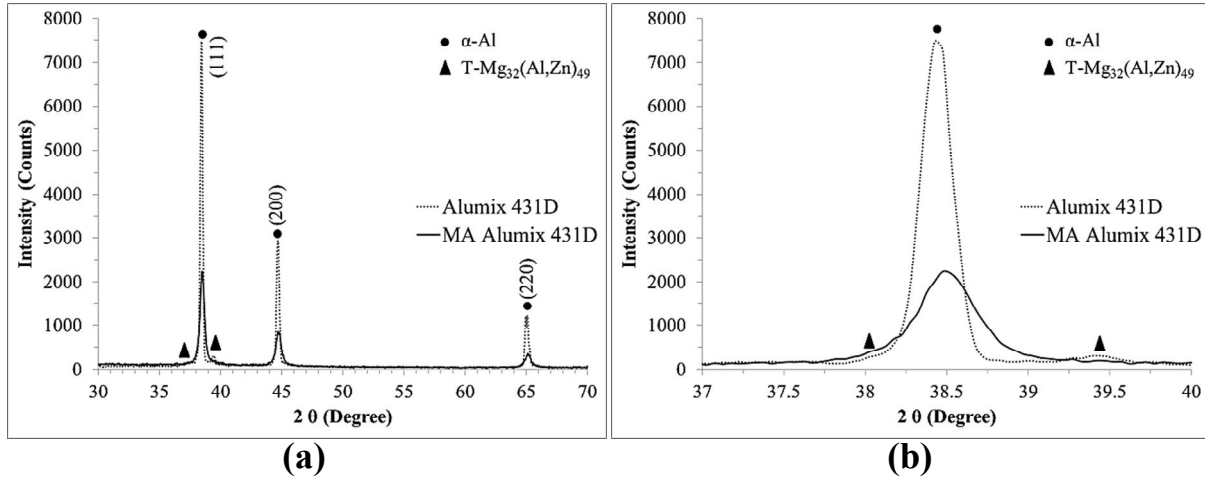


Fig. 4.5. (a) XRD patterns of Alumix 431D and MA Alumix 431D powders. (b) The α -Al (111) diffraction peak of Alumix 431D and MA Alumix 431D powders (Paper AI II).

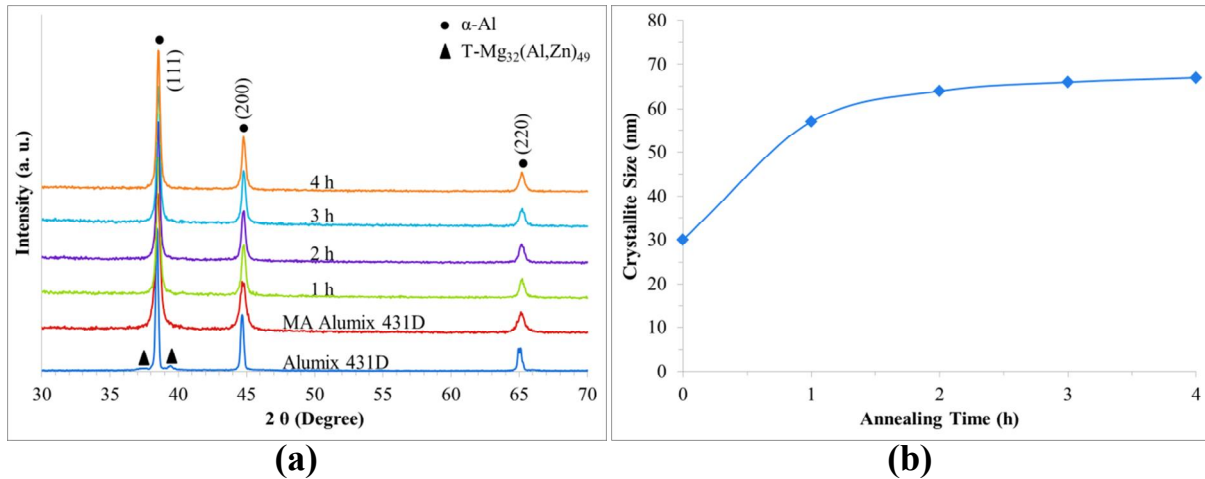


Fig. 4.6. (a) The XRD patterns and (b) the crystallite sizes of MA Alumix 431D powder annealed at 400 °C for different times (Paper AI II).

The XRD patterns of MA Alumix 431D powder annealed at 400 °C for 1 h to 4 h are illustrated in Fig. 4.6 (a). During annealing at 400 °C for different times, no significant microstructural change is detectable, suggesting that the MA Alumix 431D powder show good thermal stability. The crystallite size of MA Alumix 431D powder annealed at 400 °C

for 4 h was determined to be about 70 nm (Fig. 4.6 (b)), implying that the nanostructured 7075 Al alloy processed by HEM has a good tendency to maintain the nano features when a heat treatment is applied. This favorable resistance to grain growth could result from the homogenous distribution of nanosized Al oxides and carbides in the microstructure of MA Alumix 431D powder particles.

For detailed information on the above subject also see **Paper Al II**.

4.4 Analysis of the Compressibility.

The **Paper Al III** included in the appendix concerns the effects of mechanical alloying on the compressibility characteristics of Alumix 431D powder. In this section, the results presented in **Paper Al III** are briefly reviewed and discussed.

The compressibility curves of Alumix 431D and MA Alumix 431D powders are presented in Fig. 7.7. Alumix 431D is a ready-to-press blend and contains approximately 1.5 wt% lubricant to facilitate the pressing step. This powder exhibits excellent compressibility and reaches a relative density in green state of about 97 % at a pressing pressure of 600 MPa. Mechanical alloying has a very detrimental effect on the compressibility of Alumix 431D powder, and MA Alumix 431D powder reaches only a relative density in green state of about 82 % at a pressing pressure of 600 MPa. In addition, the powder compacts cold pressed at the pressing pressures of 100 MPa and 200 MPa were very fragile and broke during the ejection step. Then, we were unable to measure the relative green densities of these compacts.

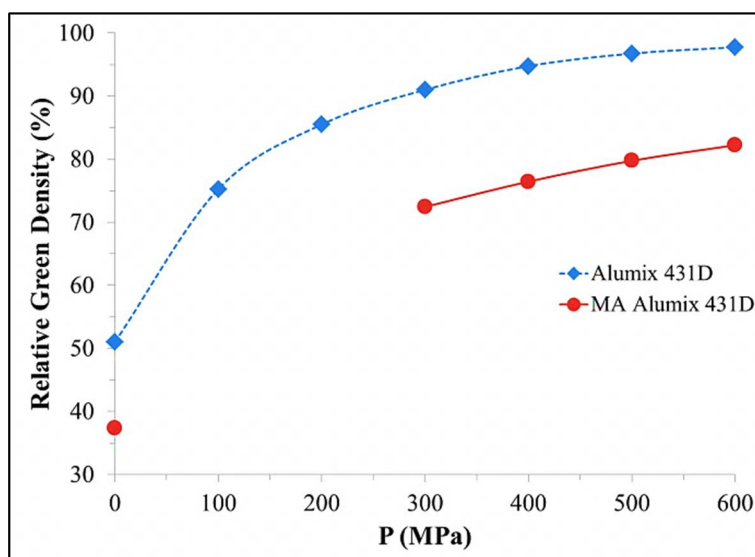


Fig. 4.7. The compressibility curves of Alumix 431D and MA Alumix 431D powders (Paper Al III).

The poor compressibility of MA Alumix 431D powder can primarily be attributed to its fine average particle size and narrow particle size distribution. In addition, mechanical alloying promotes a high degree of deformation and reduces the grain size of the starting

powder to nanometer levels, which leads to a significant increase in the strength and, as a result, to an unfavorable compressibility for the MA Alumix 431D powder.

In Fig. 4.8, the compressibility data for the as-received and as-milled Alumix 431D powders are represented in a diagrams of $P^{(1/2)}$ versus $\ln(1/(1-D))$ to visualize the validity of the Panelli and Ambrosio equation [6] (Equation 2.2) for uniaxial cold compaction of the mentioned powders. This equation fits reasonably the experimental results. K_p value obtained for the MA Alumix 431D powder (0.06) suggests that this powder has a low capacity for plastic deformation through uniaxial cold compaction, most probably resulting from the high hardness of MA Alumix 431D powder and its unfavorable particle size characteristics. K_p value of MA Alumix 431D powder is comparable with the K_p value previously reported for a milled 6061 Al alloy powder (~ 0.07) [7] and is far lower than that calculated for Alumix 431D powder, namely, 0.17.

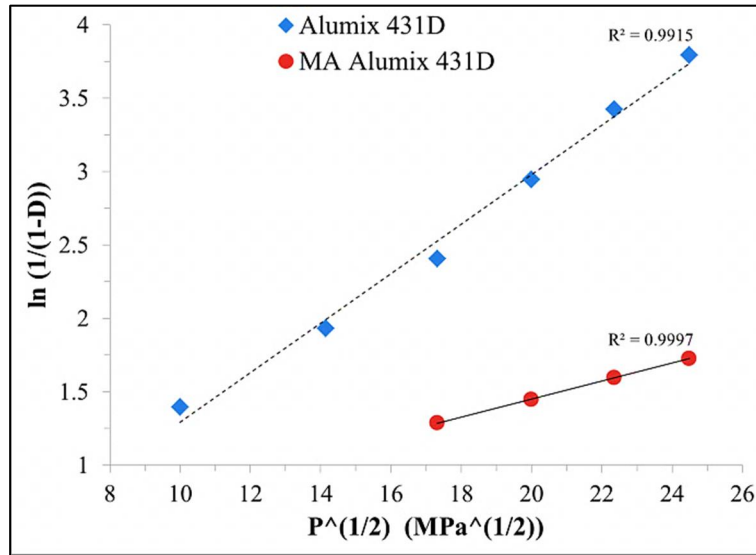


Fig. 4.8. Compressibility data of the as-received and as-milled Alumix431D powders fitted to Panelli and Ambrosio equation (Paper Al III).

Acrawax C is a commercially available lubricant that is widely used in the compaction of metallic powders. The effect of the content of atomized Acrawax C on the relative green density and ejection force of MA Alumix 431D powder compacts are shown in Fig. 4.9. A higher content of Acrawax C results in a higher relative green density and a lower ejection force. However, the effect of Acrawax C is more noticeable for the ejection forces of MA Alumix 431D powder compacts (Fig. 4.9 (b)). For example, the use of 1.5 wt% Acrawax C allows the ejection force of the MA Alumix 431D powder compact cold pressed at a pressing pressure of 600 MPa to decrease from 15 kN to 5 kN. The observed decrease in the ejection force can effectively enhance the working life of the employed pressing die. The obtained results suggest that Acrawax C is highly beneficial to the cold compaction of MA Alumix 431D powder, and the use of 1.5 wt% Acrawax C can significantly ease the cold compaction of MA Alumix 431D powder.

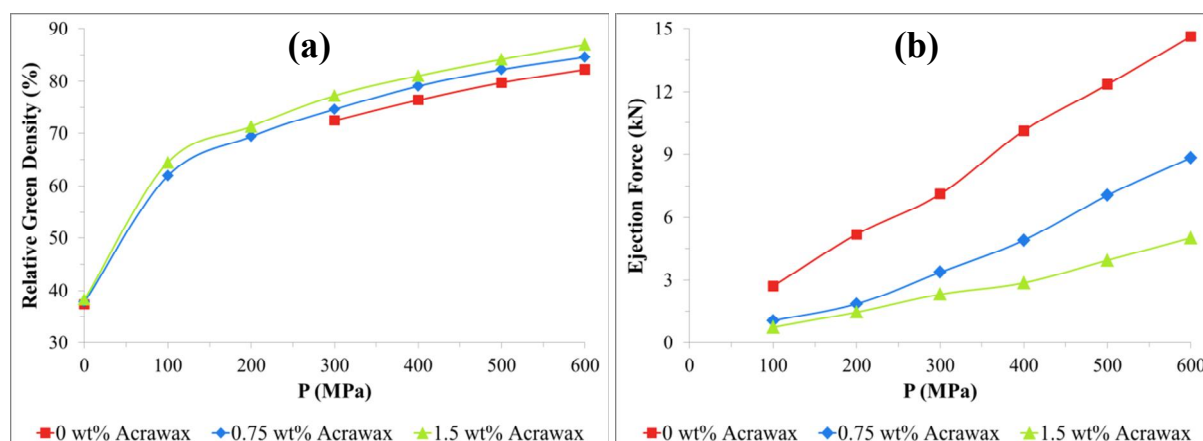


Fig. 4.9. (a) The relative green densities and (b) the ejection forces of MA Alumix431D powder compacts as a function of Acrawax C content (Paper Al III).

4.5 Conventional Sintering.

4.5.1 Effects of Sintering Temperature and Time.

Based on the results presented in the previous section and with the aim of improving the compressibility of MA Alumix 431D powder, this powder was initially mixed with 1.5 wt% Acrawax C. Next, both Alumix 431D and MA Alumix 431D powders were uniaxially cold pressed at 600 MPa into cylindrical billets measuring 10 mm in diameter and 5 mm in height. The relative green densities of Alumix 431D and MA Alumix 431D powder compacts were measured to be 96 % and 84 %, respectively. The green compacts were finally sintered using the heating cycle and sintering parameters introduced in the section 3.5. To develop an optimal sintering process for Alumix 431D and MA Alumix 431D powders, the effects of sintering temperature and time were studied.

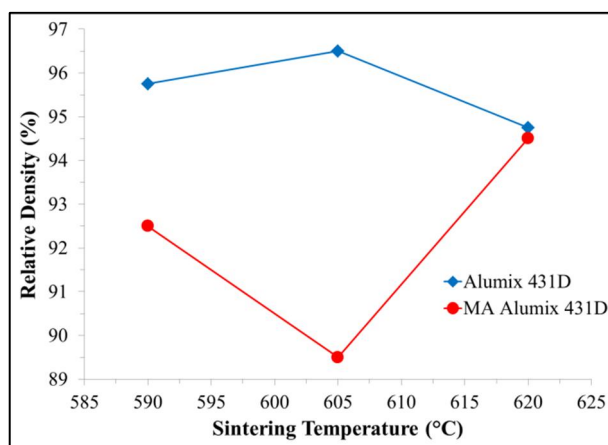


Fig. 4.10. Relative sintered densities of Alumix 431D and MA Alumix 431D compacts sintered at different temperatures for 30 min.

The effect of sintering temperature on the sintered densities of Alumix 431D and MA Alumix 431D compacts is shown in Fig. 4.10. When assessing the effect of sintering temperature on sintered density, a peak was found for Alumix 431D compacts sintered at 605 °C. Below this temperature the Alumix 431D compact did not sinter properly. When sintered at 620 °C there was a drop in sintered density and the Alumix 431D compact became noticeably distorted due to excessive liquid formation, which is considered unsuitable for an industrial production environment. Considering all above, 605 °C is taken to be the optimum sintering temperature for Alumix 431D compacts, which is also in good agreement with the optimum sintering temperature suggested by previous research works on the sintering of Alumix 431D premix [8, 9]. In the case of MA Alumix 431D compacts, sintering temperature has a complex effect on the sintered density. Regardless of the sintering temperature, the MA Alumix 431D compacts did not distort significantly through sintering. Based on the results obtained for the relative sintered density, 620 °C can be selected as the optimum sintering temperature for MA Alumix 431D compacts.

Table 4.2 clearly shows that an increase in sintering time has an adverse effect on the relative densities of Alumix 431D and MA Alumix 431D compacts sintered at 605 °C and 620 °C, respectively. The reason for this negative effect is not exactly known. However, it can be postulated that with longer sintering times, closed pores containing trapped gases are given enough time to expand on heating, therefore decreasing the density of the compacts. At the sintering temperatures employed, it is possible that small changes in pressure would affect pore size given the presence of mobile liquid phases [10].

Table 4.2. Sintered densities of Alumix 431D and MA Alumix 431D compacts sintered at 605 °C and 620 °C, respectively, for different times. Densities reported as % of theoretical.

Compact – Sintering T (°C)	Green Density (%)	Sintered Density (%)		Hardness (HV1)	
		30 min	60 min	30 min	60 min
Alumix 431 D - 605	96 ± 0.5	96.5 ± 0.2	95 ± 0.5	89 ± 1.5	91 ± 2
MA Alumix 431D - 620	84 ± 0.5	94.5 ± 0.3	90 ± 0.2	80 ± 5	63 ± 3

Considering all above, the highest quality of sinter for Alumix 431D and MA Alumix 431D compacts were achieved when sintering at 605 °C and 620 °C, respectively, for 30 minutes. As shown in Fig. 4.11, the general aspects of microstructure are very similar for the Alumix 431D and MA Alumix 431D compacts sintered using the optimized sintering parameters. A low level of residual porosity persisted after sintering. That which remained was small, isolated, and fairly rounded. Well-defined grain boundaries are present in the microstructure of sintered Alumix 431D compact along which a secondary phase is precipitated (Fig. 4.11 (a)). Overall, development of strong inter-particle bonds, homogenous

distribution of alloying elements, and a reduction in porosity confirms that a high quality sinter has been achieved for both Alumix 431D and MA Alumix 431D compacts.

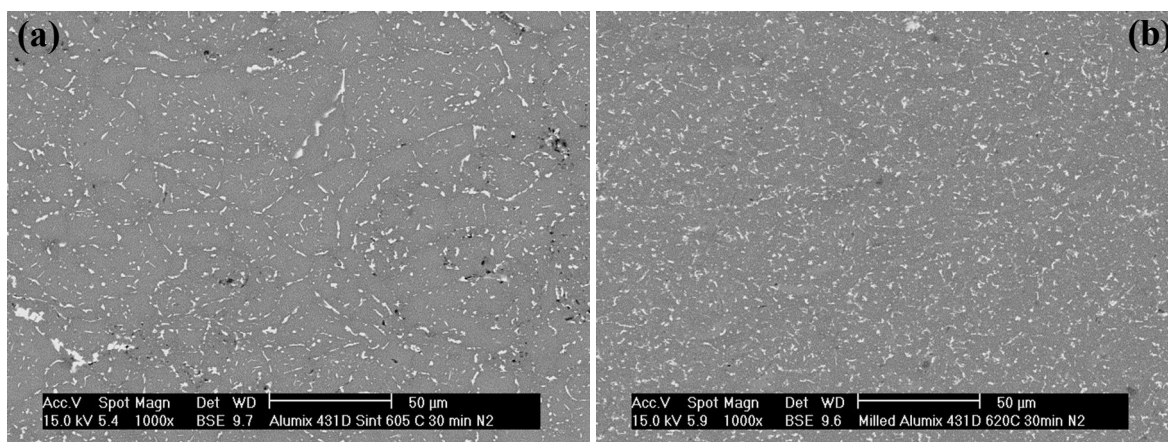


Fig. 4.11. Microstructures of the (a) Alumix 431D and (b) MA Alumix 431D compacts sintered at 605 °C and 620 °C, respectively, for 30 min.

Fig. 4.12 contains the XRD patterns of Alumix 431D and MA Alumix 431D compacts sintered using the optimized sintering parameters, where the dominant phases are found to be α -Al and MgZn_2 . In the case of MA Alumix 431D, some weak diffraction peaks are located at an angular position of about 30 °, which cannot be easily recognized.

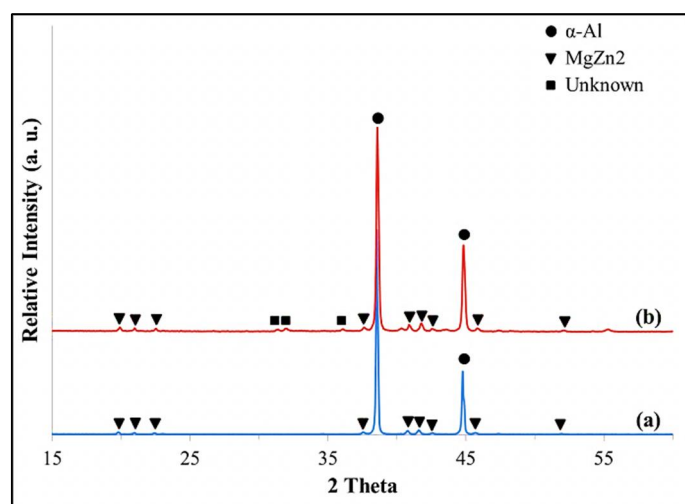


Fig. 4.12. The XRD patterns of (a) Alumix 431D and (b) MA Alumix 431D compacts sintered at 605 °C and 620 °C, respectively, for 30 min.

The hardness of the Alumix 431D and MA Alumix 431D compacts sintered using the optimized sintering parameters were measured to be 89 and 80 HV, respectively, suggesting that cold pressing and sintering is not a suitable route for consolidating MA Alumix 431D powder. The reason is that during conventional sintering, nanostructured MA Alumix 431D powder is exposed to high temperatures for a long time, which leads to crystallite growth and

formation of coarse second phase particles. In addition, a high percentage of residual porosity is still presented in the microstructure of sintered MA Alumix 431D compact, which can have detrimental effects on mechanical properties. In contrast, cold pressing and sintering seems to be a favorable consolidation route for Alumix 431D powder.

4.5.2 Simultaneous Thermal Analysis (STA).

A series of STA tests were carried out on Alumix 431D and MA Alumix 431D powders to determine melting and other thermal events that took place during sintering of these powders. Fig. 4.13 represents the STA results obtained for the powders.

In the Alumix 431D sample (Fig. 4.13 (a)), “A” refers to the elimination of admixed pressing lubricant. In this study, de-lubrication was carried out at 400 °C which seems to be high enough for the complete elimination of pressing lubricant. The first endothermic peak at 475 °C (“B”) can be attributed to a low-temperature eutectic reaction between the MgZn_2 and $\text{Al}_2\text{Mg}_3\text{Zn}_3$ phases and the Al solid solution ($\alpha\text{-Al}$) matrix of the master alloy particles, leading to the formation of a transient liquid phase which promotes the sintering process [11-13]. The large endothermic peaks, which appear upon heating above 500 °C (“C” and “D”), are believed to be melting events attributable to the different constituents within Alumix 431D powder.

In the MA Alumix 431D sample, the first two exothermic peaks (“E” and “F”) are believed to be related to the precipitation and growth of intermetallic phases [9]. The next endothermic peak (“G”) is very broad and can be attributed to the dissolution of intermetallic precipitates. This peak may also be the result of several melting events taking place in the temperature range of 450 °C to 550 °C. Finally, the large endothermic peak starting at 585 °C (“H”) is believed to be associated with melting of the solid solution matrix ($\alpha\text{-Al}$) of MA Alumix 431D powder particles.

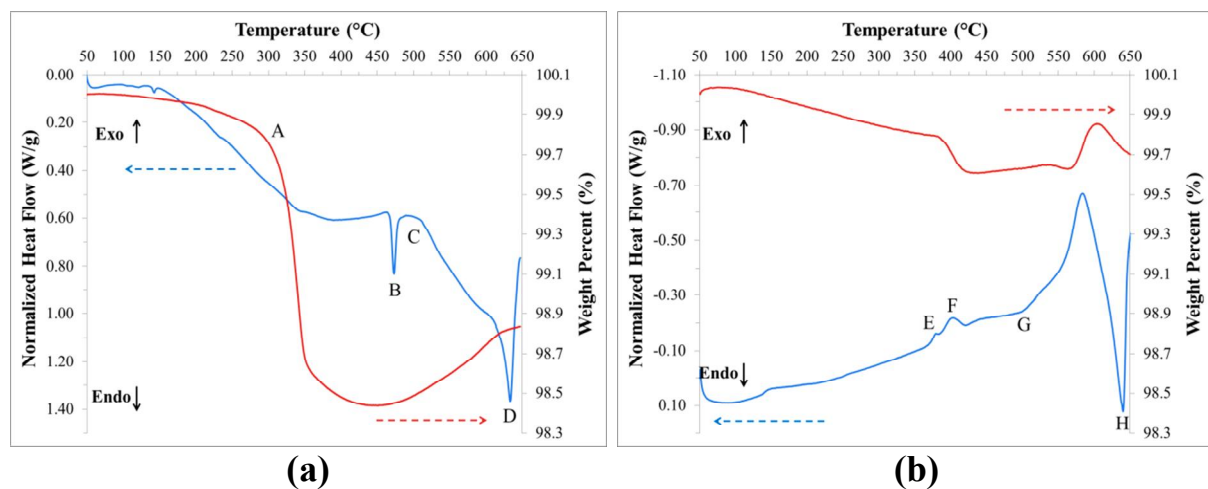


Fig. 4.13. Simultaneous thermal analysis (STA) of the (a) Alumix 431D and (b) MA Alumix 431D powders. The blue and red curves represent DSC and TGA data, respectively.

Based on the results of STA and considering that both Alumix 431D and MA Alumix 431D powders contain pre-alloyed particles, the used sintering temperatures in this study can promote supersolidus liquid phase sintering (LPS).

4.6 Field Assisted Hot Pressing (FAHP)

The Alumix 431D powder contains 1.5 percent pressing lubricant by weight. As shown in Fig. 4.13 (a), this pressing lubricant starts to burn off upon heating above 300 °C, which can raise the internal pressure of the graphite die used for FAHP and, as a result, can cause the die to explode during the FAHP process. Then, Alumix 431D powder was not consolidated by FAHP. The schematic temperature-load profile used for the FAHP of samples at 400 °C is presented in Fig. 3.4 of chapter 3.

Fig. 4.14 shows the displacement of a graphite die punch units as a function of sample temperature for different FAHP temperatures. The 1st shrinking regime occurred when the applied pressure was increased to 50 MPa at room temperature. The 2nd shrinking regime occurred with increasing temperature while the applied pressure of 50 MPa remained constant. The 3rd shrinking regime occurred with increasing pressure up to 70 MPa while temperature was kept constant at the required FAHP temperature. During the heating stage, MA Alumix 431D powder began to shrink at about 100 °C (2nd shrinking).

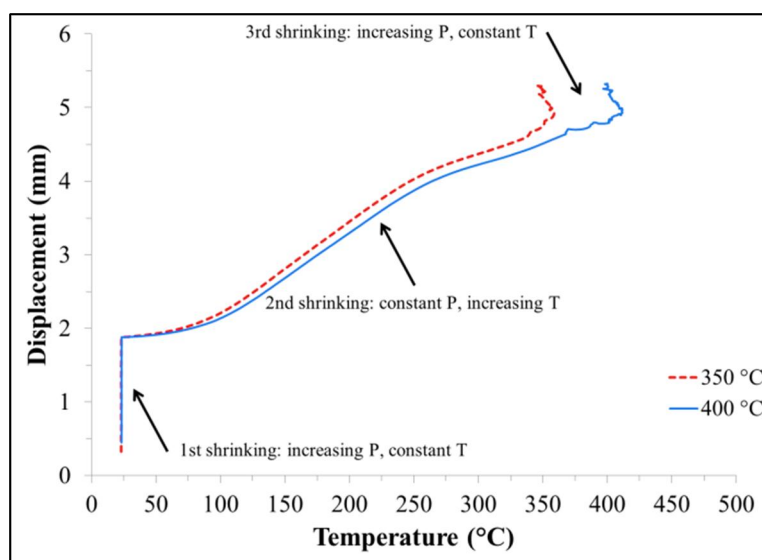


Fig. 4.14. Displacement of graphite die punch units as a function of sample temperature during FAHP for MA Alumix 431D powder consolidated at temperatures of 350 °C and 400 °C.

Fig. 4.15 shows that FAHP temperature affects significantly the density of the bulk samples processed by this technique. The relative density of the sample consolidated by FAHP at 350 °C was measure to be 96 %, suggesting that this temperature is too low for MA Alumix 431D powder. However, only a 50-degree increase in FAHP temperature was enough

to process a bulk sample with a relative density of about 99.5 %. As the main objective was to consolidate nanostructured MA Alumix 431D powder at the lowest temperature possible, 400 °C was considered as the optimum FAHP temperature for MA Alumix 431D powder. Similar to density, a higher processing temperature resulted in a higher hardness for the bulk samples consolidated by FAHP from MA Alumix 431D powder. The MA Alumix 431D compact consolidated by FAHP at 400 °C for 10 minutes shows a hardness value of 213 HV1 which is considered very high for commercial Al alloys.

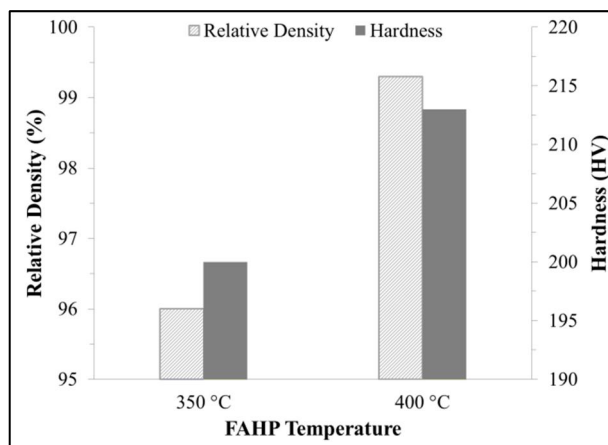


Fig. 4.15. Relative densities and hardness values of the MA Alumix 431D compacts consolidated by FAHP at the temperatures of 350 °C and 400 °C for 10 min.

Fig. 4.16 illustrates the microstructure of the bulk sample consolidated from MA Alumix 431D powder by FAHP at a temperature of 400 °C for 10 minutes. A homogeneous distribution of the ultra-fine second phase particles is visible throughout the microstructure. These particles should have precipitated during the FAHP process as no intermetallic phase was present in the microstructures of MA Alumix 431D powder particles (Fig. 4.4 (b)). Additionally, the powder particles appear to be welded together and initial MA Alumix 431D powder particles are no longer distinguishable. As expected, very limited residual porosity (marked with the black circles in Fig. 4.16 (b)) is present in the microstructure, which can be characterized as isolated and rounded.

Fig. 4.17 presents a comparison between the XRD patterns obtained for MA Alumix 431D powder and the compact consolidated from this powder by FAHP at 400 °C for 10 minutes. The obtained results feature the presence of the MgZn_2 intermetallic phase in the microstructure of MA Alumix 431D compact, confirming that MgZn_2 precipitation occurs during FAHP processing presumably due to thermal and strain activation.

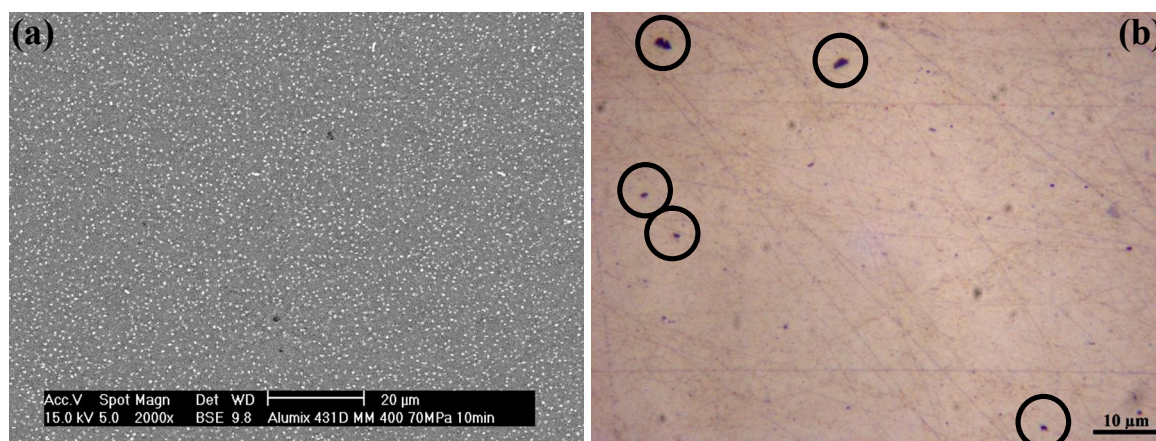


Fig. 4.16. Cross section microstructures of the compact consolidated from MA Alumix 431D powder by FAHP at 400 °C for 10 min, (a) SEM and (b) optical microscope micrographs.

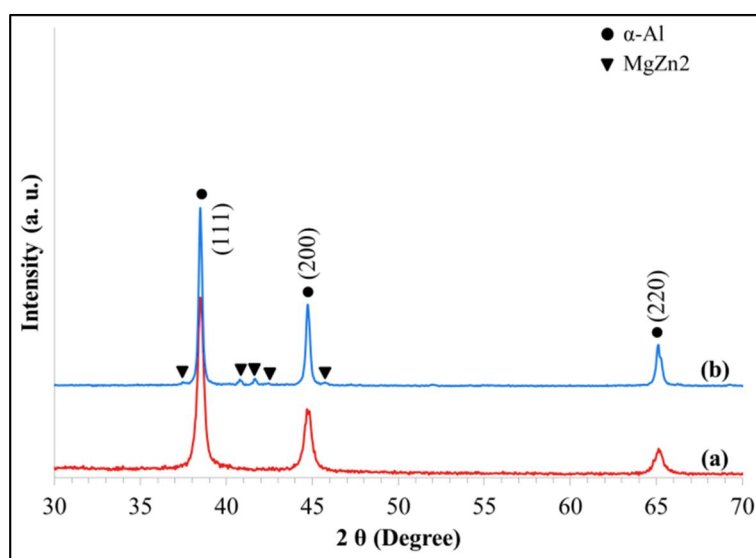


Fig. 4.17. The XRD patterns of (a) MA Alumix 431D powder and (b) MA Alumix 431D compact consolidated by FAHP at 400 °C for 10 min.

The XRD results also suggest that the crystallite size of the nanostructured 7075 Al alloy may have increased during the FAHP process as the XRD peaks of the MA Alumix 431D compact are narrower when compared to those of the MA Alumix 431D powder. The crystallite size of the MA Alumix 431D compact was measured to be about 75 nm using the Williamson–Hall method, which shows that the nanostructured 7075 Al alloy had actually experienced some crystallite growth during FAHP processing. However, the crystallite size of the bulk 7075 Al alloy is still under 100 nm, which definitely contributes to the high hardness value obtained for the MA Alumix 431D compact (213 HV). Considering the low temperature and short time employed for FAHP processing, we actually did not expect the nanostructured 7075 Al alloy to experience a large amount of grain growth during the FAHP process.

4.7 Effects of Green Density on the Hot Deformation of a 7075 Al PM Alloy.

Studies on the hot deformation behavior of porous Al alloys are relatively scarce [14-17]. Due to the lack of knowledge in the field [16] and the importance of constitutive information for the modeling of powder processing routes such as powder extrusion and powder forging [18, 19], in the **Paper Al IV** included in the appendix the effects of the relative green density, deformation temperature, and strain rate on the hot deformation behavior and flow stress of de-lubricated powder compacts cold pressed from Alumix 431D premix were evaluated by performing hot compression tests. In addition, a constitutive equation that is capable of predicting the peak flow stress of powder compacts and considers the relative green density, deformation temperature, and strain rate was proposed. This section summarizes the presented results in the **Paper Al IV**. For detailed information on the employed methodology and the full results related to this section, refer to **Paper Al IV**.

For the majority of compacts, the true stress-true strain curves obtained during the hot compression of de-lubricated Alumix 431D powder compacts with different relative green densities are characterised by a peak stress at a critical strain after which the flow stress remained nearly constant (see Figs. 2-4 of the paper Al IV). As the strain rate and relative green density decreased or the deformation temperature increased, a decrease in the peak stress level was observed.

The relationship between strain rate, deformation temperature, and the peak flow stress of a powder compact can be represented by the Zener-Hollomon parameter in an exponential equation containing relative green density compensated deformation activation energy (Q) and material constants (β and A) (Equation 4.1).

$$Z = \dot{\epsilon} \exp\left(\frac{Q}{RT}\right) = A \exp(\beta\sigma) \quad (4.1)$$

Depending on the relative green density, the deformation activation energy (Q) of the compacts ranged from 157 to 192 kJ/mol (see Table 2 of the Paper Al IV). The relative green density was found to have a significant influence on the hot deformation activation energy (Q) and β constant of a powder compact. As the relative green density increases, larger hot deformation activation energies (Q) and lower β constants were observed. The results of the present study quantitatively showed that the presence of pores in the structures of porous materials reduces their resistance to deformation. In addition, the flow stress of powder compacts with high β constants is less sensitive to deformation parameters, such as deformation temperature and strain rate.

4.8 Hot Deformation of a 7075 Al PM Alloy.

One of the hurdles to overcome in the field of PM is the presence of pores in the sintered products. To reduce the residual porosity, sintered materials can be hot deformed to full

density [20]. In this study, the hot deformation of a 7075 Al PM alloy was studied by performing hot compression tests on pre-sintered Alumix 431D powder compacts.

4.8.1 PM Processing.

First, the Alumix 431D powder was uniaxially cold pressed into cylindrical compacts measuring 10 mm in diameter and 15 mm in height. Prior to hot compression, the green compacts with a relative green density of about 96 % were subjected to a presintering treatment (heating to 400 °C and holding at 400 °C for 20 min, followed by heating to 525 °C and soaking at this temperature for 45 min). The resultant compacts achieved a sintered density of 2.5 g/cm³, i. e. 90 % of the full theoretical density (2.79 g/cm³). The appreciable swelling during the presintering treatment of Alumix 431D compacts can be attributed to the formation of a transient liquid phase at about 475 °C (see Fig. 4.13 (a)).

Microstructure of the presintered Alumix 431D compact is shown in Fig. 4.18. After the presintering treatment, a homogeneous distribution of intermetallic phases was found throughout the microstructure, and Al and master alloy particles, which are present in the microstructure of Alumix 431D premix (Fig. 4.1 (b)), were no longer distinguishable. Additionally, the detection of the initial interfaces of powder particles became difficult as the powder particles appear to be welded together. The presence of porosity in the presintered microstructure is shown by the black regions in SEM micrograph (Fig. 4.18 (a)). The etched microstructure of the presintered Alumix 431D compact (Fig. 4.18 (b)) features a dual grain structure. In other words, the presintered microstructure contains some large equiaxed grains. In addition, some regions composed of fine grains are also detectable. It seems likely that these regions originated from the initial master alloy particles present in the microstructure of Alumix 431D premix. The hardness of the presintered Alumix 431D compact was measure to be 52 ± 2 HV1.

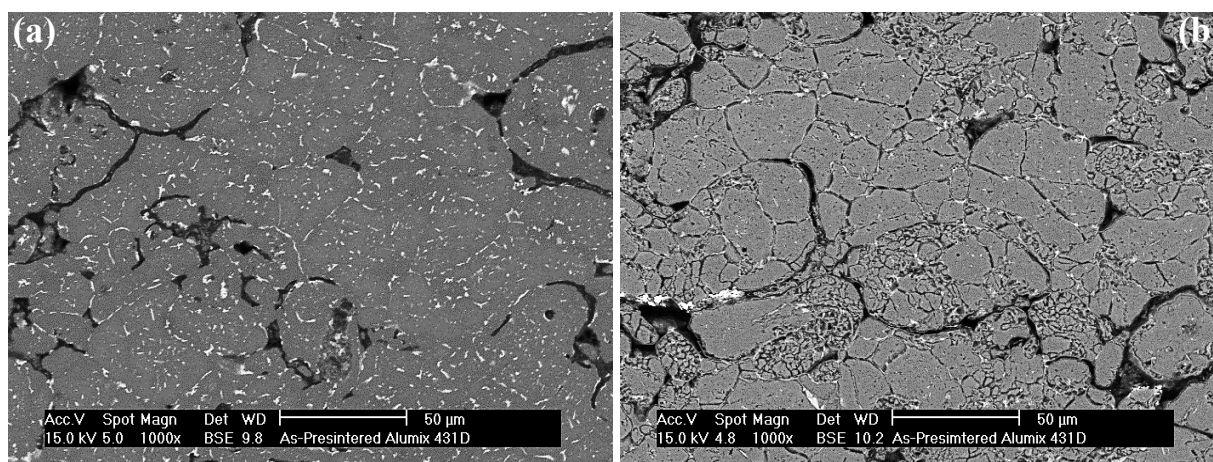


Fig. 4.18. (a) As-presintered and (b) etched cross-section microstructures of the presintered Alumix 431D compact.

4.8.2 Hot Compression Tests

Hot compression tests were performed on presintered Alumix 431D compacts at temperatures ranging from 200 °C to 500 °C and at true strain rates ranging from 0.001 s⁻¹ to 10 s⁻¹. Examples of the resultant true stress-true strain plots are shown in Fig. 4.19. As shown here, the true stress-true strain curves exhibited a peak stress at a critical strain after which the flow stress increased slightly or remained nearly constant. As the deformation temperature increased or the strain rate decreased, a decrease in the peak stress level was observed.

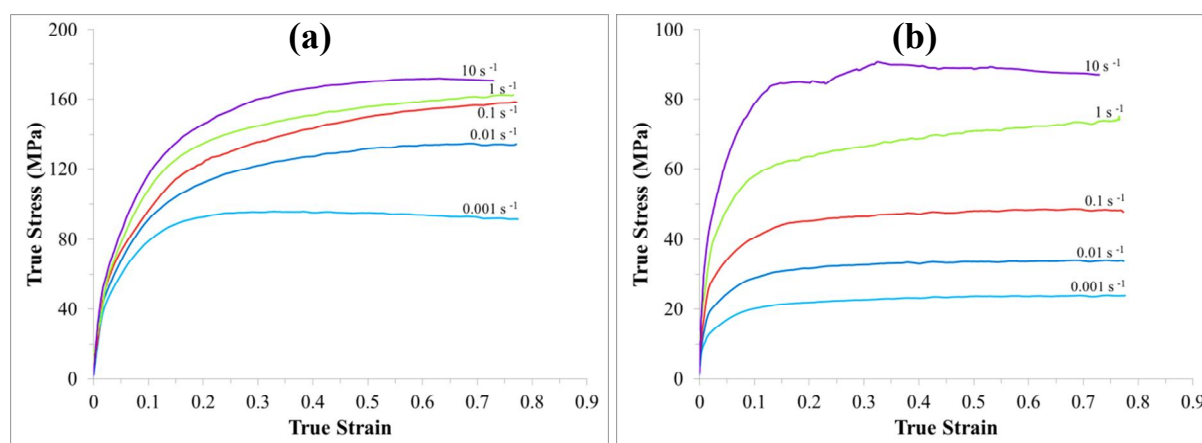


Fig. 4.19. True stress–true strain curves of the presintered Alumix 431D compacts hot-compressed at deformation temperatures of (a) 250 °C and (b) 400 °C and at different strain rate.

4.8.3 Processing Maps.

The processing maps developed for strains of 0.1, 0.5, and 0.8 are shown in Fig. 4.20. The contour numbers in these figures represent the efficiency of the power dissipation through dynamic metallurgical mechanisms (η); and the hatched regions represent regions of flow instability, where the instability parameter (ξ) is negative. The regions labeled “Cracking” correspond to regions with negative η values that resulted from the severe cracking or fragmentation of the specimens during compression testing. Although the features of the three maps are basically similar, the expansion of instability and cracking regions with increasing strain suggest that strain has an important effect on the processing maps of presintered Alumix 431D compacts.

As shown in Fig. 4.20, all of the processing maps include a large instability region. This region expands significantly with increasing strain. This expansion is particularly noticeable for “Log Strain Rate” greater than -0.1 (strain rates greater than 0.1 s⁻¹). Fig. 4.20 clearly shows that the workability of 7075 Al PM alloy is not good at high strain rates. Consequently, the instability region located at these strain rates expands with increasing strain. The cracking of presintered Alumix 431D compacts at a deformation temperature of 500 °C can be attributed to the negative effect of a melting phenomenon on the material’s

deformability. The processing map developed for a strain of 0.1 (Fig. 4.20 (a)) exhibits two domains with high efficiency of the power dissipation (η). These domains are normally considered as the suitable conditions for hot deformation. Domain I is basically similar for all of the processing maps. In contrast to domain I, the increase in strain affects domain II, and this domain shifts to lower deformation temperatures and strain rates with increasing strain.

The map depicting a strain of 0.8 (Fig. 4.20 (c)) exhibits two domains of stable flow (domains I & II) with peak efficiencies of about 30 % in the following temperature and strain rate ranges: 275-350 °C / 0.001-0.01 s⁻¹ and 350-450 °C / 0.01-0.3 s⁻¹, respectively. The average hardness values of the samples hot-compressed at domains I and II were measured to be 80 HV and 114 HV, respectively. Considering the low strain rates and hardness values associated with domain I, domain II can be considered as the safe and optimized domain for the hot deformation of presintered Alumix 431D compacts. The processing map also contains large flow instability and cracking regions which should be prevented for hot working of the material under study.

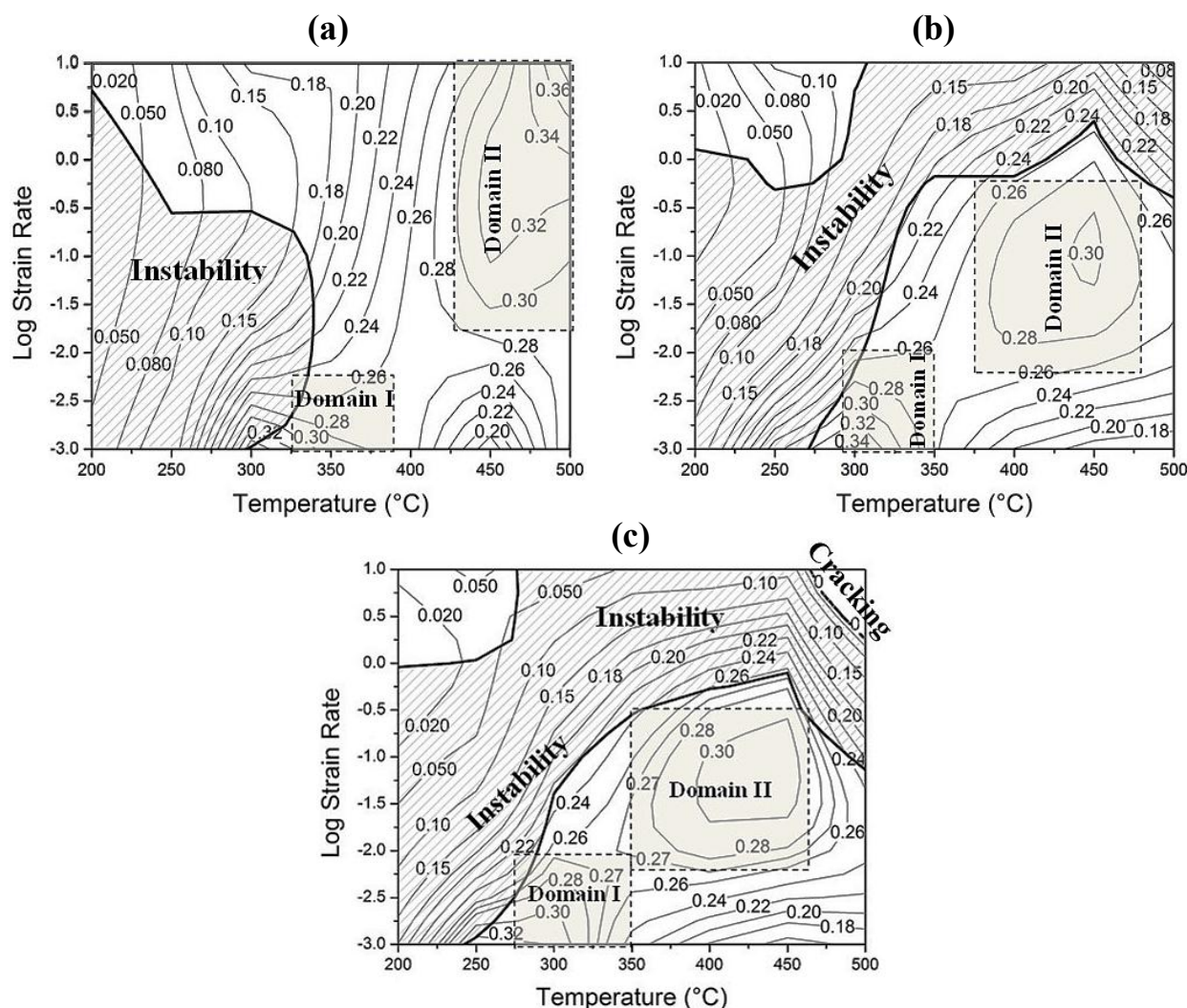


Fig. 4.20. Processing maps of the presintered Alumix 431D compacts developed at strains of (a) 0.1, (b) 0.5, and (c) 0.8.

Side views of the specimens hot-compressed at different temperatures and strain rates to a strain of 0.8 are presented in Fig. 4.21. The 7075 Al PM alloy exhibited good workability within domain II and produced crack-free, uniformly deformed specimens, suggesting that the developed processing maps successfully identified the safe domain for the hot deformation of presintered Alumix 431D compacts. As expected, the specimens severely cracked or fragmented in the cracking region (the intensity of which increased with increasing strain rate). Fig 4.22 illustrates the specimens hot-compressed to different strains at a temperature of 400 °C and a strain rate of 0.1, confirming that within domain II presintered Alumix 431D compacts can be hot-compressed to high strain levels without experiencing inhomogeneous deformation (i.e., flow localization) and/or cracking.

The stress-strain curves obtained for domain II (Fig. 4.19 (b)) featured flow hardening behavior with a low hardening rate. During the hot deformation of porous materials such as the presintered compacts under study, flow hardening mechanisms such as strain and densification hardening occur simultaneously. The latter mechanism results from a continuous increase in density during deformation. For example, the effect of strain on the relative density of presintered Alumix 431D compacts hot-compressed at a deformation temperature of 400 °C and a strain rate of 0.1 is illustrated in Fig. 23, implying that presintered Alumix 431D compacts can be consolidated to almost full density just by open-die, uniaxial hot compression. Domains such as domain II that possess a high efficiency of the power dissipation (η) and good workability have generally been associated with dynamic restoration mechanisms, such as dynamic recovery and recrystallization [21]. At the beginning of deformation, the dislocation density [22] and the density of the powder compact increase rapidly, which lead to a sharp increase in the flow stress. However, as deformation continues, the activation of dynamic restoration mechanisms neutralizes the effect of hardening mechanisms. Consequently, the slope of the true stress-true strain curve flattens and deformation continues with a lower work hardening rate.

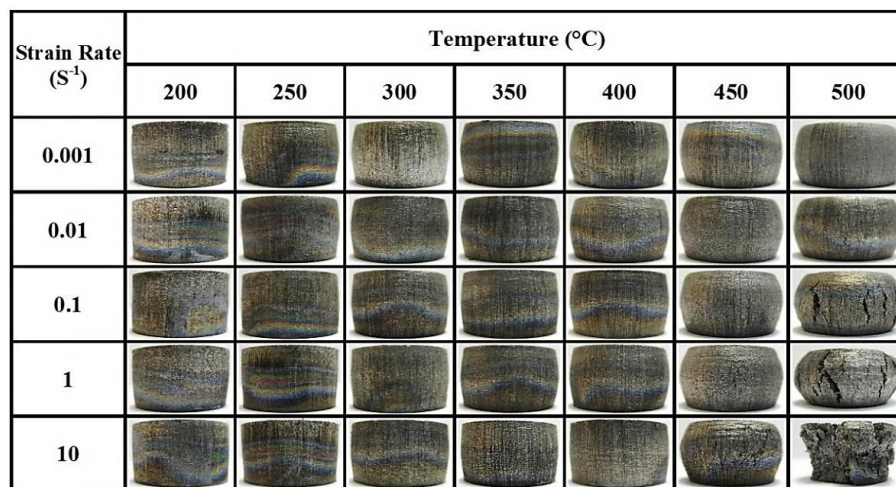


Fig. 4.21. Side views of the specimens hot-compressed at different temperatures and strain rates to a strain of 0.8.

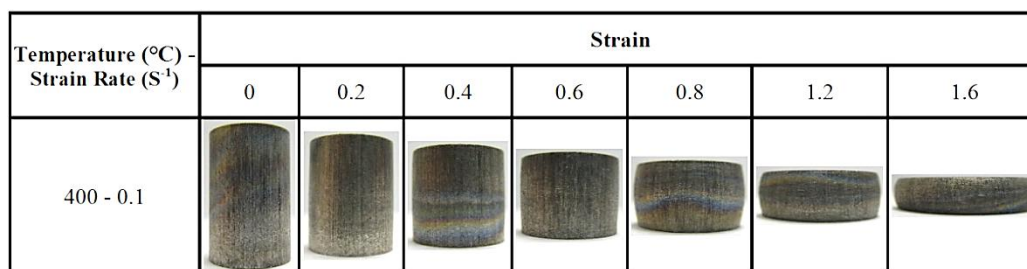


Fig. 4.22. Side views of the specimens hot-compressed at a deformation temperature of 400 °C and a strain rate of 0.1 to different strains.

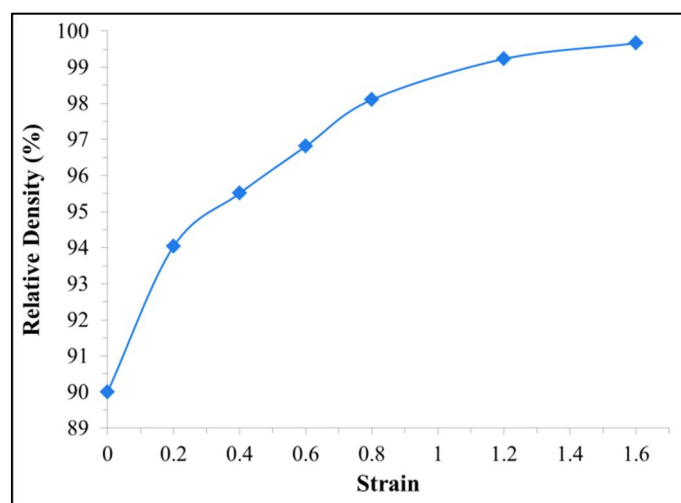


Fig. 4.23. The effect of strain on the relative density of presintered Alumix 431D compacts hot-compressed at a deformation temperature of 400 °C and a strain rate of 0.1.

4.8.4 Kinetics of Hot Deformation.

The kinetic rate equation (Equation 4.2) is normally obeyed in the deterministic domains of a processing map [23, 24]. The variation of the flow stress at a strain of 0.1 (near peak flow stress) with strain rate on a natural logarithmic scale is shown in Fig. 4.24 (a). The average slope of the straight-line fits obtained at the temperatures and strain rates covering domain II of the processing map developed for a strain of 0.1 was considered to be an estimate of the value of m (the strain rate sensitivity of flow stress) for the mentioned domain. Then, this value was then used to calculate the value of n ($=1/m$, the stress exponent in Equation 4.2). The value of n was determined to be 6.67 for domain II.

$$\dot{\epsilon} = A\sigma^n \exp(-Q/RT) \quad (4.2)$$

The value of “Ln (flow stress)” at a strain of 0.1 as a function of “1000/T” (T: absolute deformation temperature) is shown in Fig. 4.24 (b). The average slope of the straight-line fits obtained at the temperatures and strain rates covering domain II of the processing map developed for a strain of 0.1 was used to calculate the value of Q (the activation energy of hot

deformation) for this domain. The value of Q obtained from Fig.4.24 (b) was 202 kJ/mol, which is higher than that of the aged 7150 alloy (158.8–161.4 kJ/mol) previously reported by Sheppard and Jackson [25] but close to the values of the solution-treated 7012 alloy (200–230 kJ/mol) [26] and the homogenized and furnace-cooled 7050 Al alloy (223 kJ/mol) [27].

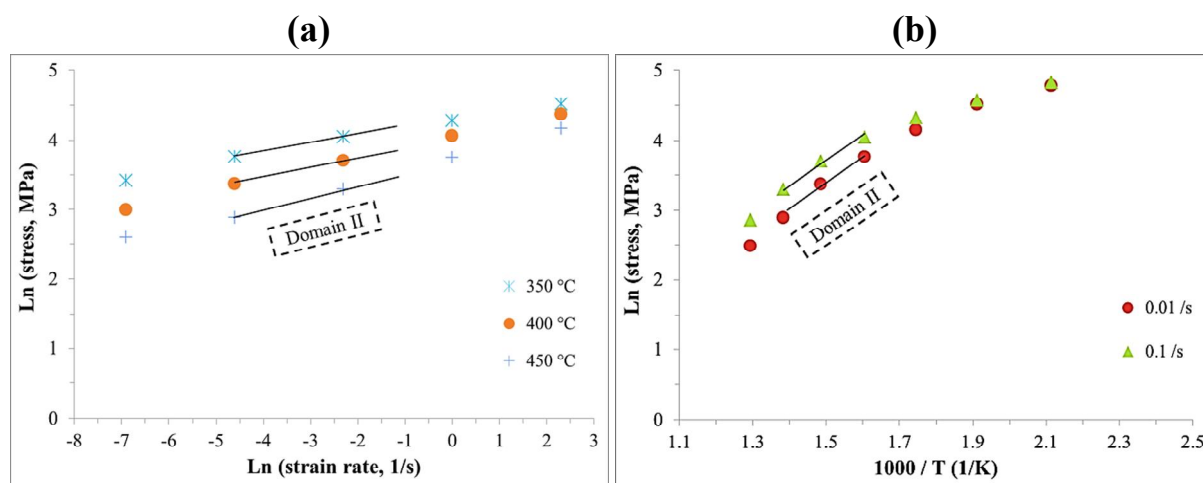


Fig. 4.24. (a) Variation of flow stress (strain 0.1) with strain rate on a natural logarithmic scale for the presintered Alumix 431D compacts. (b) Arrhenius plot showing the variation of flow stress (strain 0.1) with inverse of absolute deformation temperature for the presintered Alumix 431D compacts.

The hot deformation activation energy (Q) is an important physical parameter serving as indicator of deformation difficulty degree in plasticity deformation [28]. Namely, as the deformation activation energy increases, deformation becomes more difficult. It is believed that the content of alloying elements in solution has an important effect on the Q value of 7xxx series Al alloys, and the Q value of this alloy series increases with the increasing content of Zn, Mg, and Cu in solution. A stationary dislocation in a solid solution can be pinned by the solute atoms if they are able to diffuse to the dislocation, and hence an additional increment of stress will be required to free the dislocation from its energetically favorable position. In addition, any dislocation moving through a solid solution will encounter friction drag thus raising the energy required for movement. Hence any increase in foreign atoms held in solution will increase the activation energy [28]. It should also be considered that the value of Q has dependences on some other factors. For example, the presence of pores in the structure of porous materials reduces their resistance to deformation (Paper Al IV). Consequently, a powder compact has a lower Q value than the bulk alloy with similar chemical composition and microstructure.

4.8.5 Microstructures of the Hot-compressed Specimens.

Microstructures of the hot-compressed specimens at a strain rate of 0.1 s^{-1} and deformation temperatures within domain II (350 °C to 450 °C) of the processing maps developed for presintered Alumix 431D compacts are shown in Fig. 4.25.

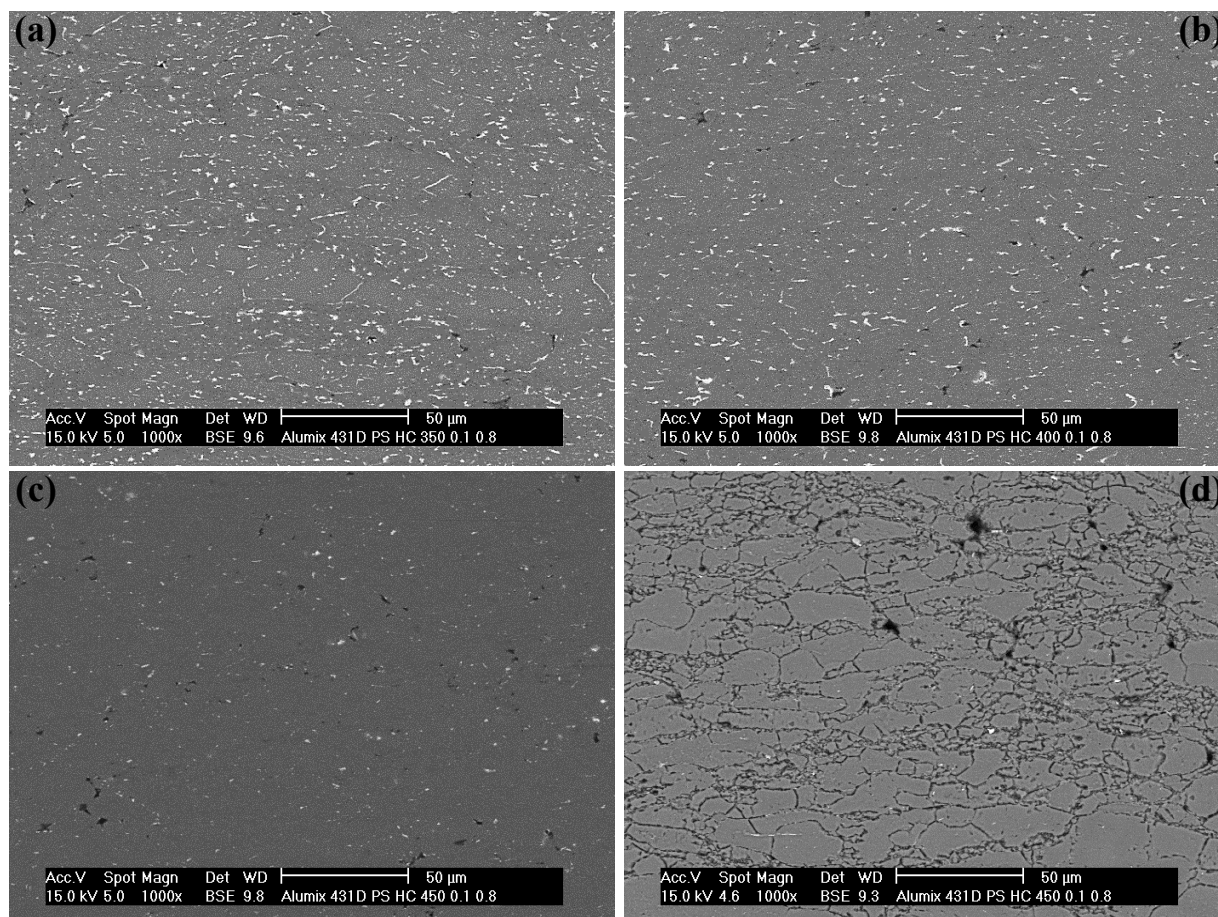


Fig. 4.25. As-deformed microstructures of the specimens hot-compressed at a strain rate of 0.1 s^{-1} and deformation temperatures of (a) 350 °C, (b) 400 °C, and (c) 450 °C (strain= 0.8). (d) Etched microstructure of the specimen hot-compressed at a strain rate of 0.1 s^{-1} and a deformation temperature of 450 °C to a strain of 0.8.

The samples deformed at different temperatures (Figs. 4.25 (a) to (c)) share the same microstructural features. For all of the samples, there is found to be an Al rich matrix in which a secondary phase(s) and some residual porosity are homogenously distributed. However, a higher deformation temperature leads to a lower amount of secondary phase present in the as-deformed microstructure. Fig. 4.26 shows that as-deformed hardness increases with increasing deformation temperature within domain II, implying that dissolution of the secondary phase present in the microstructure of a presintered Alumix 431D compact (Fig. 4.18 (a)) through the hot compression process has an improving effect on the as-deformed hardness. Considering the obtained microstructures and hardness values for the samples deformed within domain II of the processing maps developed for presintered

Alumix 431D compacts, the optimum condition for hot deformation of these compacts is determined to lie between 400-450 °C and 0.01-0.1 s⁻¹.

The etched microstructure of the hot-compressed sample at a strain rate of 0.1 s⁻¹ and a deformation temperature of 450 °C is shown in Fig. 4.25 (d). The as-deformed microstructure contains some large and elongated grains perpendicular to the hot compression direction. Some regions composed of fine grains are also detectable in the microstructure. It seems likely that these regions originated from similar regions with fine and equiaxed grains observed in the microstructure of presintered Alumix 431D compact (Fig. 4.18 (b)). According to McQueen et al. [29], dynamic recovery (DRV) results in large, elongated grains, whereas dynamic recrystallization (DRX) results in new equiaxed grains. Considering the as-deformed microstructure, DRV appears to be the predominant restoration mechanism acting during the hot compression of presintered Alumix 431D compact. Due to their high stacking fault energies, Al alloys show a very high rate of DRV during hot deformation. As a result, DRX may be partly or completely prevented during the hot deformation of Al alloys.

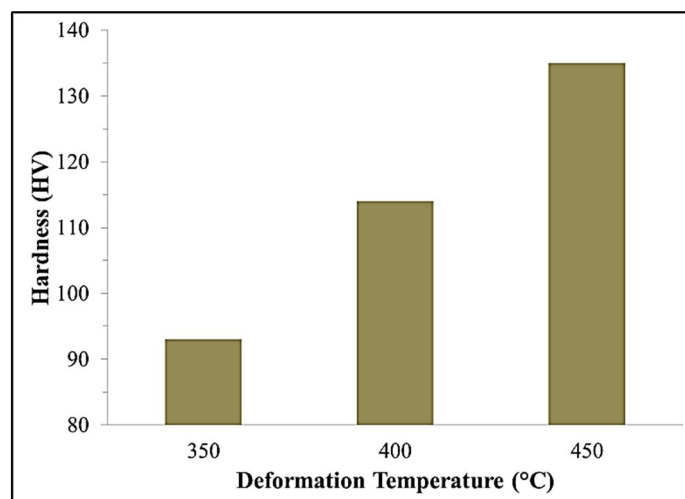


Fig. 4.26. As-deformed hardness of the specimens hot-compressed at a strain rate of 0.1 s⁻¹ and deformation temperatures of 350 °C, 400 °C, and 450 °C (strain= 0.8).

Fig. 4.27 presents a comparison between the XRD pattern obtained for a presintered Alumix 431D compact and those of the specimens hot-compressed at a strain rate of 0.1 s⁻¹ and deformation temperatures within domain II (350 °C to 450 °C) of the processing maps developed for presintered Alumix 431D compacts.

MgZn₂ is the major intermetallic phase present in the microstructure of a presintered Alumix 431D compact. Weakening of the XRD peaks related to the MgZn₂ phase after hot compression confirms the dissolution of this intermetallic phase into the α -Al matrix of the compacts through hot compression, the amount of which increases with increasing deformation temperature.

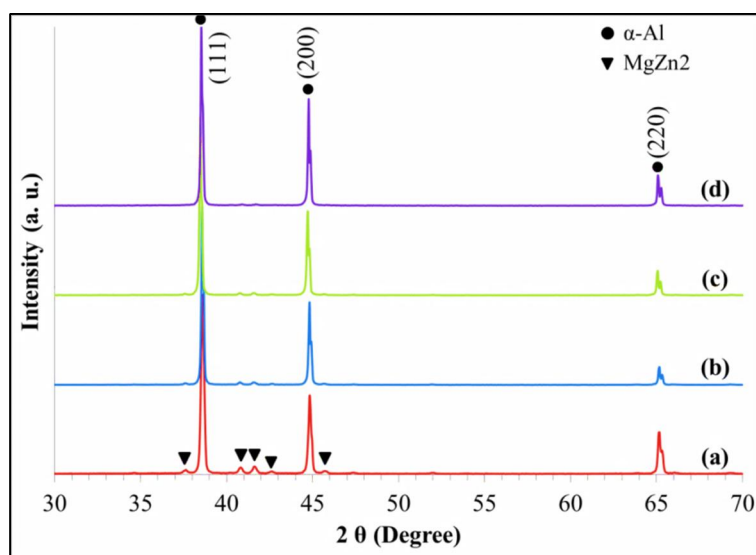


Fig. 4.27. The XRD patterns of (a) presintered Alumix 431D compact and the specimens hot-compressed at a strain rate of 0.1 s^{-1} and at deformation temperatures of (b) 350 °C, (c) 400 °C, and (d) 450 °C.

4.9 Hot Deformation of a Nanocrystalline 7075 Al PM Alloy.

In recent years, processing of nanostructured Al alloys by mechanical alloying and characterization of mechanically alloyed Al-based powders has been the subject of several investigations. The powders processed by mechanical alloying are then consolidated by PM routes. To date, the nanostructured Al-based powders processed by mechanical alloying have mostly been consolidated by powder extrusion. Hot deformation behavior of bulk and microcrystalline Al alloys has widely been studied. However, there are no systematic studies on the hot deformation behavior of nanocrystalline Al alloys. Therefore, this study focused on the hot deformation behavior and workability characteristics of a nanocrystalline 7075 Al alloy processed by mechanical alloying.

4.9.1 PM Processing.

The MA Alumix 431D powder was first mixed with 1.5 wt% Acrawax C to facilitate the cold pressing step. Then, the prepared mixture was uniaxially cold pressed at 600 MPa into cylindrical compacts measuring 10 mm in diameter and 12 mm in height. Prior to hot compression, the green compacts were subjected to a delubrication (heating to 400 °C and holding at 400 °C for 30 min) treatment, after which the compacts were furnace cooled to room temperature. The relative densities of delubricated compacts were measured to be about 85 %. The appreciable residual porosity present in the microstructure of delubricated MA Alumix 431 compacts can have negative effects on their workability.

Microstructure of the delubricated MA Alumix 431D compact is shown in Fig. 4.28. After the delubrication treatment, a homogeneous distribution of coarse second phase particles was found throughout the microstructure. As no intermetallic phase was present in

the microstructure of MA Alumix 431D powder (Fig. 4.4 (b)), it can be postulated that these second phase particles precipitated from the supersaturated Al solid solution (α -Al) matrix of MA Alumix 431D powder particles during a sluggish furnace cooling. Although some powder particles appear to be welded together, the initial interfaces of powder particles are easily detectable. The presence of porosity in the delubricated microstructure is shown by the black regions. A high level of residual porosity persisted after the delubrication treatment. The hardness of the delubricated MA Alumix 431D compact was measure to be 80 ± 10 HV.

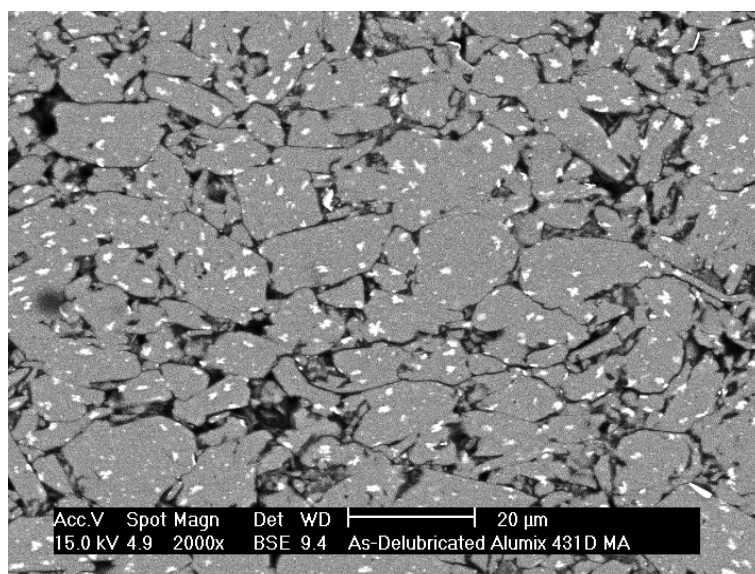


Fig. 4.28. Cross-section microstructure of the delubricated MA Alumix 431D compact.

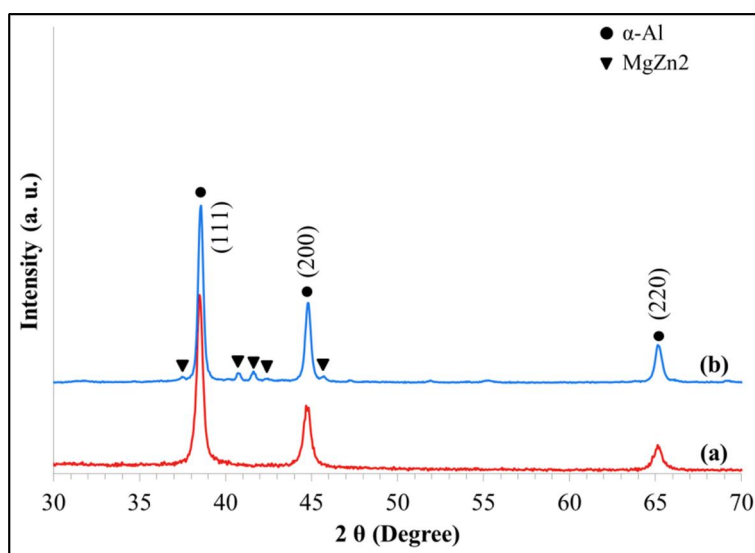


Fig. 4.29. The XRD patterns of (a) MA Alumix 431D powder and (b) delubricated MA Alumix 431D compact.

The XRD patterns of MA Alumix 431D powder and delubricated MA Alumix 431D compact are presented in Fig. 4.29, showing that MgZn_2 is the major intermetallic phase

present in the microstructure of delubricated MA Alumix 431D compact, most probably precipitated from the Al solid solution (α -Al) matrix of MA Alumix 431 powder particles during the cooling step of delubrication due to low cooling rates. The XRD peaks of delubricated MA Alumix 431D compact look slightly narrower than those of MA Alumix 431D powder, which can be related to an increase in crystallite size and/or a decrease in lattice strain due to the delubrication treatment. The crystallite size of delubricated MA Alumix 431D compact was calculated to be about 40 nm, which is in good agreement with the results obtained by the isothermal annealing of MA Alumix 431D powder (Fig. 4.6 (b)).

4.9.2 Hot Compression Tests.

Hot compression tests were performed on delubricated MA Alumix 431D compacts at temperatures ranging from 200 °C to 550 °C and at true strain rates ranging from 0.001 s⁻¹ to 10 s⁻¹. The specimens fragmented at every strain rate and deformation temperatures of 200 °C and 250 °C, implying that these temperatures are too low for the hot deformation of delubricated MA Alumix 431D compacts. Therefore, the data obtained for the mentioned temperatures were not used further analysis.

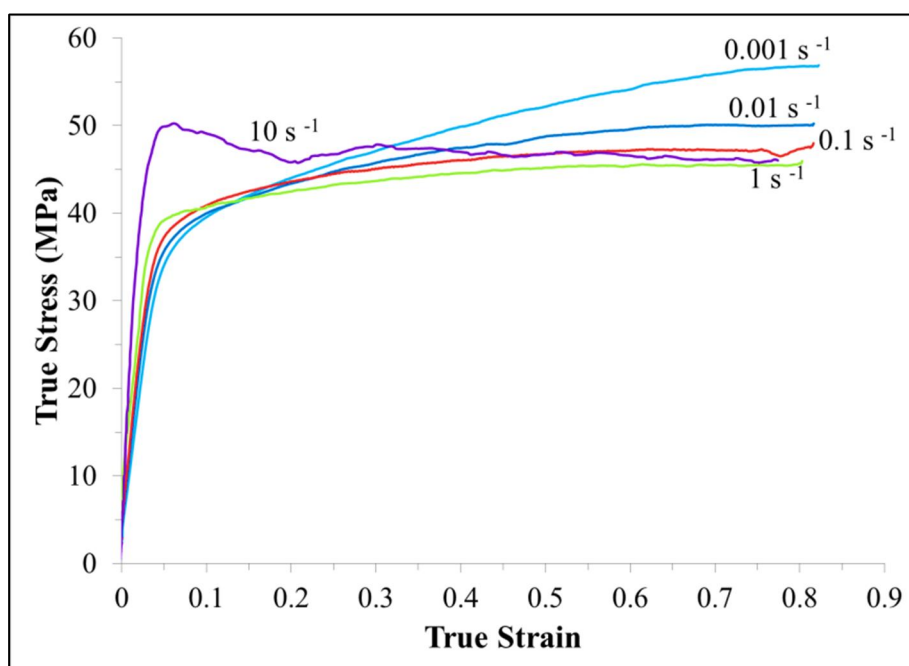


Fig. 4.30. True stress–true strain curves of the delubricated MA Alumix 431D compacts hot-compressed at a deformation temperature of 400 °C and at different strain rate.

An example of the resultant true stress-true strain plots is illustrated in Fig. 4.30. As shown here, the true stress-true strain curves exhibited a peak flow stress at a critical strain after which the flow stress increased moderately or remained nearly constant. Also, a higher strain rate resulted in a lower work hardening rate. As a general trend, when the deformation

temperature increased or the strain rate decreased, a decrease in the peak stress level was observed. This trend was far more noticeable for the deformation temperature than for the strain rate. Furthermore, at high strain levels like 0.5 or 0.8 and due to severe cracking of delubricated MA Alumix 431D compacts, the above-mentioned trend for the effect of strain rate on flow stress at a constant strain level became partly or completely reverse, leading to negative strain rate sensitivities. Due to the high degree of residual porosity (15%), delubricated MA Alumix 431D compacts were notably brittle and cracked severely during hot compression, the amount of which increased with increasing strain rate. The presence of voids causes a significant decrease in local ductility which increases the likelihood of fracture during hot deformation [30].

4.9.3 Processing Maps.

Due to severe cracking of delubricated MA Alumix 431D compacts during hot compression and its effects on the obtained true stress-true strain curves, we were unable to develop any *instability maps* for the hot deformation of nanostructured 7075 Al alloy. Consequently, only the *efficiency of power dissipation* maps developed for strains of 0.1, 0.5, and 0.8 are shown in Fig. 4.31. The contour numbers in these figures represent the efficiency of the power dissipation through dynamic metallurgical mechanisms (η). The regions labeled “Cracking” correspond to regions with negative η values that resulted from the severe cracking or fragmentation of the specimens during compression testing. The considerable alteration and expansion of cracking region(s) with increasing strain suggest that strain has an important effect on the efficiency maps of delubricated MA Alumix 431D compacts.

The efficiency map developed for a strain of 0.1 (Fig. 4.31 (a)) includes a small cracking region at high deformation temperatures (475 °C to 525 °C) and low strain rates (0.001 s⁻¹ to 0.01 s⁻¹). This region expands significantly with increasing strain and covers the major area of the efficiency maps developed for strains of 0.5 and 0.8 (Figs. 4.31 (b) and (c)). Besides, as the deformation strain increases from 0.5 to 0.8, another cracking region starts to appear at low deformation temperatures (300 °C to 350 °C) and high strain rates (1 s⁻¹ to 10 s⁻¹). Fig. 4.31 suggests that the nanocrystalline 7075 Al alloy processed by mechanical alloying of Alumix 431D powder possesses poor workability, which can be attributed to the microstructural characteristics of MA Alumix 431D powder. The MA Alumix 431D powder particles have an ultra-fine microstructure with a homogenous distribution of nano-sized Al oxide and carbide dispersoids and a high amount of alloying elements in solid solution, all making it difficult for dislocations to move and slip and, consequently, resulting in a poor workability for the nanocrystalline 7075 Al alloy.

The efficiency map developed for a strain of 0.1 (Fig. 4.31 (a)) exhibits a domain with high efficiency of the power dissipation (η). Both the area and the peak efficiency of domain I decrease noticeably with increasing strain, and domain I is eventually replaced by a cracking region at a strain of 0.8 (Fig. 4.31 (c)), all suggesting that this domain cannot be

considered as a safe and suitable domain for hot deformation of delubricated MA Alumix 431D compacts.

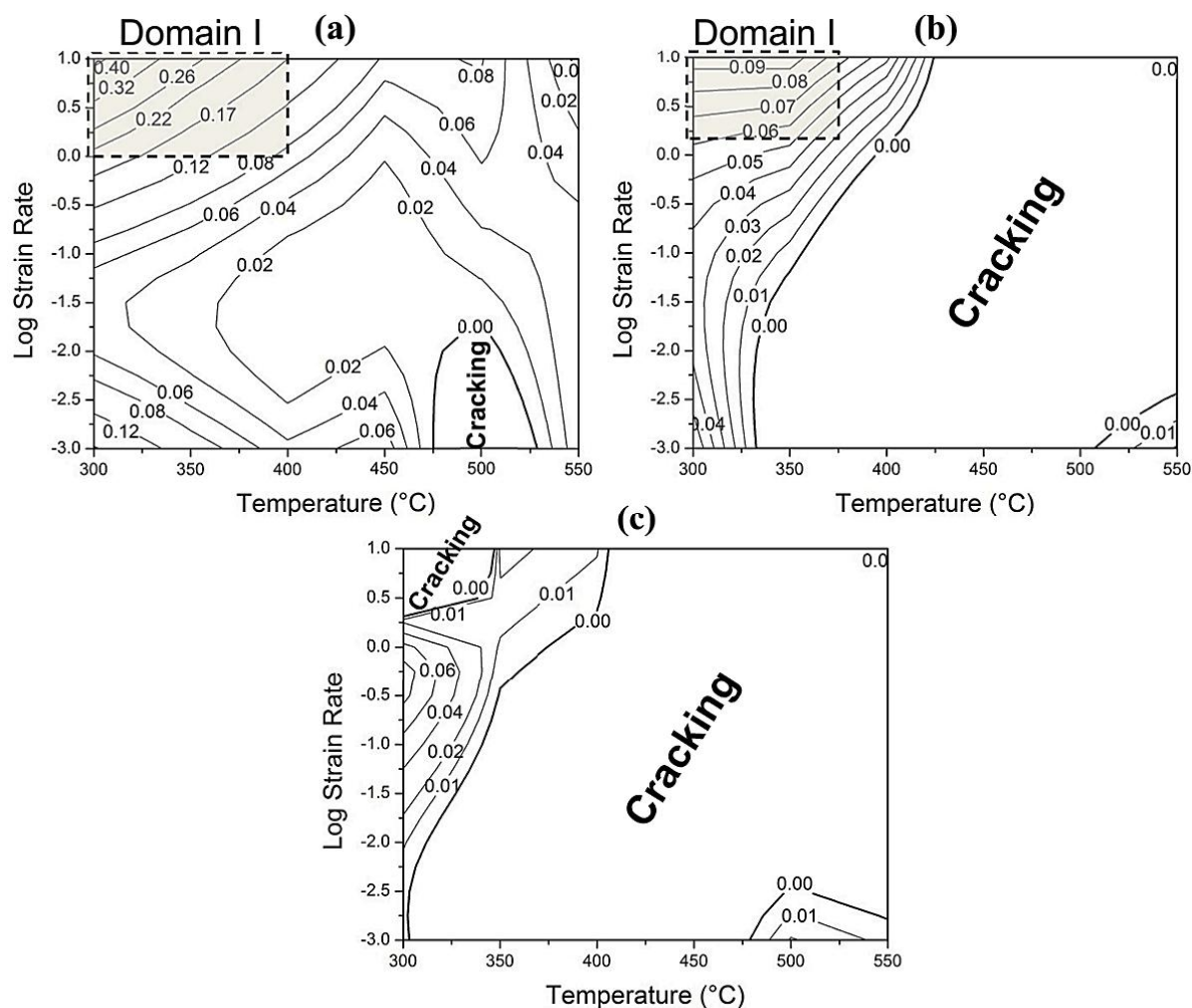


Fig. 4.31. Processing maps of the delubricated MA Alumix 431D compacts developed at strains of (a) 0.1, (b) 0.5, and (c) 0.8.

Determining the optimized condition for hot deformation of the nanocrystalline 7075 Al alloy just based on the efficiency maps developed for delubricated MA Alumix 431D compacts is impossible and misleading. Side views of the specimens hot-compressed at different temperatures and strain rates to a strain of 0.8 are presented in Fig. 4.32, confirming that the delubricated MA Alumix 431D compacts are highly susceptible to cracking during hot compression. This can be attributed to both the poor workability of the nanocrystalline 7075 Al alloy and the appreciable residual porosity present in the microstructure of delubricated MA Alumix 431 compacts (about 15 %). The compacts hot-compressed in the temperature range of 400-500 °C and a strain rate of 0.001 s^{-1} produced crack-free, uniformly deformed specimens. It seems likely that the nanocrystalline 7075 Al alloy shows reasonable workability at the mentioned temperatures and strain rate. Considering all above, the optimum hot working window for delubricated MA Alumix 431D compacts was determined

to lie between 400-500 °C and 0.001-0.01 s⁻¹. As shown in Fig. 4.32, the specimens experienced inhomogeneous deformation (i.e., flow localization) and/or cracking in the domain I, confirming that this domain is not suitable for hot deformation of delubricated MA Alumix 431D compacts.

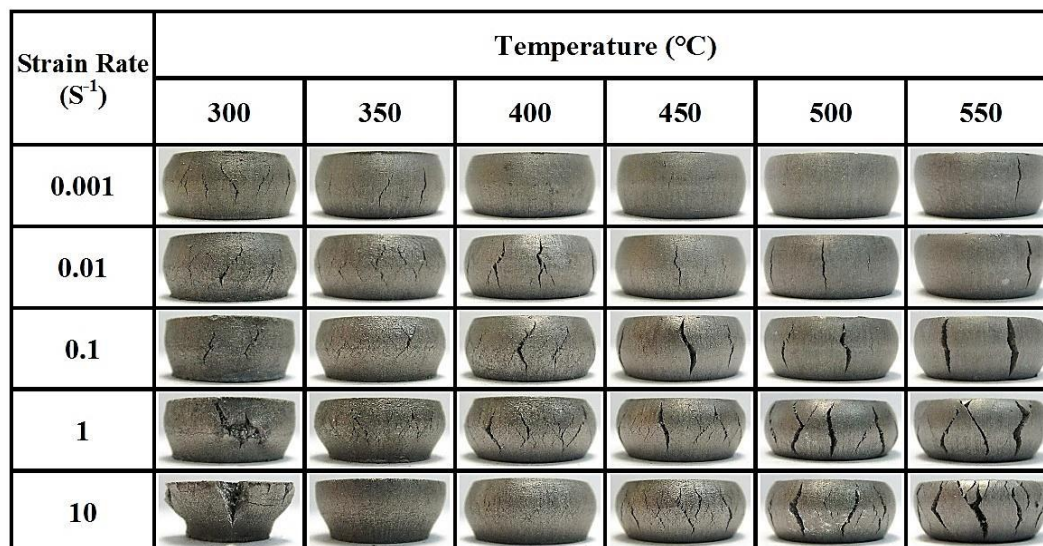


Fig. 4.32. Side views of the specimens hot-compressed at different temperatures and strain rates to a strain of 0.8.

4.9.4 Microstructures of the Hot-compressed Specimens.

Microstructures of the hot-compressed specimens at a deformation temperature of 450 °C and a strain rate of 0.001 s⁻¹ (within the optimum hot deformation window determined for delubricated MA Alumix 431D compacts) are shown in Fig. 4.33. The coarse second phase precipitates present in the microstructure of the delubricated MA Alumix 431D compact (Fig. 4.28) are no longer visible in the microstructure of the hot-compressed specimen. Because of the very fine grain sizes and consequent high density of interfaces, nanocrystalline materials, including those prepared by mechanical alloying method, show extremely high diffusion rates [31]. Consequently, the short exposure time to high temperatures during hot compression testing was long enough for the second phase precipitates present in the microstructure of the delubricated MA Alumix 431D compact to dissolve entirely into the Al solid solution (α -Al) matrix of the nanocrystalline 7075 Al alloy. After hot compression, the samples were air-quenched to room temperature. Therefore, there was not enough time for re-formation of coarse precipitates. After hot compression, MA Alumix 431D powder particles seem to be welded together and the initial interfaces of powder particles are hardly recognizable (Fig 4.33 (b)). Limited residual porosity (surrounded by the black circle in Fig. 4.33 (b)) is still present in the microstructure of the hot-compressed sample. The effect of deformation strain on the relative density of the specimen hot-compressed at a deformation temperature of 450 °C and a strain rate of 0.001 s⁻¹ is shown in Fig. 4.34. Although the delubricated MA Alumix

431D compact has a high level of residual porosity (15 %) in its microstructure, uniaxial hot compression to a low strain of 0.8 is enough for the deformed specimen to achieve a high relative density of about 98.5 %. Then, it can be postulated that delubricated MA Alumix 431D compacts can be deformed to full density by a proper deformation process such as hot extrusion.

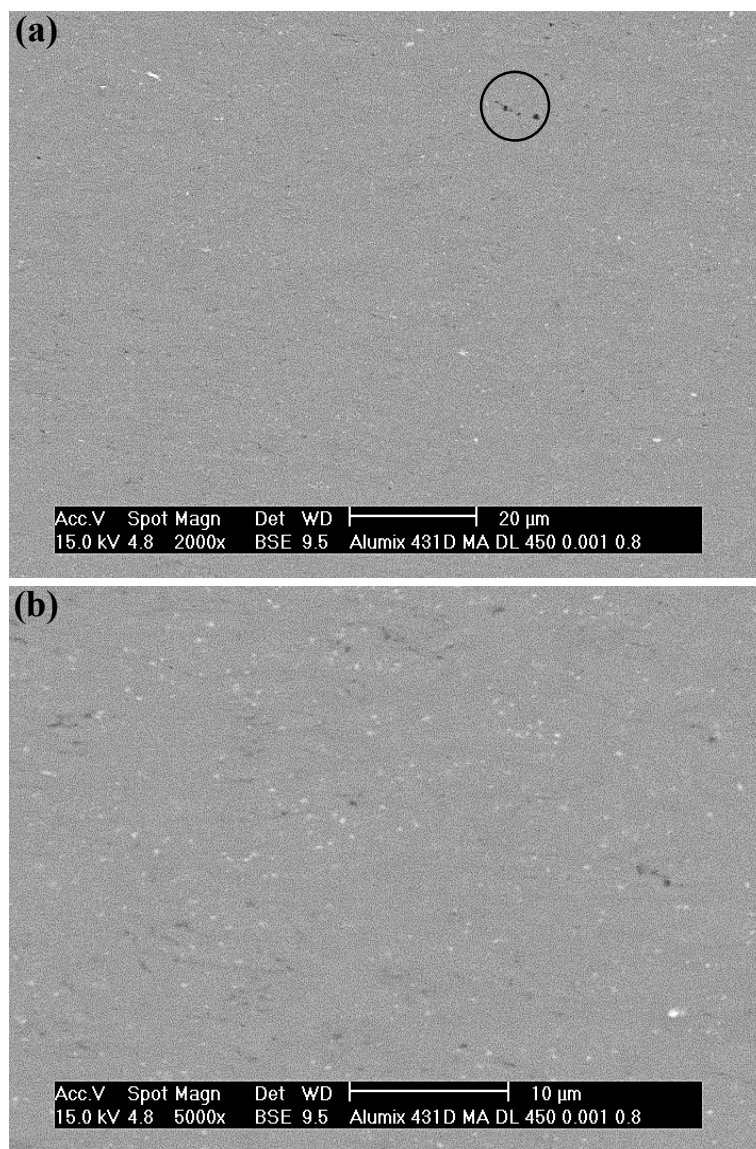


Fig. 4.33. As-deformed microstructure of the specimen hot-compressed at a deformation temperature of 450 °C and a strain rate of 0.001 s⁻¹ (strain= 0.8), (a) 2000x and (b) 5000x magnifications.

The XRD patterns of delubricated MA Alumix 431D compact and the specimen hot-compressed at a deformation temperature of 450 °C and a strain rate of 0.001 s⁻¹ are compared in Fig 4.35. The XRD peaks of the MgZn₂ phase are not present in the pattern obtained for the hot-compressed specimen, confirming the dissolution of this intermetallic phase during hot deformation. As a result, after hot compression a high amount of alloying elements is kept in solid solution, which leads to high hardness values for the specimens hot-

compressed at a strain rate of 0.001 s^{-1} and deformation temperatures of $400 \text{ }^{\circ}\text{C}$, $450 \text{ }^{\circ}\text{C}$, and $500 \text{ }^{\circ}\text{C}$ (Table 4.3). Table 4.3 features the favorable resistance of the nanostructured 7075 Al alloy, processed by mechanical alloying, to crystalline growth during high temperature processing, which keeps the crystallite sizes of the specimens hot-compressed at deformation temperatures up to $500 \text{ }^{\circ}\text{C}$ about 100 nm .

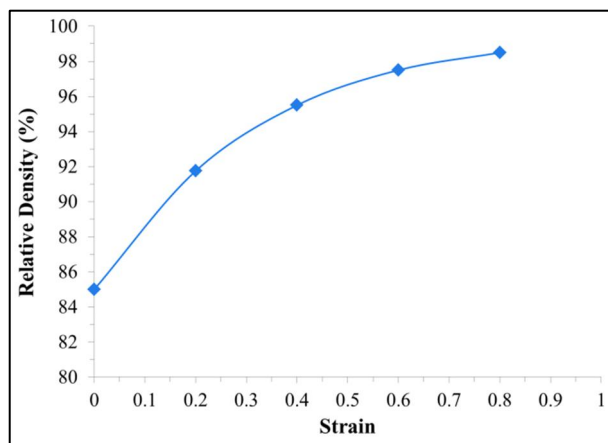


Fig. 4.34. The effect of strain on the relative density of delubricated MA Alumix 431D compacts hot-compressed at a deformation temperature of $450 \text{ }^{\circ}\text{C}$ and a strain rate of 0.001 .

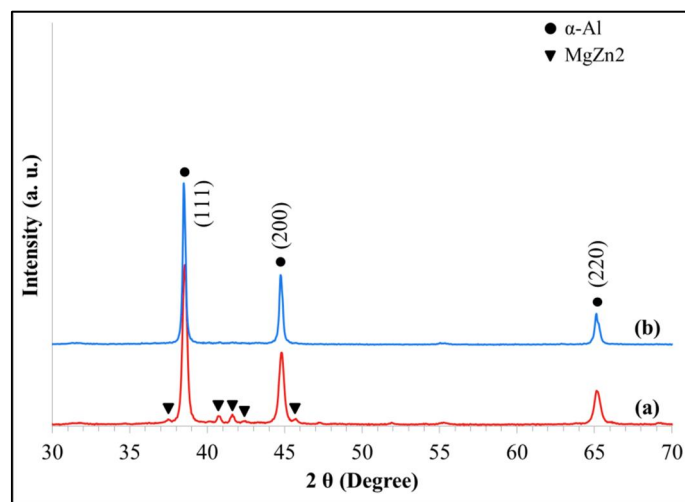


Fig. 4.35. The XRD patterns of (a) delubricated MA Alumix 431D compact and (b) the specimens hot-compressed at a deformation temperature of $450 \text{ }^{\circ}\text{C}$ and a strain rate of 0.001 s^{-1} .

Both the relative density and crystallite size of the specimen hot compressed at a deformation temperature of $400 \text{ }^{\circ}\text{C}$ and a strain rate of 0.001 s^{-1} are comparable with those of the bulk sample consolidated from MA Alumix 431D powder by FAHP (Section 4.6). However, the hardness of the hot-compressed specimen (245 HV) is higher than that of the specimen processed by FAHP (213 HV). A comparison between the microstructures of the mentioned specimens (Fig. 4.33 and 4.16) suggests that this difference in hardness can be

attributed to the higher amount of alloying elements in solid solution for the hot-compressed specimen than for the specimen processed by FAHP.

Table 4.3. Crystallite size and hardness values of the specimens hot-compressed at a strain rate of 0.001 s^{-1} and deformation temperatures within the optimum hot deformation window determined for delubricated MA Alumix 431D compacts (strain= 0.8).

Property	Deformation Temperature (°C)		
	400	450	500
Crystallite Size (nm)	80	91	111
Hardness (HV)	245 ± 6	238 ± 8	229 ± 8

4.10 Hot Extrusion of a 7075 Al PM Alloy.

In the section 4.8, the hot deformation behavior and workability characteristics of a 7075 Al PM alloy were thoroughly studied, and the optimum condition for hot deformation of presintered Alumix 431D compacts was determined to lie between 400-450 °C and 0.01-0.1 s^{-1} . In this section, the mentioned hot deformation parameters are used for the hot extrusion of presintered Alumix 431D compacts.

It should be explained that the extrusion ratio (R) and the effective plastic strain (ϵ_{eff}) introduced into the material during extrusion are defined as [32]:

$$R = A_0/A_1 = (\pi d_0^2)/(\pi d_1^2) \quad (4.3)$$

$$\epsilon_{\text{eff}} = \ln(R) = \ln(A_0/A_1) = 2 \ln(d_0/d_1) \quad (4.4)$$

where A_0 and d_0 are cross-sectional area and diameter of billet before extrusion, and A_1 and d_1 are cross-sectional area and diameter of the extrusion product. In this study, d_0 and d_1 were 25 mm and 5 mm, respectively. Then, R and ϵ_{eff} are calculated to be 25 and 3.2. The mean extrusion strain rate ($\dot{\epsilon}$) is generally calculated using the following equation [33]:

$$\dot{\epsilon} = (6 V d_0^2 \tan \alpha / (d_0^3 - d_1^3)) \ln(R) \quad (4.5)$$

Where V is the average ram speed, and α is the dead-metal zone semi-angle. In this study, the value of α was 60 °. As mentioned before, the optimum strain rate for hot deformation of presintered Alumix 431D compacts was determined to range between 0.01-0.1 s^{-1} . Using the Equation 4.5, the optimum ram speed for the extrusion of presintered Alumix 431D compacts is calculated to range between 0.04-0.4 mm/s. Therefore, the ram speed for this study was controlled in such a way that the average ram speed for hot extrusion of presintered Alumix 431D compacts lied in the optimum range.

The **Paper Al V** included in the appendix basically concerns the processing of a 7075 Al alloy by hot extrusion of presintered Alumix 431D compacts. For comparison purposes, the green and delubricated Alumix 431D compacts were also hot extruded using the same parameters used for hot extrusion of the presintered Alumix 431D compacts. Extrusion of the cylindrical Alumix 431D compacts (25 mm in diameter and 15 mm thick) was performed at 400 °C to 450 °C without caning and degassing, using an extrusion ratio (R) of 25:1 to ensure full density after extrusion.

No porosity was present in the microstructures of the extruded alloys. Heat treatment prior to extrusion was found to have an important effect on the degree of alloy development in powder compacts and, as a direct consequence, remarkably affected the extrusion process and the as-extruded microstructures and mechanical properties of the extrusion products. Hot extrusion caused banded structures for the alloys consolidated from the green and delubricated compacts. Thanks to a recrystallized grain structure and the homogeneous distribution of fine second phase particles in its microstructure, the alloy consolidated from the presintered Alumix 431D compact by hot extrusion showed excellent mechanical properties, which were far better than those of the extrusion products consolidated from green and delubricated Alumix 431D compacts.

For detailed information on this section also see **Paper Al V**.

4.11 Hot Extrusion of a Nanocrystalline 7075 Al PM Alloy.

In the section 4.9, the hot deformation behavior and workability characteristics of a nanocrystalline 7075 Al PM alloy were thoroughly studied, and the optimum condition for hot deformation of delubricated MA Alumix 431D compacts was determined to lie between 400-500 °C and 0.001-0.01 s⁻¹. In this section, the optimized hot deformation parameters are used for the hot extrusion of delubricated MA Alumix 431D compacts.

4.11.1 PM Processing.

The MA Alumix 431D powder was first mixed with 1.5 wt% pressing lubricant (Acrawax C). Then, 15.5 g of the prepared mixture was uniaxially cold pressed at 600 MPa into cylindrical compacts measuring 25 mm in diameter. Prior to hot extrusion, the green compacts were subjected to the delubrication treatment previously introduced in the sub-section 4.9.1. The sub-section 4.9.1 also provides detailed information on the microstructural characteristics of the delubricated MA Alumix 431D compact.

4.11.2 Hot Extrusion.

As mentioned before, the optimum strain rate range for hot deformation of delubricated MA Alumix 431D compacts was found to be 0.001-0.01 s⁻¹. Using the Equation 4.5, the

optimum ram speed range for the extrusion of delubricated MA Alumix 431D compacts is calculated to be 0.004-0.04 mm/s. Therefore, the ram speed for this study was controlled in such a way that the average ram speed was kept in the optimum range.

First we tried to extrude the delubricated MA Alumix 431D compacts at 400 °C, but our attempts were unsuccessful because the force needed for extrusion at 400 °C was beyond the maximum force we could apply to our extrusion setup. Consequently, extrusion of the mentioned compacts was performed at 500 °C without caning and degassing using an extrusion ratio (R) of 25:1, and the delubricated MA Alumix 431D compacts were extruded to form rods 5 mm in diameter and approximately 250 mm long. After extrusion, the extruded rods were air cooled to room temperature.

4.11.3 Extruded Material.

Fig. 4.36 illustrates the microstructure of the bulk alloy consolidated from a delubricated MA Alumix 431D compact by hot extrusion at 500 °C. No porosity is visible in the microstructure. The relative density of the extruded alloy was measured to be very close to 100 %, suggesting that the employed extrusion ration (R) of 25:1 was high enough to process a full-density bulk material (a bulk material with a relative density of 100 %).

There is a homogeneous distribution of the ultra-fine second phase particles in the microstructure of the extruded alloy. These particles should have precipitated during or after the extrusion process as they are much finer than the ones present in the microstructure of the delubricated MA Alumix 431D compact (Fig. 4.28). Some isolated larger second phase particles are also seen in the microstructure (Fig. 4.36 (a)). Additionally, the powder particles present in the microstructure of the delubricated MA Alumix 431D compact appear to be completely welded together as the initial interfaces of powder particles are no longer detectable in the as-extruded microstructure.

The XRD patterns of delubricated MA Alumix 431D compact and the bulk alloy consolidated from a delubricated MA Alumix 431D compact by hot extrusion at 500 °C are compared in Fig 4.37. The XRD peaks of the MgZn_2 phase are almost undetectable in the pattern obtained for the extruded specimen, suggesting that the coarse MgZn_2 precipitates present in the microstructure of the delubricated MA Alumix 431D compact (Fig. 4.28) dissolve into the α -Al matrix during heating to the extrusion temperature. As seen in Fig. 4.36, some ultra-fine second phase particles precipitate during hot extrusion and/or subsequent cooling to room temperature. However, these precipitates are too low in amount or too small in size for effective detection by XRD. The crystallite size of the bulk 7075 Al alloy processed by hot extrusion was measured to be about 230 nm using the Williamson–Hall method, which shows that the nanostructured 7075 Al alloy had experienced some crystallite growth during the extrusion process. This crystalline growth could have been promoted by the high extrusion temperature employed, prolonged exposure to high

temperatures during the extrusion process, and the high effective plastic strain ($\epsilon_{\text{eff}} = 3.2$) introduced into the material through extrusion.

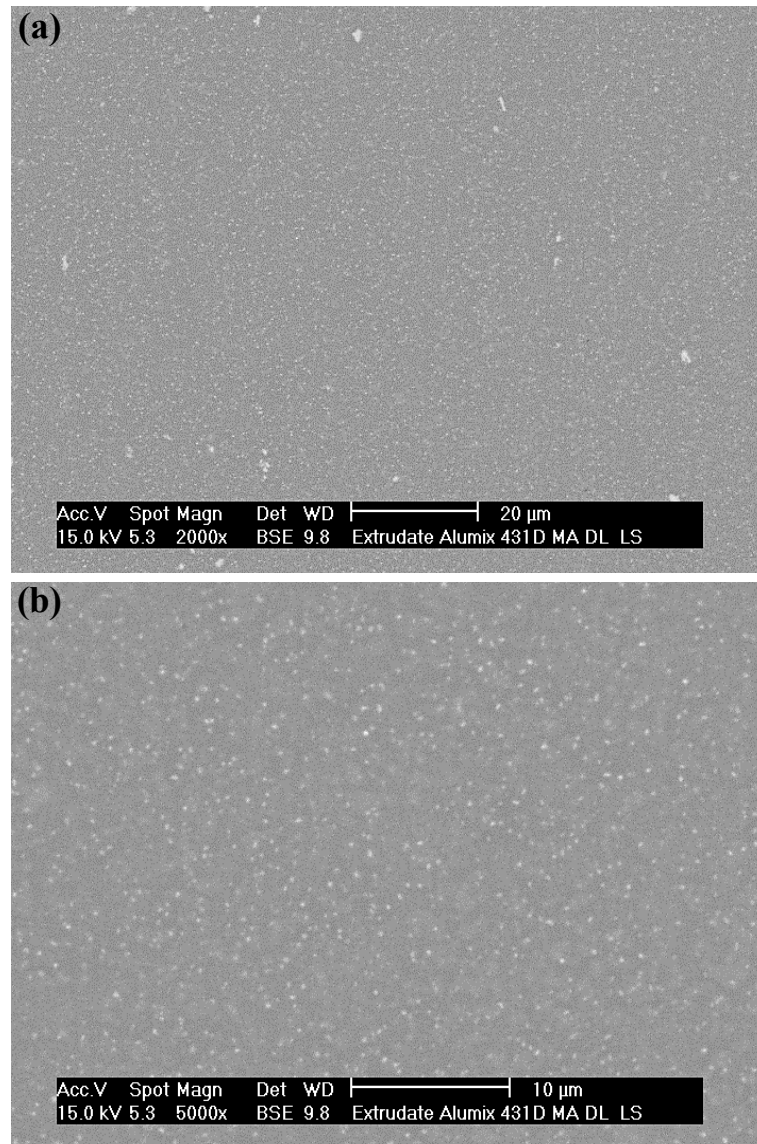


Fig. 4.36. Longitudinal section microstructure of the bulk alloy consolidated from delubricated MA Alumix 431D compacts by hot extrusion at 500 °C, (a) 2000x and (b) 5000x magnifications.

The most convenient means of mechanical assessment is ambient temperature tests. The rods extruded from delubricated MA Alumix 431D compacts were tested in the as-extruded state (F), and the averages of those tests were calculated as shown in Table 4.4. Data obtained for the rods extruded from presintered Alumix 431D compacts, the Alumix 431D cold pressed and sintered parts after T6 heat treatment (solution treated and artificially aged) [9], and wrought 7075 Al alloy extruded rods after T6 heat treatment [34] are also reported for comparison purposes. Comparing the MA Alumix 431D extrusion-F system with the Alumix 431D extrusion-F and Alumix 431D sintered-T6 systems shows that the products consolidated from MA Alumix 431D powder are significantly superior. It is also worthy to

note that the tensile properties of the MA Alumix 431D extrusion-F system are about 8 percent superior to those measured for the wrought 7075 Al alloy extrusion-T6 system and some 20 to 30 percent superior to those previously reported for the rods extruded from mechanically alloyed 7010 Al alloy powder after T6 heat treatment [35]. In this study, Alumix 431D premix was mechanically alloyed to produce a nanocrystalline 7075 Al alloy powder, which was subsequently consolidated by hot extrusion without canning and degassing. Considering the superior mechanical properties obtained for the rods extruded from delubricated MA Alumix 431D compacts, clearly the approach adopted in the processing of bulk ultrafine-grained 7075 Al alloy is highly beneficial.

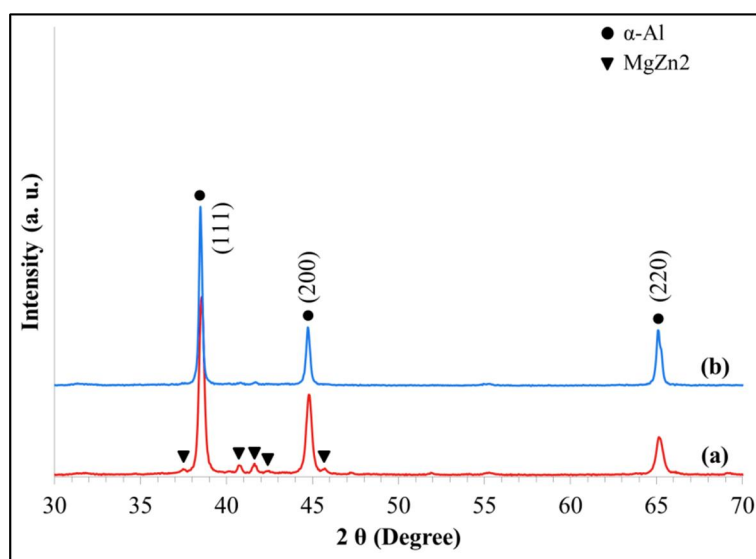


Fig. 4.37. The XRD patterns of (a) delubricated MA Alumix 431D compact and (b) the bulk alloy consolidated from delubricated MA Alumix 431D compacts by hot extrusion at 500 °C.

Table 4.4. Mechanical properties of the MA Alumix 431D extruded rods. Data on Alumix 431D extruded rods, Alumix 431D sintered parts [9], and 7075 Al alloy extruded rods [34] included for comparison purposes.

System	Hardness (HV)	Yield Strength (MPa)	Tensile Strength (MPa)	Elongation (%)	Compressive Strength (MPa)
MA Alumix 431D Extrusion - F	165 ± 3	525 ± 10	575 ± 13	2.5 ± 0.5	667 ± 12
Alumix 431D Extrusion - F	108 ± 2	305 ± 21	463 ± 19	12.5 ± 1.5	502 ± 22
Alumix 431D Sintered – T6	-	444	448	0.9	-
7075 Al alloy Extrusion - T6	-	483	538	7	-

4.12 Partial Conclusions

Through the work completed in this study the following conclusions have been reached:

1. The content of PCA used for the mechanical alloying of Alumix 431D powder considerably affected the optimum milling time, the as-milled apparent density, and the powder extraction efficiency. The employment of 1 wt% stearic acid as PCA resulted in the optimum balance among the aforementioned items and, consequently, was considered as the optimum content of PCA for this study. In addition to the content of PCA, the method of addition of PCA was found to be of great importance.
2. Alumix 431D powder was highly responsive to conventional sintering, as it was able to reach a relative density of about 96.5 % through sintering at 605 °C for 30 min. Alumix 431D achieved a hardness value of 89 HV in the as-sintered state. Cold pressing and sintering seemed to be a suitable consolidation route for Alumix 431D powder. However, the results obtained for MA Alumix 431D powder confirmed that this powder could not be effectively consolidated by conventional sintering. Simultaneous thermal analysis (STA) studies helped us to understand better the sintering mechanisms of Alumix 431D and MA Alumix 431D powders.
3. Bulk nanocrystalline 7075 Al samples were consolidated from MA Alumix 431D powder by field assisted hot pressing (FAHP) technique. FAHP temperature was found to have an important effect on the relative density and hardness of the processed bulk samples. FAHP at a low temperature of 400 °C for 10 min was able to process fully dense bulk samples with a crystallite size of about 75 nm and a hardness value of 213 HV, showing that the MA Alumix 431D powder can be effectively consolidated by the FAHP technique.
4. The data obtained through the hot compression of presintered Alumix 431D and delubricated MA Alumix 431D compacts were analyzed to develop processing maps. Strain was found to have important effects on the processing maps of both compacts. Presintered Alumix 431D compacts showed good workability at moderate deformation temperatures (350-450 °C) and strain rates (0.01-0.3 s⁻¹) while delubricated MA Alumix 431D compacts were extremely susceptible to cracking during hot compression. The optimum hot working window for delubricated MA Alumix 431D compacts was determined to lie between 400-500 °C and 0.001-0.01 s⁻¹. Both presintered Alumix 431D and delubricated MA Alumix 431D compacts exhibited significant increases in density through hot compression, and it was confirmed that full density could be achieved for both compacts by hot deformation.
5. The heat treatment prior to extrusion had a significant effect on the degree of alloy development in Alumix 431D powder compacts. Banded structures consisting of two repeating bands were observed in the bulk samples extruded from the green and

delubricated Alumix 431D compacts, in which the master alloy and Al particles were distinguishable. Thanks to a recrystallized grain structure and the homogeneous distribution of fine second phase particles in its microstructure, the bulk sample extruded from the presintered Alumix 431D compact showed excellent mechanical properties, which were far better than those of the bulk samples extruded from the green and delubricated Alumix 431D compacts.

6. Hot extrusion without canning and degassing was capable of processing full density bulk samples from delubricated MA Alumix 431D compacts. However, prolonged exposure to high temperatures caused the nanocrystalline 7075 Al alloy (processed by mechanical alloying) to experience some crystalline growth during the extrusion process, and the crystallite size of the bulk 7075 Al alloy extruded from delubricated MA Alumix 431D compacts was measured to be about 230 nm. The tensile properties of the MA Alumix 431D extrudate were even superior to those reported for the wrought 7075 Al alloy extrudate after T6 heat treatment, confirming that hot extrusion without canning and degassing was highly beneficial for the processing of bulk ultrafine-grained 7075 Al alloy from delubricated MA Alumix 431D compacts.

References

- [1] J.B. Fogagnolo, F. Velasco, M.H. Robert, J.M. Torralba, *Mater. Sci. Eng. A*, 342 (2003) 131-143.
- [2] J.B. Fogagnolo, M.H. Robert, J.M. Torralba, *Mater. Sci. Eng. A*, 426 (2006) 85-94.
- [3] P. Le Brun, L. Froyen, B. Munar, L. Delaey, *Scand. J. Metall.*, 19 (1990) 19-22.
- [4] L. Lu, Y.F. Zhang, *J. Alloys Compd.*, 290 (1999) 279-283.
- [5] Y.F. Zhang, L. Lu, S.M. Yap, *J. Mater. Process. Technol.*, 89-90 (1999) 260-265.
- [6] R. Panelli, F. Ambrosio Filho, *Powder Metall.*, 41 (1998) 131-133.
- [7] J.B. Fogagnolo, E.M. Ruiz-Navas, M.H. Robert, J.M. Torralba, *Mater. Sci. Eng. A*, 355 (2003) 50-55.
- [8] J.M. Martín, F. Castro, *Journal of Materials Processing Technology*, 143-144 (2003) 814-821.
- [9] A.D.P. LaDelpha, H. Neubing, D.P. Bishop, *Materials Science and Engineering: A*, 520 (2009) 105-113.
- [10] W.G.E. Moshe, in, Dalhousie University, Halifax, Nova Scotia, 2010.
- [11] N.A. Belov, D.G. Eskin, A.A. Aksenov, *Multicomponent Phase Diagrams: Applications for Commercial Aluminum Alloys*, Elsevier, Amsterdam, 2005.
- [12] W. Yuan, J. Zhang, C. Zhang, Z. Chen, *J. Mater. Process. Technol.*, 209 (2009) 3251-3255.
- [13] M.A. Jabbari Taleghani, E.M. Ruiz Navas, J.M. Torralba, *Materials & Design*, 55 (2014) 674-682.
- [14] P.T. Wang, *Powder Technology*, 66 (1991) 21-32.
- [15] P.T. Wang, M.A. Zaidi, *Powder Technology*, 66 (1991) 9-19.
- [16] P.T. Wang, M.E. Karabin, *Powder Technology*, 78 (1994) 67-76.

- [17] M. yan Zhan, Z. Chen, H. Zhang, W. Xia, *Mechanics Research Communications*, 33 (2006) 508-514.
- [18] S. Serajzadeh, A. Karimi Taheri, *Mechanics Research Communications*, 30 (2003) 87-93.
- [19] H. Mirzadeh, A. Najafizadeh, *Mater. Sci. Eng. A*, 527 (2010) 1160-1164.
- [20] R.E.D. Mann, R.L. Hexemer Jr, I.W. Donaldson, D.P. Bishop, *Materials Science and Engineering: A*, 528 (2011) 5476-5483.
- [21] N. Srinivasan, Y.V.R.K. Prasad, P. Rama Rao, *Mater. Sci. Eng. A*, 476 (2008) 146-156.
- [22] Y. Deng, Z. Yin, J. Huang, *Mater. Sci. Eng. A*, 528 (2011) 1780-1786.
- [23] K.P. Rao, Y.V.R.K. Prasad, *Mater. Sci. Eng. A*, 527 (2010) 6589-6595.
- [24] K.P. Rao, Y.V.R.K. Prasad, K. Suresh, *Mater. Des.*, 32 (2011) 4874-4881.
- [25] T. Sheppard, A. Jackson, *Materials Science and Technology*, 13 (1997) 203-209.
- [26] E. Cerri, E. Evangelista, A. Forcellese, H.J. McQueen, *Materials Science and Engineering: A*, 197 (1995) 181-198.
- [27] S. Liu, J. You, X. Zhang, Y. Deng, Y. Yuan, *Materials Science and Engineering: A*, 527 (2010) 1200-1205.
- [28] N. Jin, H. Zhang, Y. Han, W. Wu, J. Chen, *Materials Characterization*, 60 (2009) 530-536.
- [29] H.J. McQueen, E. Evangelista, M.E. Kassner, *Mater. Res. Adv. Tech.*, 82 (1991) 336-345.
- [30] G.E. Dieter, *Mechanical Metallurgy*, SI Metric ed., McGraw-Hill London, UK, 1988.
- [31] C. Suryanarayana, *Progress in Materials Science*, 46 (2001) 1-184.
- [32] S. Kaneko, K. Murakami, T. Sakai, *Materials Science and Engineering: A*, 500 (2009) 8-15.
- [33] M.M. Peres, J.B. Fogagnolo, A.M. Jorge Jr, C.S. Kiminami, W.J. Botta F., C. Bolfarini, *Materials Science Forum*, 570 (2008) 97-102.
- [34] J.R. Davis, *Aluminum and Aluminum Alloys*, ASM International, Materials Park, Ohio, USA, 1993.
- [35] A. Bhaduri, V. Gopinathan, P. Ramakrishnan, A.P. Miodownik, *Materials Science and Engineering: A*, 221 (1996) 94-101.

RESULTS AND
DISCUSSION FOR
AZ91 MG PM ALLOY

5

CHAPTER 5 SUMMARY OF RESULTS AND DISCUSSION

FOR AZ91 MG PM ALLOY

5.1 AZ91 Mg Alloy Powders

The raw materials used for this study were two different kinds of pre-alloyed Mg-Al-Zn powder produced by mechanical grinding (Ecka Granules, Germany) and atomization (ESM Special Metals & Technology, USA), respectively, with a chemical composition equivalent to that of AZ91 Mg alloy (8.8 wt% Al, 0.6 wt% Zn, 0.2 wt% Mn, 0.03 wt% Si, and the balance Mg).

Fig. 5.1 illustrates the morphology and cross-section microstructure of the mechanically ground AZ91 powder, showing that the powder particles possess the irregular, plate-like morphology that is typical of Mg-based powders produced by the mechanical grinding of casting ingots [1]. The microstructure of powder particles was comprised of a dark gray matrix in which some gray phases were randomly distributed. The EDS analyses (data not shown) determined that the dark gray matrix was enriched in Mg while the gray precipitates were enriched in Mg and Al. These precipitates are highlighted using black ovals. The average particle size ($D(0.5)$) and particle size distribution ($D(0.9) - D(0.1)$) of the mechanically ground AZ91 powder was measured to be 105 μm and 183 μm , respectively. The hardness of the powder was measure to be about 90 HV0.01. This hardness appears to be relatively high for Mg-based powders, which implies that the particles of mechanically ground AZ91 powder may have experienced some work hardening through the mechanical grinding process.

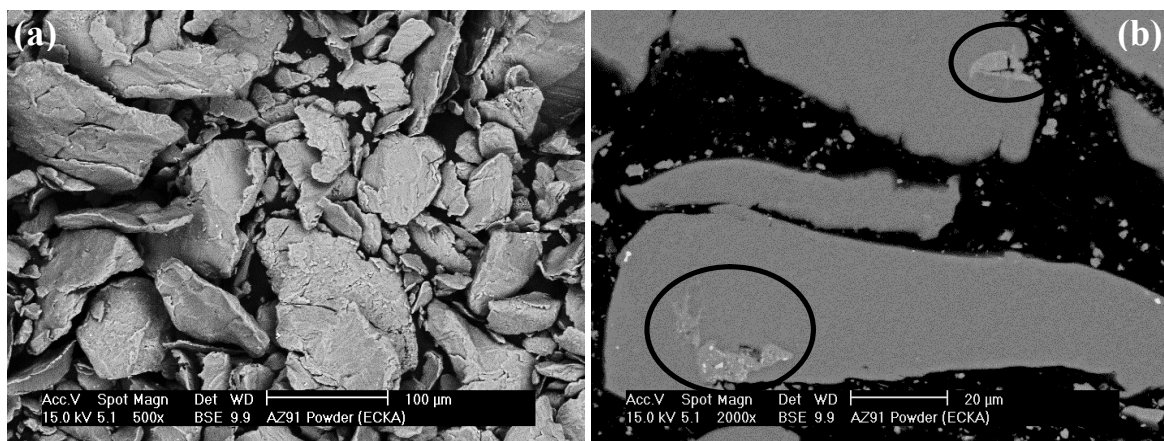


Fig. 5.1. (a) Morphology and (b) cross-section microstructure of the AZ91 powder produced by mechanical grinding.

Fig. 5.2 illustrates the morphology and cross-section microstructure of the atomized AZ91 powder, showing that the powder particles possess the spherical morphology that is typical of Mg-based powders produced by atomization [1]. The powder particles appear light grey and have a very fine cellular microstructure. A network of second phases is slightly visible in the microstructure of the atomized AZ91 powder particles. The second phases are believed to be enriched with the alloying elements. The average particle size ($D(0.5)$) and particle size distribution ($D(0.9) - D(0.1)$) of the atomized AZ91 powder was measured to be 70 μm and 142 μm , respectively. The hardness of the powder was measured to be about 73 HV0.01.

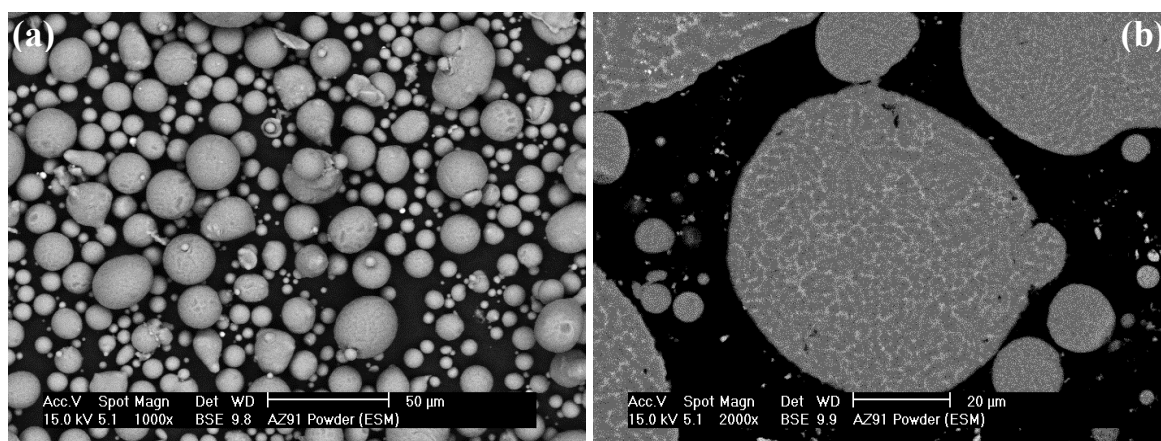


Fig. 5.2. (a) Morphology and (b) cross-section microstructure of the AZ91 powder produced by atomization.

5.2 Mechanical Alloying

To produce a nanocrystalline AZ91 Mg alloy, the mechanically ground AZ91 powder was high-energy milled in a horizontal attritor (CM01 Simoloyer, ZOZ, Germany) using the following milling parameters: ball-to-powder weight ratio: 20/1; ball diameter: 5 mm; ball material: AISI 420 stainless steel; milling time: 14 h, milling speed: 700 rpm; and milling atmosphere: Ar. Stearic acid (2 wt%) was employed as the process control agent (PCA). It should be explained that the attritor mill used for the mechanical alloying of AZ91 powder was the same attritor mill used for the milling of Alumix 431D powder. Consequently, the milling time and the content of PCA for AZ91 powder were selected based on the optimization process carried out for Alumix 431D powder.

Special precautions should be taken during unloading of the Mg-based powders after high energy milling. Immediately after high energy milling, the milled powder is hot (or at least warm) and, therefore, the lid should not be immediately opened. Furthermore, after opening the lid and prior to unloading, the milled powder must be exposed to atmosphere for a couple of hours. Otherwise, the powder may catch fire during unloading because of interaction with the oxygen.

5.3 Mechanical Alloyed AZ91 Powder

The **Paper Mg I** included in the appendix analyzes the effects of mechanical alloying and subsequent isothermal annealing on the microstructural characteristics of the AZ91 powder. To this end, the mechanically ground powder was high-energy milled using the milling parameters mentioned in the previous section. Then, the mechanically alloyed powder was isothermally annealed. In this section, the results presented in **Paper Mg I** are briefly reviewed and discussed.

The mechanically alloyed AZ91 (MA AZ91) powder exhibited irregular, semi-equiaxed morphology (Fig. 5.3 (a)), which implies that the employed milling time, i.e. 14 h, was sufficient for the high-energy milling process to reach its steady state, in which there is a balance between the cold welding and fracturing of powder particles. After the milling process, no second phase precipitates were visible in the microstructure of the MA AZ91 powder, and the particles of the MA AZ91 powder possessed a grey matrix with no specific microstructural feature (Fig. 5.3 (b)). The average particle size ($D(0.5)$) and particle size distribution ($D(0.9) - D(0.1)$) of MA AZ91 powder were measured to be $37\ \mu\text{m}$ and $100\ \mu\text{m}$, respectively, suggesting that the high-energy milling process had significant effects on the particle size characteristics of the mechanically ground AZ91 powder. The hardness of MA AZ91 powder was measured to be $125 \pm 6\ \text{HV}0.01$.

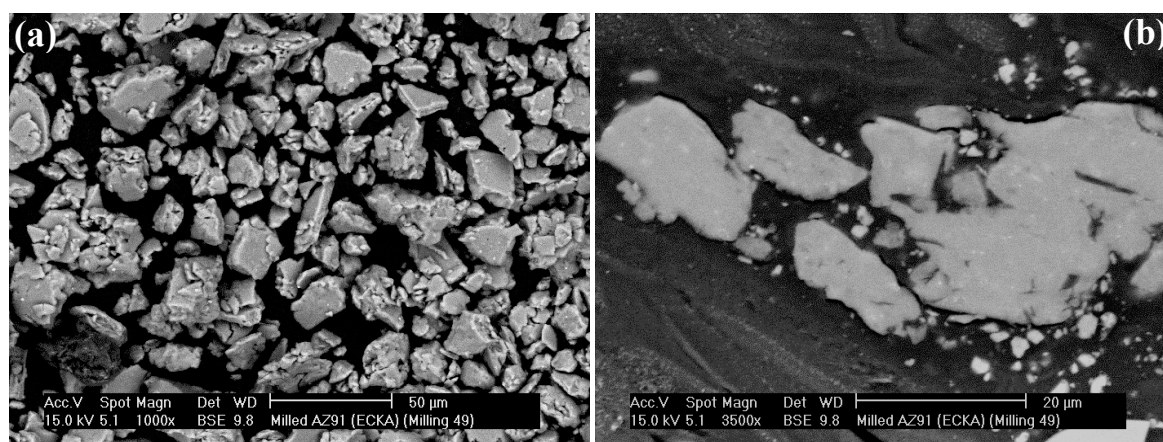


Fig. 5.3. (a) Morphology and (b) cross-section microstructure of the MA AZ91 powder.

The XRD patterns of AZ91 (produced by mechanical grinding) and MA AZ91 powders are presented in Fig. 5.4. The microstructure of the AZ91 powder particles was composed of the $\beta\text{-Mg}_{17}\text{Al}_{12}$ precipitates and the $\alpha\text{-Mg}$ solid solution matrix. This structure is typical of AZ91 castings [2]. High-energy milling remarkably affected the intensities and widths of the diffraction peaks of the $\alpha\text{-Mg}$ phase, and the mentioned peaks became weaker and wider through high-energy milling. This phenomenon can be attributed to the reduction in particle size, the refinement of crystallite size, and the enhancement of lattice strain, all promoted by the severe plastic deformation of the AZ91 powder particles during the milling process.

Moreover, the diffraction peaks of the β -Mg₁₇Al₁₂ phase are barely detectable in the XRD pattern of MA AZ91 powder, which can be related to the dissolution of the β -Mg₁₇Al₁₂ phase in the α -Mg matrix of the powder particles. Another possibility is that high-energy milling caused the β -Mg₁₇Al₁₂ phase to be refined into very small dispersoids distributed in the α -Mg phase, which are hardly detectable by XRD. The grain sizes of AZ91 casting products normally range between 10 μ m and 150 μ m [2, 3]. The AZ91 powder used for this study had been produced by the mechanical grinding of AZ91 casting ingots. Considering the production method, it can be concluded that the grains of this powder should have had micrometer dimensions. The crystallite size and lattice strain of MA AZ91 powder were calculated to be 25 nm and 0.53 %. A high lattice strain implies that the AZ91 powder particles went through severe plastic deformation during the milling process and, as a result, contained a high density of microstructural defects. The values obtained for crystallite size and lattice strain are in good agreement with those previously reported for high-energy milled Al-based powders [4, 5]. Various models have been proposed to describe the mechanism of formation of nanostructures by high-energy milling [6].

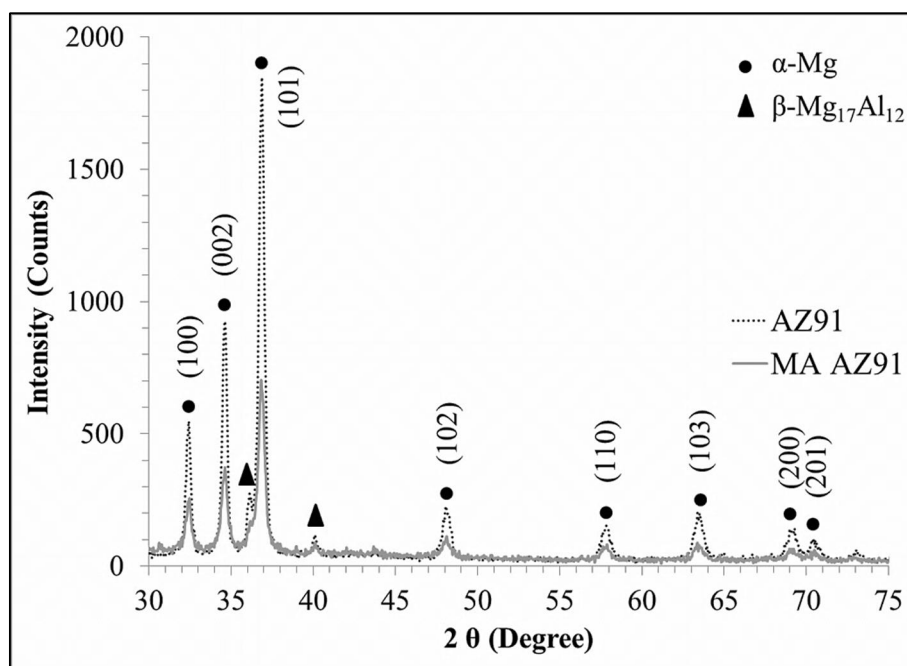


Fig. 5.4. The XRD patterns of AZ91 (dotted) and MA AZ91 (solid) powders (Paper Mg I).

The crystallite size of MA AZ91 powder annealed at 300 °C for 4 h was determined to be 80 nm (Fig. 5.5), suggesting that the nanostructured AZ91 alloy processed by mechanical alloying had a good thermal stability. This favorable thermal stability could result from the homogenous distribution of nanosized Mg oxides and carbides in the structure of MA AZ91 powder particles. The surfaces of Mg-based powders are covered with a thin, stable oxide layer of 3-5 nm [7], which can be fragmented and introduced into the structure of powder particles by high-energy milling. Moreover, Mg may react with PCA and form nanosized Mg

carbides during the milling process. The growth of MA AZ91 grains at high temperatures can then be hindered by the Mg oxide and carbide dispersoids.

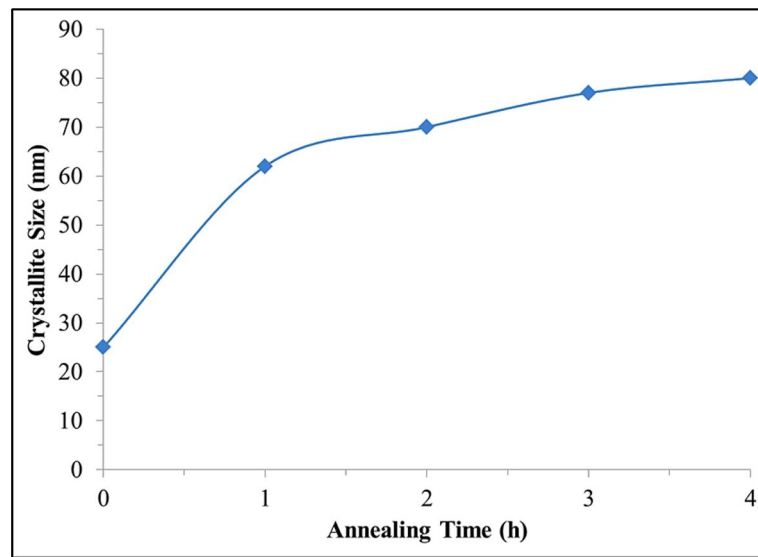


Fig. 5.5. The crystallite sizes of MA AZ91 powder annealed at 300 °C for different times (Paper Mg I).

For detailed information on the above subject also see **Paper Mg I**.

5.4 Analysis of the Compressibility.

The **Paper Mg II** included in the appendix concerns the compressibility of AZ91 powder (produced by mechanical grinding). Besides, the effect of mechanical alloying on the compressibility characteristics of the above-mentioned powder has been examined in the **Paper Mg III**.

The compressibility curves of AZ91 (produced by mechanical grinding) and MA AZ91 powders are presented in Fig. 5.6 (a).

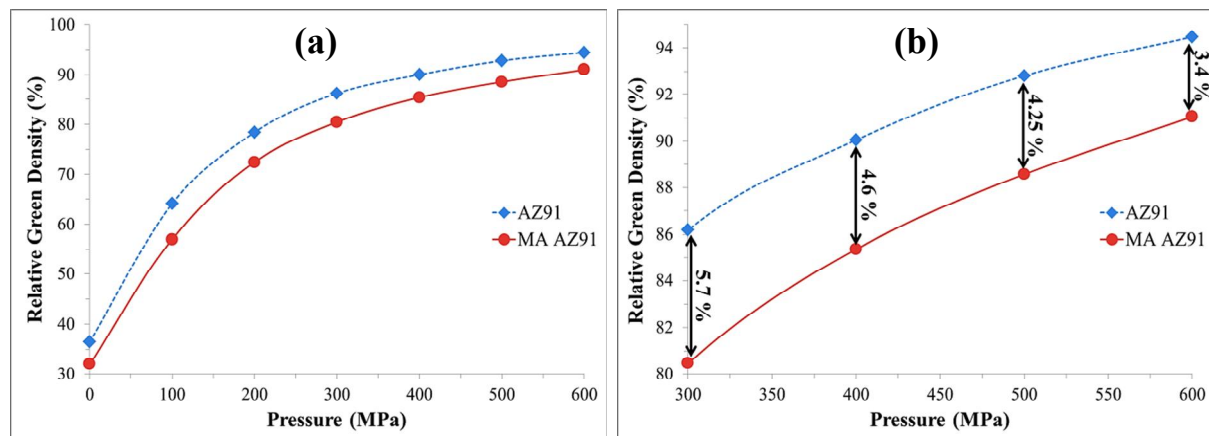


Fig. 5.6. (a) The compressibility curves of AZ91 and MA AZ91 powders. (b) The same curves at pressing pressures greater than 300 MPa (Paper Mg III).

Both curves illustrate the typical compressibility behavior of metallic powders [8]; i.e., the relative green density increases with increasing compaction pressure, albeit at a decreasing densification rate. It is also observed that, compared with MA AZ91 powder, AZ91 powder exhibits a higher densification rate at low pressing pressures ($P \leq 200$ MPa). This stage of densification is mainly attributed to the rearrangement of powder particles. A higher densification rate at this stage may imply that the morphology and particle size distribution of AZ91 powder were more beneficial to the rearrangement stage of densification than those of MA AZ91 powder. However, at pressures above 300 MPa, the densification rate of MA AZ91 powder surpasses slightly that of AZ91 powder, leading to a decrease in the difference between the relative green densities of AZ91 and MA AZ91 powder compacts (Fig. 5.6 (b)). Both AZ91 and MA AZ91 powders exhibited relatively good compressibility and reached relative green densities of 94 % and 91 %, respectively, at a compaction pressure of 600 MPa.

In Fig. 5.7, the compressibility data for the AZ91 (produced by mechanical grinding) and MA AZ91 powders are represented in a diagrams of $P^{(1/2)}$ versus $\ln(1/(1-D))$ to visualize the validity of the Panelli and Ambrosio equation [9] (Equation 2.2) for uniaxial cold compaction of the mentioned powders. This equation fits reasonably the experimental results.

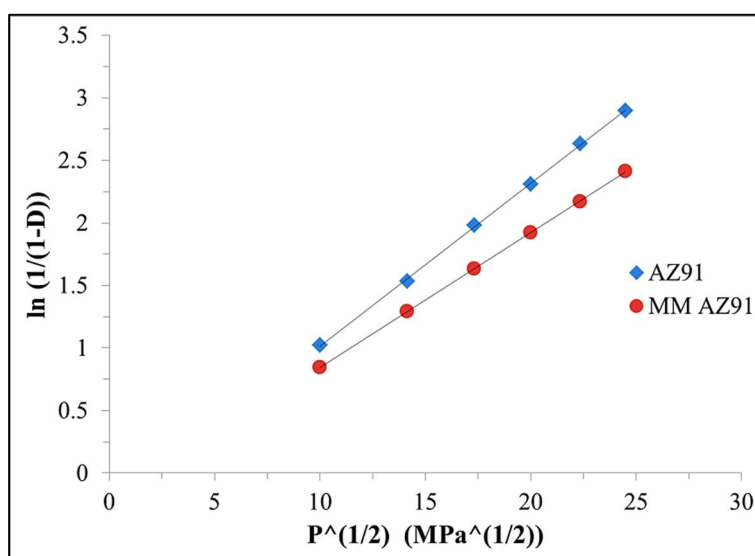


Fig. 5.7. The compressibility data for the mechanically ground AZ91 and MA AZ91 powders fitted to the Panelli and Ambrosio equation (Paper Mg III).

The K_{pan} constant calculated for the AZ91 powder, 0.13, is close to the K_{pan} constant obtained for a gas-atomized pure Al powder (0.17) [10] and is far higher than that reported for a 6061 Al alloy powder (0.057) [11], suggesting that this powder has a high capacity for plastic deformation. It should be noted that, aside from its plastic deformability, the morphology and size distribution of a powder can also affect its K_{pan} constant. For example, it is reported that, compared with an equiaxed morphology, a flattened or flake-like morphology provides a higher K_{pan} constant for a given powder [11]. However, there has not

been any systematic study of the effect of the morphology and particle size characteristics of a powder on its K_{pan} constant. As a result, the exact effect of these parameters on the K_{pan} constant is not known. Considering the poor workability of Mg and its alloys at room temperature and considering the fact that AZ91 alloy with nearly 10 wt% of alloying elements is generally considered a casting alloy, it can be postulated that the morphology and size distribution of the AZ91 powder may affect its K_{pan} constant. The K_{pan} constant of the AZ91 powder decreased from 0.13 to 0.1 as a result of mechanical alloying. The higher hardness of MA AZ91 powder, its semi-equiaxed morphology, and its smaller average particle size along with a narrower particle size distribution can all be responsible for the reduction observed in the K_{pan} constant.

The effect of atomized Acrawax C on the relative green densities and ejection forces of AZ91 and MA AZ91 powder compacts, cold-pressed at 600 MPa, is shown in Fig. 5.8. For both powders, a higher content of Acrawax C resulted in a higher relative green density and a lower ejection force. However, the effect of Acrawax C content on the relative green density and ejection force was more noticeable for the AZ91 powder. The AZ91 powder had a larger average particle size than the MA AZ91 powder and, as a result, a lower specific surface area, resulting in a higher Acrawax C-to-powder surface ratio for the AZ91 powder. It should also be noted that the average particle size of atomized Acrawax C, namely, 6 μm , is far smaller than those of the AZ91 and MA AZ91 powders (105 μm and 37 μm , respectively). Optimizing the average particle size of Acrawax C may, therefore, enhance its efficiency as a pressing lubricant for the two powders. Considering the slight improving effect of Acrawax C on the compressibility of AZ91 and MA AZ91 powders, we decided not to use any pressing lubricant for uniaxial cold compaction of the Mg-based powders.

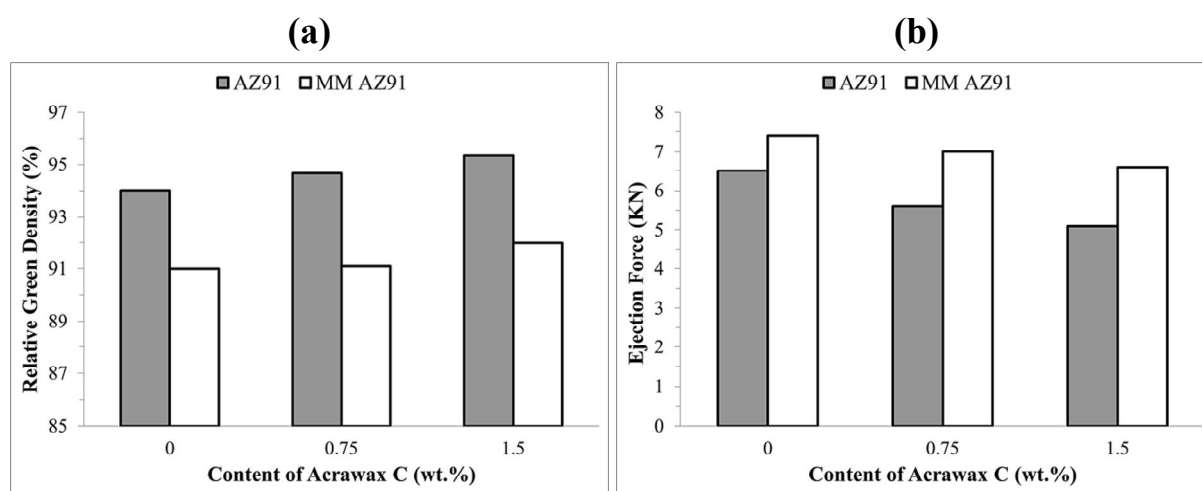


Fig. 5.8. (a) The relative green densities and (b) the ejection forces of AZ91 and MA AZ91 powder compacts as a function of Acrawax C content (Paper Mg III).

For detailed information on the above subject also see **Papers Mg II** and **Mg III**.

5.5 Conventional Sintering.

5.5.1 Effects of Sintering Temperature and Time.

Mechanically ground AZ91, atomized AZ91, and MA AZ91 powders were uniaxially cold pressed at 600 MPa into cylindrical billets measuring 10 mm in diameter and 5 mm in height. The relative green densities of the resultant powder compacts were measured to be 94 %, 96 %, and 90 %, respectively. The green compacts were finally sintered using the heating cycle and sintering parameters introduced in the section 3.5. To develop an optimal sintering process for the mentioned powders, the effects of sintering temperature and time were first studied.

The effect of sintering temperature on the relative densities of the powder compacts sintered in a high-purity Ar atmosphere for 1 h is shown in Fig. 5.9.

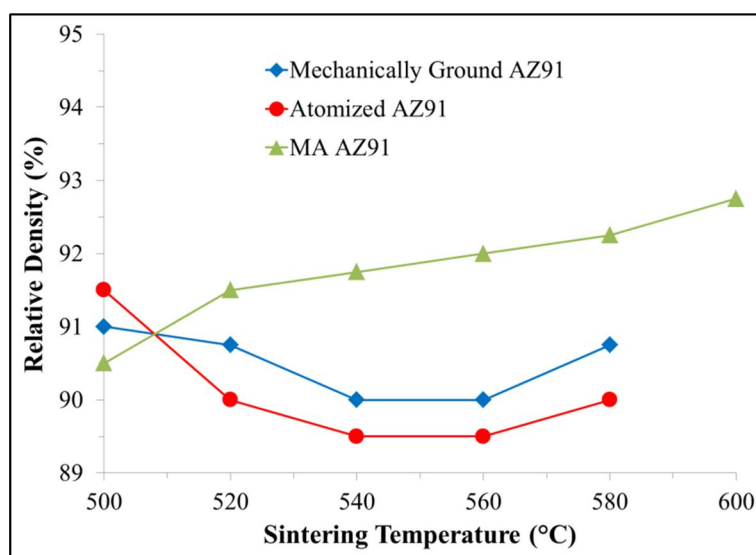


Fig. 5.9. Relative densities of mechanically ground AZ91, atomized AZ91, and MA AZ91 compacts sintered in at different temperatures for 1 h in a high-purity Ar atmosphere.

When assessing the effect of sintering temperature on relative density, a maximum was found for mechanically ground and atomized AZ91 compacts sintered at 500 °C. When sintered at 520 °C and above, there was a minimum in sintered density (at 540 °C) and the compacts became noticeably distorted. In fact, a higher sintering temperature resulted in a higher degree of distortion most probably due to excessive liquid phase formation, which is generally considered unsuitable for an industrial production environment. Besides, some small balls (solid drops) formed on the surfaces of the compacts sintered at 540 °C and above. Distortion and formation of surface balls can both be attributed to the formation of a liquid phase with unfavorable wettability during sintering, amount of which increased with increasing sintering temperature. Atomized AZ91 compacts suffered more from distortion and surface ball-formation compared to their mechanically ground AZ91 counterparts.

Considering all above, 500 °C is taken to be the optimum sintering temperature for the mechanically ground and atomized AZ91 compacts. In the case of MA AZ91 compacts, a higher sintering temperature resulted in a higher sintered density. The MA AZ91 compacts did not distort significantly through sintering. Based on the results illustrated in the Fig. 5.9, 600 °C can be selected as the optimum sintering temperature for MA AZ91 compacts.

Table 5.1 clearly shows that an increase in sintering time from 1 h to 3 h not only does not improve, but also tends to adversely affect the properties of different AZ91 compacts sintered at their optimum sintering temperatures in a high-purity Ar atmosphere. It seems that the oxide layer which normally covers the surface of Mg-based powders is very persistent, and, as a result, increasing the time of sintering from 1 h to 3 h does not help the AZ91 powder particles develop a better bonding with their neighbors. In the case of MA AZ91 compact, prolonging the time of sintering at 600 °C most probably promotes crystallite growth for the nanostructured AZ91 Mg alloy processed by mechanical alloying, resulting in a noticeable decrease in the hardness of sintered compacts.

Table 5.1. Properties of different AZ91 compacts sintered at their optimum sintering temperatures for different times in a high-purity Ar atmosphere. Densities reported as % of theoretical.

Compact - Sintering T (°C)	Green Density (%)	Sintered Density (%)		Hardness (HV1)	
		1 h	3 h	1 h	3 h
Mech. Ground AZ91 - 500	94 ± 0.5	91 ± 0.2	91.3 ± 0.3	38 ± 2	39 ± 2
Atomized AZ91 - 500	96 ± 0.5	91.5 ± 0.2	91 ± 0.4	41 ± 2	39 ± 2
MA AZ91 - 600	90 ± 0.5	92.8 ± 0.3	92 ± 0.3	80 ± 4	68 ± 1.5

5.5.2 Effect of Sintering Atmosphere.

The effect of sintering atmosphere on the sintered properties of different AZ91 compacts is shown in Table 5.2. The effect was the same for all AZ91 compacts. When sintered in the nitrogen (N₂) atmosphere rather than the argon (Ar) atmosphere, AZ91 compacts reached higher sintered densities and hardness values, indicating that the atmosphere plays an active role in the sintering of AZ91 powder compacts and that it is not simply inert. The positive effect of nitrogen atmosphere on sintering was most noticeable for the MA AZ91 compact probably due to the small average particle size of MA AZ91 powder (37 µm), the high percentage of porosity present in the structure of MA AZ91 compact (10 %), and the high sintering temperature employed (600 °C). The first two factors provide a large free surface area within the powder compact which can react with nitrogen at a high sintering temperature of 600 °C. Then, a key feature in the beneficial use of nitrogen may be the formation of magnesium nitride (Mg₃N₂), which can occur because the interior region of the powder compact is essentially oxygen free. The formation of Mg₃N₂ reduces the pressure in the pore

spaces, which unbalances the meniscus forces, inducing pore filling and hence densification [12]. Pore filling may thus be an important densifying mechanism in the sintering of Mg-based powders. Considering all above, the highest quality of sinter for mechanically ground AZ91, atomized AZ91, and MA AZ91 compacts were achieved when sintering at 500 °C, 500 °C, and 600 °C, respectively, for 1 hour in a high-purity nitrogen atmosphere.

Table 5.2. Properties of different AZ91 compacts sintered at their optimum sintering temperatures for 1 h in high-purity Ar and N₂ atmospheres. Densities reported as % of theoretical.

Compact - Sintering T (°C)	Green Density (%)	Sintered Density (%)		Hardness (HV1)	
		Ar	N ₂	Ar	N ₂
Mech. Ground AZ91 - 500	94 ± 0.5	91 ± 0.2	92 ± 0.3	38 ± 2	41 ± 1
Atomized AZ91 - 500	96 ± 0.5	91.5 ± 0.2	92.7 ± 0.2	41 ± 2	43 ± 2
MA AZ91 – 600	90 ± 0.5	92.8 ± 0.3	95.5 ± 0.5	80 ± 4	102 ± 6

5.5.3 Microstructures of the Sintered Specimens.

Fig. 5.10 illustrates the microstructures of the mechanically ground AZ91, atomized AZ91, and MA AZ91 compacts sintered at 500 °C, 500 °C, and 600 °C, respectively, for 1 hour in a high-purity nitrogen atmosphere. Some level of residual porosity (black feature) persisted after sintering. That which remained was small, isolated, and fairly rounded for the MA AZ91 compact. The mechanically ground and atomized AZ91 compacts, however, contained larger and longer pores, and well-defined grain boundaries were still present in their microstructures after sintering. Overall, development of strong inter-particle bonds and a reduction in porosity confirms that a high quality sinter has been achieved for MA AZ91 compact while mechanically ground and atomized AZ91 compacts were not responsive to sintering and did not reach an acceptable sintered density.

Fig. 5.11 contains the XRD patterns of the mechanically ground AZ91, atomized AZ91, and MA AZ91 compacts sintered at 500 °C, 500 °C, and 600 °C, respectively, for 1 hour in a high-purity nitrogen atmosphere, where the dominant phases are found to be α -Mg and β -Mg₁₇Al₁₂. However, the XRD peaks of the β -Mg₁₇Al₁₂ phase are almost undetectable in the pattern obtained for the MA AZ91 compact, which may suggest that the alloying elements for this compact are mostly in solid solution. If so, this can contribute to the high hardness value of MA AZ91 compact through solid solution strengthening.

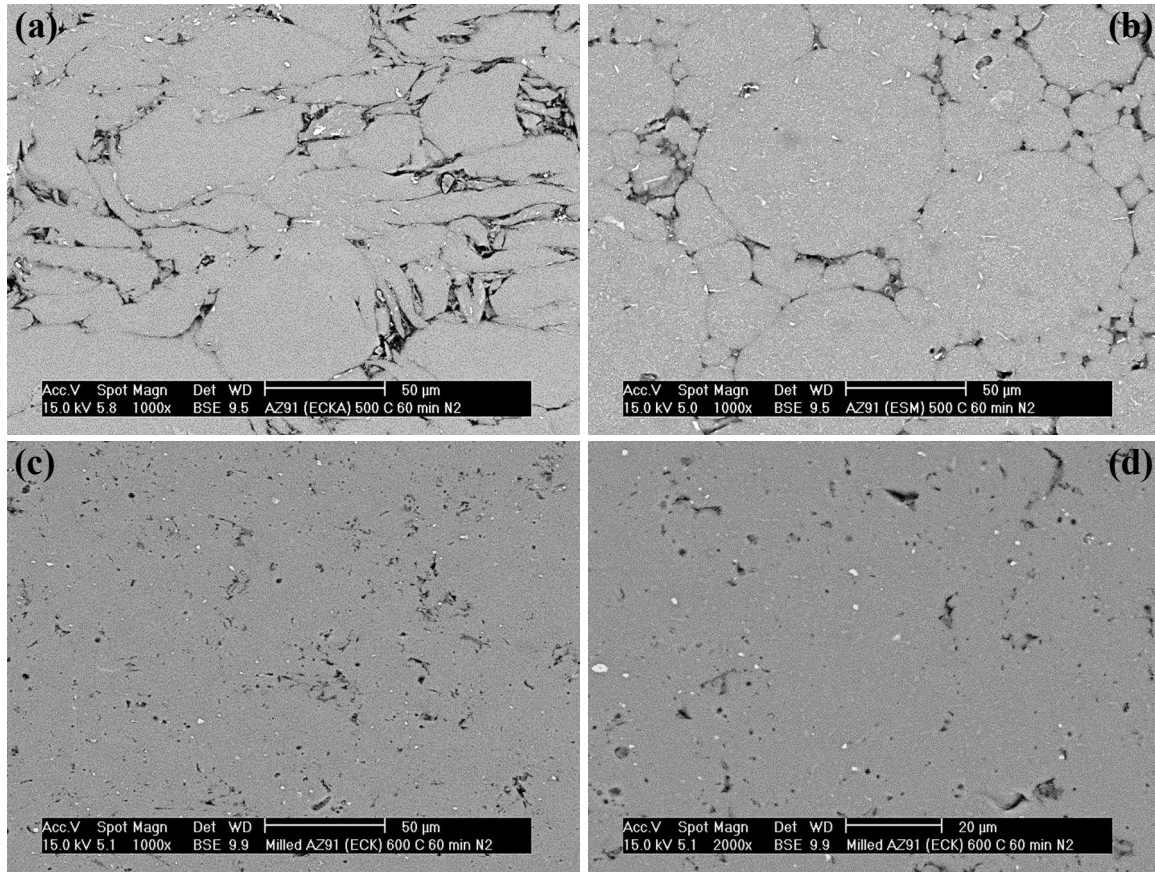


Fig. 5.10. Microstructures of the (a) mechanically ground AZ91, (b) atomized AZ91, and (c) , (d) MA AZ91 compacts sintered at 500 °C, 500 °C, and 600 °C, respectively, for 1 hour in a high-purity N₂ atmosphere.

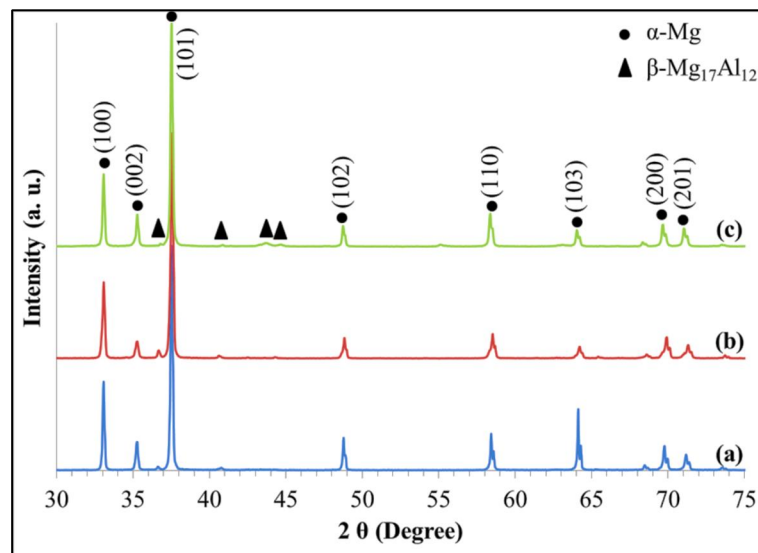


Fig. 5.11. XRD patterns of the (a) mechanically ground AZ91, (b) atomized AZ91, and (c) MA AZ91 compacts sintered at 500 °C, 500 °C, and 600 °C, respectively, for 1 hour in a high-purity N₂ atmosphere.

5.5.4 Simultaneous Thermal Analysis (STA).

A series of STA tests were carried out on mechanically ground AZ91, atomized AZ91, and MA AZ91 powders to determine melting and other thermal events that took place during sintering of them. Fig. 5.12 presents the STA results obtained for the mentioned powders using a constant flow of high-purity argon as the protective gas.

In the mechanically ground AZ91 sample (Fig. 5.12 (a)), the endothermic peak at about 420 °C (“A”) can be attributed to a low-temperature eutectic reaction between the β -Mg₁₇Al₁₂ precipitates, which are present in the microstructure of mechanically ground AZ91 powder (Fig. 5.1 (b)), and the Mg solid solution (α -Mg) matrix of powder particles, leading to the formation of a liquid phase. The large endothermic peaks, which appear upon heating above 515 °C (“B” and “C”), are believed to be melting events attributable to the different constituents of mechanically ground AZ91 powder. The weight gain under argon atmosphere, which seems to start upon heating above 500 °C (“D”), is generally considered to be due to oxidation.

In the atomized AZ91 sample (Fig. 5.12 (b)), the endothermic peak at about 460 °C (“E”) may be related to the formation of a liquid phase due to a low-temperature eutectic reaction. A set of endothermic peaks starting at 520 °C (“F”, “G”, and “H”) is believed to be associated with the melting events within powder particles. The sample starts to gain weight above 500 °C (“I”) most probably because of oxidation.

As explained in the sub-section 5.5.1, the mechanically ground and atomized AZ91 compacts sintered at 520 °C and above suffered from distortion and surface inhomogeneity which, based on the STA results, is closely related to the formation of liquid phases within powder particles. Considering the results of STA, solid state sintering can be determined as the optimum sintering mechanism for mechanically ground and atomized AZ91 powders.

In the MA AZ91 sample (Fig. 5.12 (c)), the first endothermic peak at about 420 °C (“J”) results from a low-temperature eutectic reaction between the β -Mg₁₇Al₁₂ dispersoids and the α -Mg matrix of powder particles. The next endothermic peak (“K”) is very broad and can be associated with several melting events taking place in the temperature range of 480 °C to 540 °C. Both oxidation and the melting events within powder particles should contribute to the set of peaks appearing above 560 °C (“L” and “M”) as the weight gain (starting at “N”) is significant and a mixture of endothermic and exothermic peaks is detectable. Based on the results of STA, sintering of MA AZ91 compacts at 600 °C promotes supersolidus liquid phase sintering (LPS).

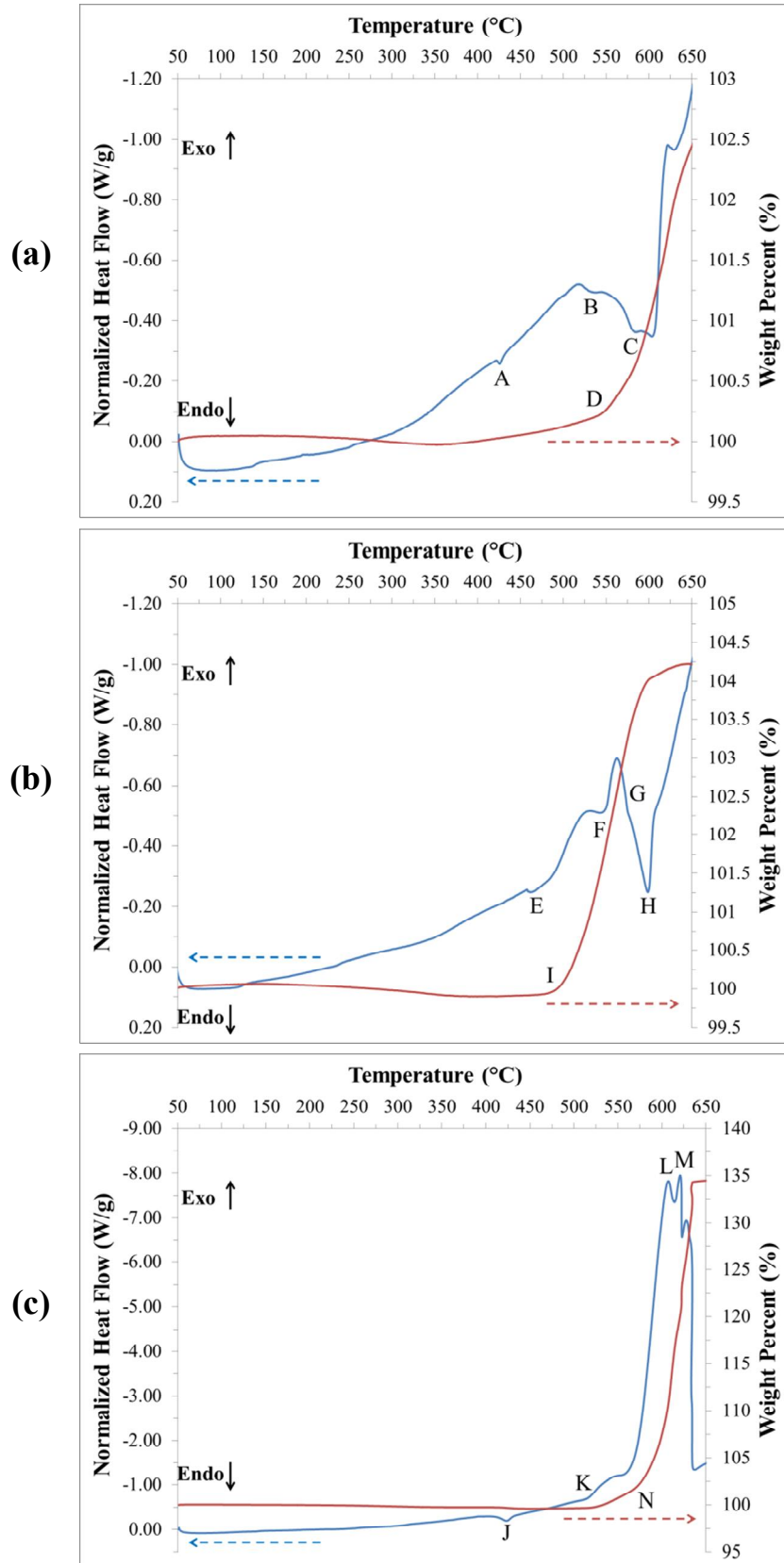


Fig. 5.12. Simultaneous thermal analysis (STA) of the (a) mechanically ground AZ91, (b) Atomized AZ91, and (c) MA AZ91 powders in a high-purity argon atmosphere. The blue and red curves represent DSC and TGA data, respectively.

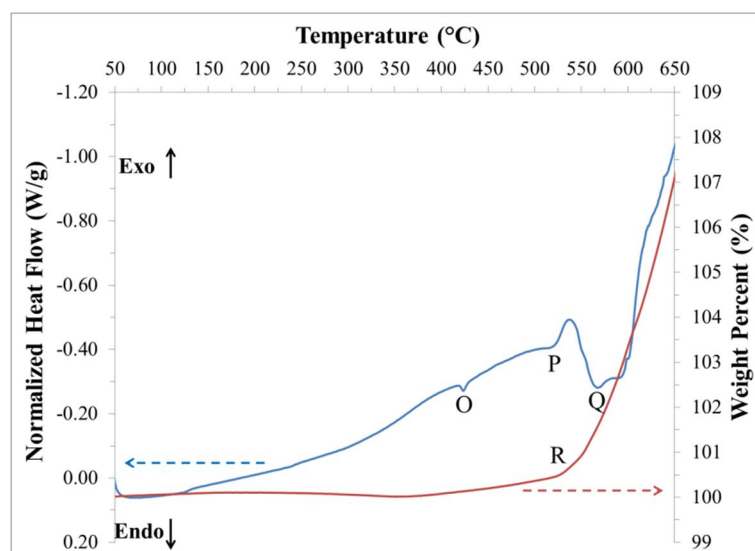


Fig. 5.13. Simultaneous thermal analysis (STA) of the mechanically ground AZ91 powder in a high-purity nitrogen atmosphere. The blue and red curves represent DSC and TGA data, respectively.

Fig. 5.13 presents the STA results obtained for the mechanically ground AZ91 powder using a constant flow of high-purity nitrogen as the protective gas. By comparing Fig. 5.13 with Fig. 5.12 (a), it is evident that the general features of the DSC curve (represented in blue) are basically similar for both protective gases. However, when tested in nitrogen, the sample gained much more weight upon heating above 500 °C (“R”), which confirms that the AZ91 powder particles react with nitrogen at temperatures higher than or equal to 500 °C. As explained in the sub-section 5.5.2, this reaction has positive effects on the sintering response of different AZ91 compacts.

5.6 Field Assisted Hot Pressing (FAHP)

The system and the temperature-load profile used for FAHP of different AZ91 powders were previously explained in detail in the section 3.6 of chapter 3. Fig. 5.14 shows the displacement of a graphite die punch units as a function of sample temperature for different AZ91 powders consolidated by FAHP at a temperature of 400 °C. The 1st shrinking regime occurred when the applied pressure was increased to 50 MPa at the room temperature. The 2nd shrinking regime occurred with increasing temperature while the applied pressure of 50 MPa remained constant. The 3rd shrinking regime occurred with increasing pressure up to 70 MPa while temperature was kept constant at the required FAHP temperature. Having a spherical morphology and a broad particle size distribution, the atomized AZ91 powder exhibited the lowest amount of shrinkage during FAHP. This is probably due to that this powder shows a higher fill density (or tap density) than the mechanically ground and MA AZ91 powders. For this study, the fill density can be defined as the density of a powder in the graphite die used for FAHP just before starting the process and increasing pressure to 50 MPa at the room temperature. The packing characteristics of a powder depend on average particle

size, particle size distribution, morphology, and surface quality. The volume occupied by a given mass largely depends on how particles are positioned during pouring, i.e. whether pores will form due to mutual support and mechanical interlocking, or whether small particles are present which will position themselves interstitially in the gaps between larger particles, or whether the particles even form a partially regular structure. Spherical powders have a higher tap density than an irregular powder of the same material. They have a lower tendency to form bridges and, because of their relatively good mobility, pack quite densely [13].

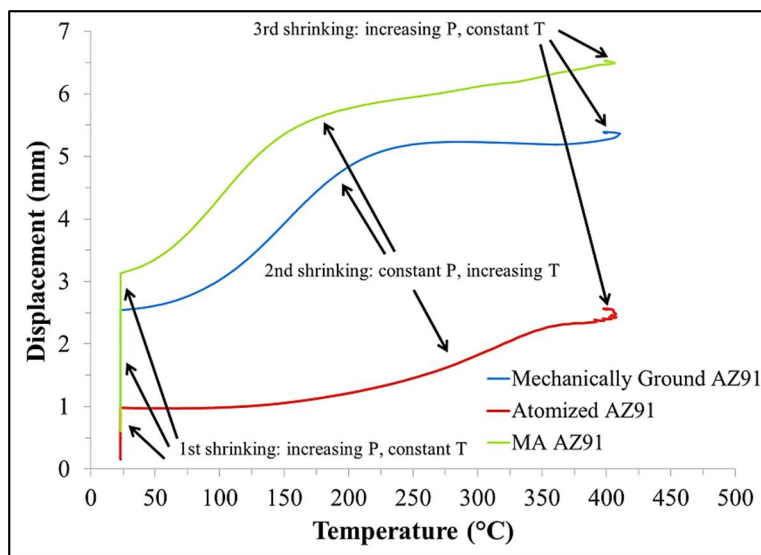


Fig. 5.14. Displacement of graphite die punch units as a function of sample temperature during for different AZ91 powders consolidated at 400 °C.

The effect of FAHP temperature on properties of the bulk samples consolidated from different AZ91 powders by FAHP is shown in Table 5.3. An increase in FAHP temperature from 350 °C to 400 °C practically did not show any positive effect on the densities of the bulk samples. However, the bulk samples consolidated at 400 °C were harder than the ones consolidated at 350 °C, which can be attributed to development of better bonding between powder particles and/or an increase in the amount of alloying elements in solid solution at the higher FAHP temperature. Considering all above, 400 °C can be determined as the optimum FAHP temperature for consolidation of different AZ91 powders. The MA AZ91 compact consolidated by FAHP at 400 °C for 10 minutes shows a hardness value of 162 HV which is considered very high for commercial Mg alloys.

Fig. 5.15 presents the XRD patterns of the bulk samples consolidated from different AZ91 powders by FAHP at a temperature of 400 °C for 10 minutes. The microstructures of the bulk AZ91 samples are basically composed of the α -Mg and β -Mg₁₇Al₁₂ phases. However, the XRD peaks of the β -Mg₁₇Al₁₂ phase are very weak, which may suggest that, after FAHP, the alloying elements are mostly in solid solution in the α -Mg phase. The crystallite size of MA AZ91 bulk sample was measured to be about 135 nm using the Williamson–Hall method [33], showing that the nanocrystalline AZ91 Mg alloy processed by mechanical alloying

experienced some crystalline growth during FAHP. However, this crystallite size is still considered extremely fine for Mg alloys and results in a high hardness value of 162 HV for the bulk material.

Table 5.3. Properties of the bulk samples consolidated from different AZ91 powders by FAHP at 350 °C and 400 °C for 10 min under vacuum. Densities reported as % of theoretical.

Powder	FAHP Temp. (°C)	Density (%)	Hardness (HV1)
Mechanical Ground AZ91	350	98 ± 0.1	69 ± 2
Mechanical Ground AZ91	400	98.2 ± 0.1	74 ± 1
Atomized AZ91	350	98.4 ± 0.1	72 ± 2
Atomized AZ91	400	98.6 ± 0.1	80 ± 2
MA AZ91	350	98.3 ± 0.1	152 ± 3
MA AZ91	400	99 ± 0.1	162 ± 4

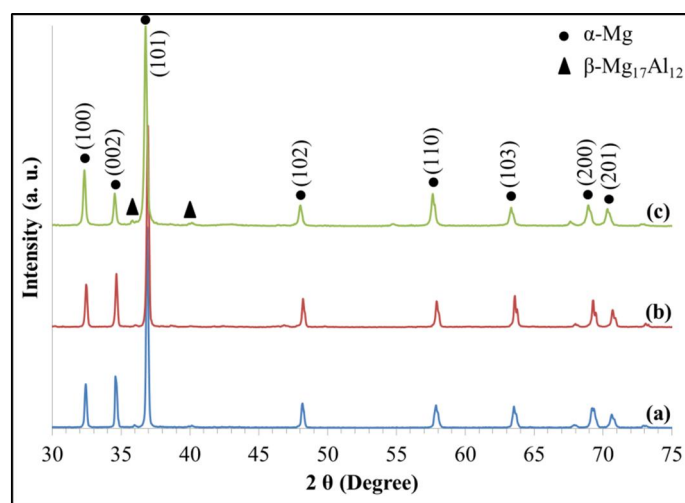


Fig. 5.15. XRD patterns of the bulk samples consolidated from (a) mechanically ground AZ91, (b) atomized AZ91, and (c) MA AZ91 powders by FAHP at 400 °C for 10 min under vacuum.

Fig. 5.16 illustrates the microstructures of the bulk samples consolidated from different AZ91 powders by FAHP at a temperature of 400 °C for 10 minutes. The powder particles appear to be welded together and well-bonded as the initial interfaces of powder particles are no longer distinguishable. As expected from the density measurement results, very limited residual porosity (black features) is present in the microstructures, which can be characterized as small, randomly distributed, and rounded. Some of the precipitates present in the microstructure of mechanically ground AZ91 powder (Fig. 5.1 (b)) persisted after FAHP and are easily visible (Fig. 15.16 (a)).

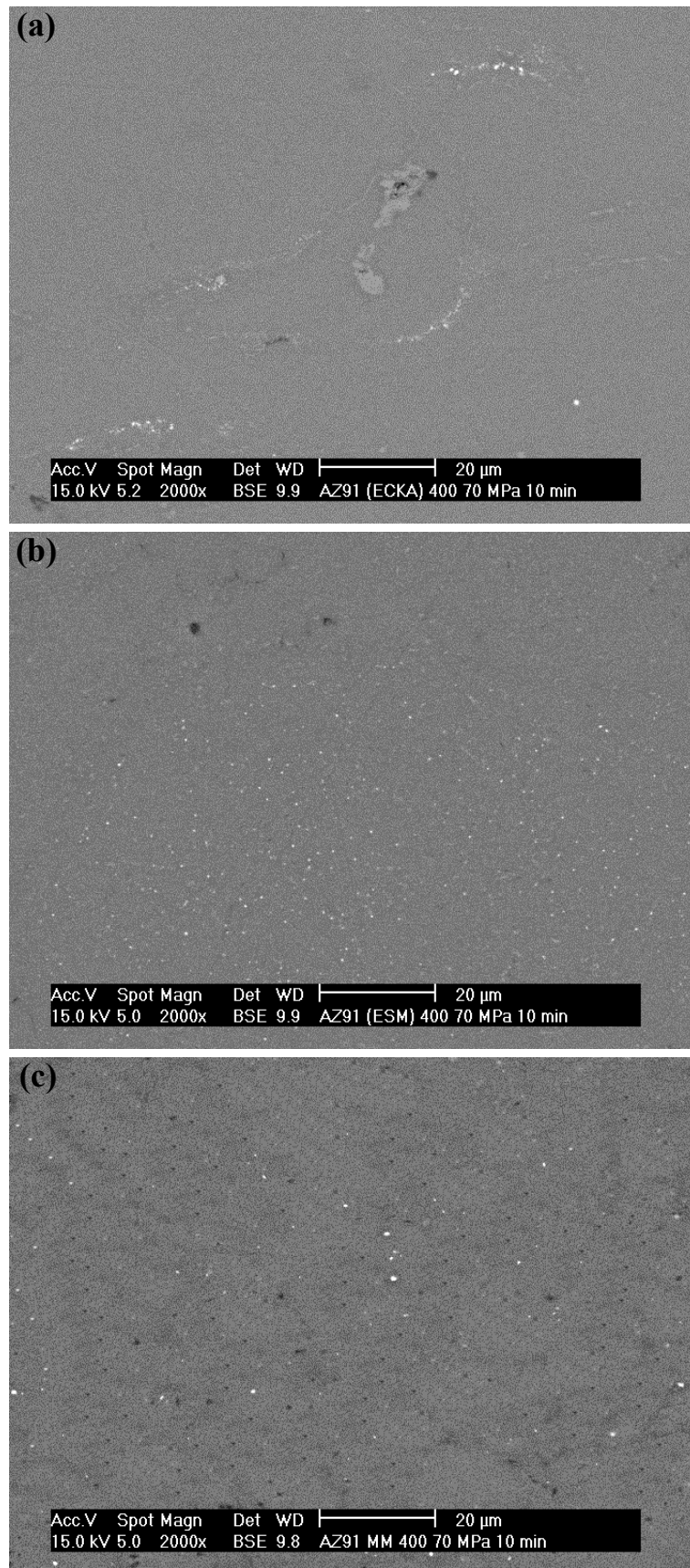


Fig. 5.16. Microstructures of the bulk samples consolidated from (a) mechanically ground AZ91, (b) atomized AZ91, and (c) MA AZ91 powders by FAHP at 400 °C for 10 min under vacuum.

5.7 Hot Deformation of an AZ91 Mg PM Alloy.

The **Paper Mg IV** included in the appendix examines the hot deformation behavior and workability characteristics of AZ91 Mg alloy powder compact (uniaxially cold pressed from mechanically ground AZ91 powder at 600 MPa) by performing hot compression tests with a Gleeble 3800 machine. To this end, green powder compacts with a relative green density of 93 % were hot-compressed at temperatures ranging from 150 °C to 500 °C and at true strain rates ranging from 0.001 s⁻¹ to 10 s⁻¹.

The true stress-true strain curves obtained at a deformation temperature of 350 °C and at different strain rates are shown in Fig. 5.17, and represent the typical deformation behavior observed for the AZ91 powder compacts. As it can be seen, the true stress-true strain curves peaked at low strains, after which the flow stress increased slightly or remained constant. The work hardening rate decreased with increasing deformation temperature or strain rate. Processing maps were developed for all of the hot compression tests at strains of 0.1, 0.5, and 0.8 (Fig. 5.18), which represented a safe deformation domain at deformation temperatures and strain rates in the ranges of 150-300 °C and 0.001-0.01 s⁻¹. Kinetic analysis of the flow stress data for the safe deformation domain yielded an activation energy of 75 kJ/mol which is lower than those previously reported for the hot compression of bulk AZ91 Mg alloy. According to the developed processing maps and the microstructures of the hot-compressed specimens, the optimum hot working window for AZ91 Mg alloy powder compacts was determined to lie between 275-325 °C and 0.001-0.01 s⁻¹.

For detailed information on this section refer to the **Papers Mg IV**.

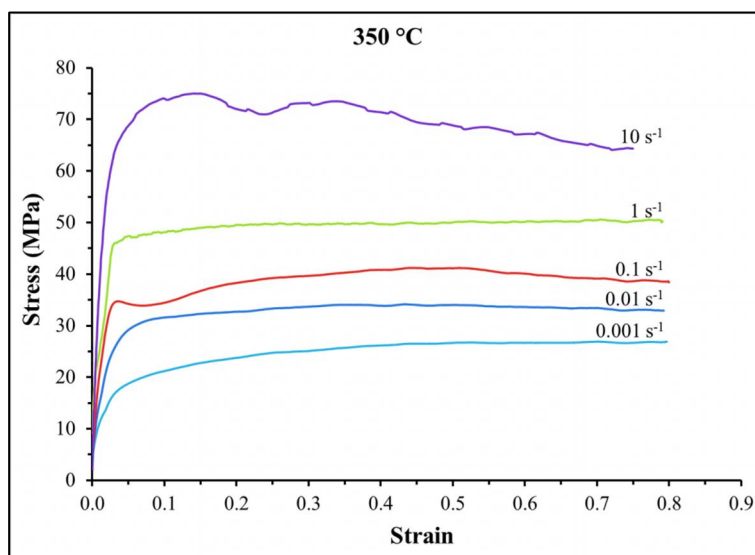


Fig. 5.17. True stress-true strain curves of the AZ91 Mg alloy powder compacts hot-compressed at a deformation temperatures of 350 °C and at different strain rates (Paper Mg IV).

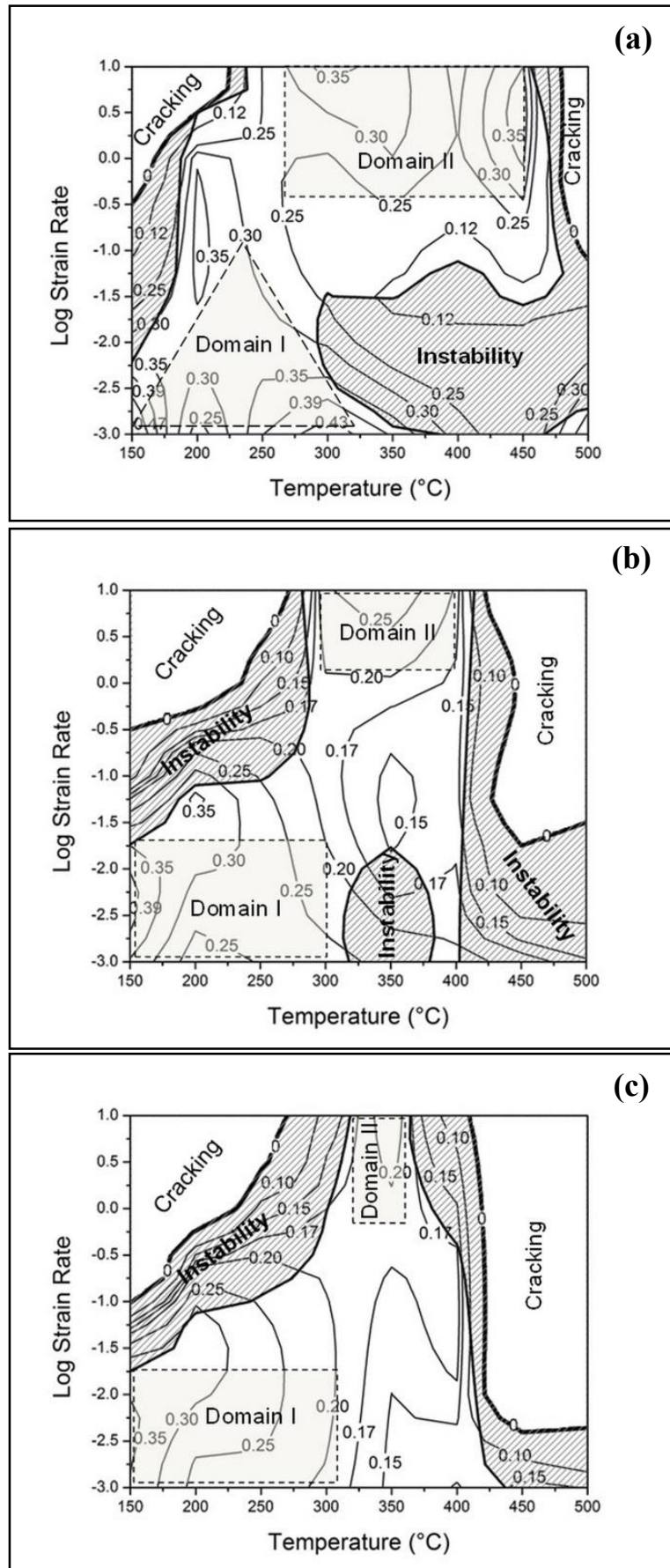


Fig. 5.18. Processing maps of AZ91 compacts developed at strains of (a) 0.1, (b) 0.5, and (c) 0.8 (Paper Mg IV).

5.8 Hot Deformation of a Nanocrystalline AZ91 Mg PM Alloy.

The **paper Mg V** included in the appendix concerns the hot deformation behavior and workability characteristics of a nanocrystalline AZ91 Mg alloy by performing hot compression tests with a Gleeble 3800 machine. To this end, the MA AZ91 powder with a crystallite size of 25 nm was uniaxially cold pressed at 600 MPa into cylindrical compacts measuring 10 mm in diameter and 12 mm in height. Then, the powder compacts with a relative green density of 91 % were hot-compressed at temperatures ranging from 150 °C to 500 °C and at true strain rates ranging from 0.001 s⁻¹ to 10 s⁻¹.

The true stress-true strain curves obtained at a deformation temperature of 350 °C and at different strain rates are shown in Fig. 5.19, and represent the typical deformation behavior observed for the MA AZ91 powder compacts. The true stress-true strain curves peaked at low strains, after which the flow stress increased moderately. In fact, the true stress-true strain curves were of flow hardening type. As a general trend, when the deformation temperature increased or the strain rate decreased, a decrease in the flow stress level was observed. Processing maps were developed for all of the hot compression tests at strains of 0.1, 0.5, and 0.8 (Fig. 5.20), which represented a safe deformation domain at deformation temperatures and strain rates in the ranges of 250-350 °C and 0.1-10 s⁻¹. The crystallite size of the nanocrystalline AZ91 Mg alloy hot-compressed within the aforementioned domain was measured to be 140 nm, which is considered very fine for Mg alloys and resulted in a high hardness value of 133 HV for the hot-compressed alloy.

For detailed information on this section refer to the **Papers Mg V**.

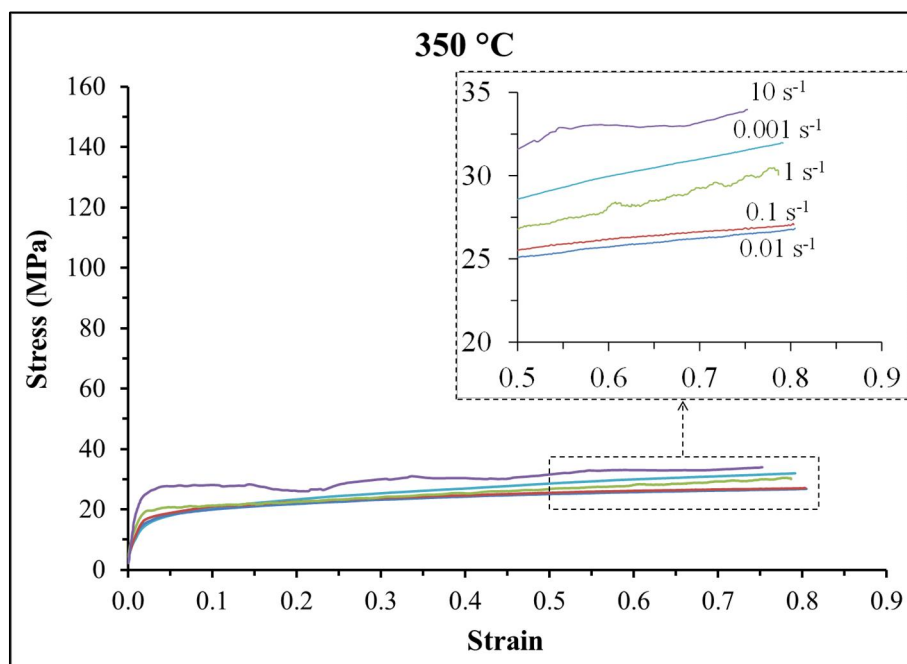


Fig. 5.19. True stress-true strain curves of MA AZ91 compacts hot-compressed at a deformation temperature of 350 °C and at different strain rates (Paper Mg V).

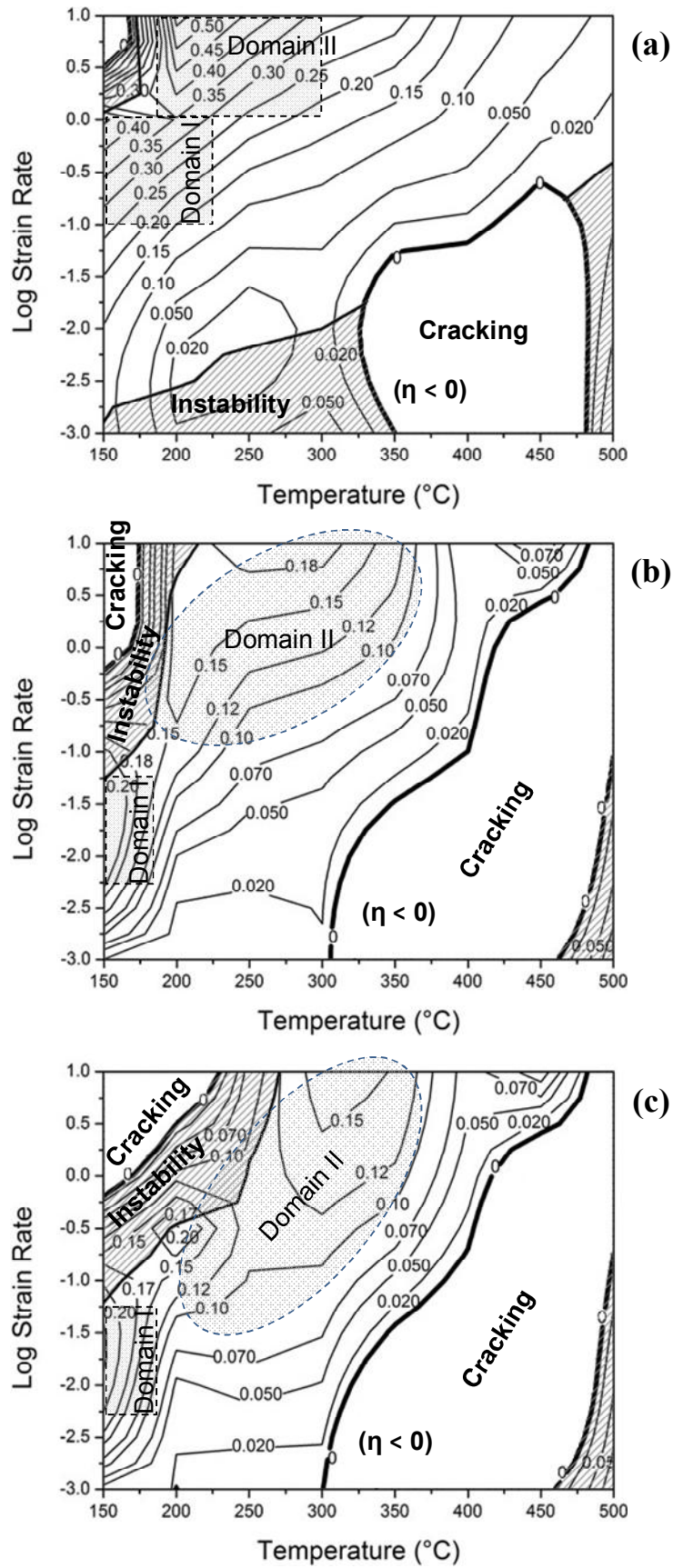


Fig. 5.20. Processing maps of MA AZ91 compacts developed at strains of (a) 0.1, (b) 0.5, and (c) 0.8 (Paper Mg V).

5.9 Partial Conclusions

Through the work completed in this study the following conclusions have been reached:

1. High-energy milling was found to be an effective technique for processing nanocrystalline AZ91 Mg alloy. Using a pre-alloyed AZ91 powder produced by mechanical grinding as the starting material, an alloy powder with a crystallite size of about 25 nm was synthesized via 14 h of mechanical alloying in an attritor mill. The nanostructured AZ91 alloy processed by high-energy milling showed good thermal stability, retaining its crystallite size of less than 100 nm after having been annealed at 300 °C for 4 h.
2. Sintering temperature was shown to have the most marked difference in the properties of the sintered AZ91 compacts. The AZ91 powders produced by mechanical grinding and atomization were not responsive to conventional sintering. The compacts cold pressed from the mentioned powders distorted significantly and formed surface inhomogeneity when sintered at temperatures higher than or equal to 520 °C due to formation of a non-wetting liquid phase. A higher sintering temperature, however, resulted in better properties for the compacts cold pressed from the AZ91 powder processed by mechanical alloying. Statistically, the effect of the sintering time on the final properties of the samples was negligible. It was also found that changing the sintering atmosphere from argon to nitrogen produced samples with improved properties.
3. Bulk samples were successfully consolidated from different AZ91 powders (produced by mechanical grinding, atomization, and mechanical alloying) by field assisted hot pressing (FAHP) technique. The average particle size, particle size distribution, and morphology of the starting AZ91 powder were found to have significant effects on the shrinking regimes of FAHP. Although not affecting the density, an increase in processing temperature improved the hardness of the bulk AZ91 samples processed by FAHP. FAHP at a low temperature of 400 °C for 10 min was able to process a fully dense bulk sample with a crystallite size of about 135 nm and a hardness value of 162 HV, showing that the nanocrystalline AZ91 powder produced by mechanical alloying can be effectively consolidated by the FAHP technique.
4. Hot compression testing was employed to study the hot deformation behavior and workability characteristics of the green compacts cold pressed from the AZ91 powders produced by mechanical grinding and mechanical alloying. To this end, the data obtained through the hot compression of the mentioned compacts were analyzed to develop processing maps. Strain was found to have important effects on the processing maps of both powders. The AZ91 alloy produced by mechanical grinding showed good workability at moderate deformation temperatures (275-325 °C) and

low strain rates ($0.001\text{--}0.01\text{ s}^{-1}$) while the AZ91 alloy processed by mechanical alloying was capable of being deformed at high strain rates. The optimum hot working window for the compacts of mechanically alloyed AZ91 powder was determined to lie between $250\text{--}350\text{ }^{\circ}\text{C}$ and $0.1\text{--}10\text{ s}^{-1}$. The AZ91 compacts exhibited significant increases in density through hot compression, which may confirm that full density can be achieved for both AZ91 powders using hot deformation processes such as powder extrusion and forging.

References

- [1] P. Burke, C. Petit, S. Yakoubi, G.J. Kipouros, Thermal Effects of Calcium and Yttrium Additions on the Sintering of Magnesium Powder, in: Magnesium Technology 2011, John Wiley & Sons, Inc., 2011, pp. 481-484.
- [2] J.-y. Li, J.-x. Xie, J.-b. Jin, Z.-x. Wang, Transactions of Nonferrous Metals Society of China, 22 (2012) 1028-1034.
- [3] E. Cerri, P. Leo, P.P. De Marco, J. Mater. Process. Technol., 189 (2007) 97-106.
- [4] J.B. Fogagnolo, M.H. Robert, J.M. Torralba, Mater. Sci. Eng., A, 426 (2006) 85-94.
- [5] N. Yazdian, F. Karimzadeh, M. Tavoosi, Journal of Alloys and Compounds, 493 (2010) 137-141.
- [6] C. Suryanarayana, Prog. Mater. Sci., 46 (2001) 1-184.
- [7] M. Wolff, T. Ebel, M. Dahms, Adv. Eng. Mater., 12 (2010) 829-836.
- [8] R.M. German, Powder Metallurgy Science, 2nd ed., MPIF, Princeton, United States, 1994.
- [9] R. Panelli, F. Ambrosio Filho, Powder Metall., 41 (1998) 131-133.
- [10] Z. Razavi Hesabi, H.R. Hafizpour, A. Simchi, Mater. Sci. Eng. A, 454-455 (2007) 89-98.
- [11] J.B. Fogagnolo, E.M. Ruiz-Navas, M.H. Robert, J.M. Torralba, Mater. Sci. Eng. A, 355 (2003) 50-55.
- [12] G.B. Schaffer, B.J. Hall, S.J. Bonner, S.H. Huo, T.B. Sercombe, Acta Materialia, 54 (2006) 131-138.
- [13] W. Schatt, W. Klaus-Peter, Powder metallurgy: processing and materials, European Powder Metallurgy Association (EPMA), Shrewsbury, UK, 1997.

CONCLUSIONS

6

CHAPTER 6 CONCLUSIONS

Using 7075 Al alloy and AZ91 Mg alloy, which show relatively high strengths when compared with all other commercial Al and Mg alloys, as the starting materials, the aim of this thesis was to produce high-performance Al and Mg alloys via powder metallurgy (PM) using different powder processing techniques and consolidation routes and to understand the effects of consolidation route and its process variables through undertaking a comprehensive study of the microstructural and mechanical characteristics of consolidated alloys.

As main conclusion can be highlighted that PM technology offers different ways to enhance the properties of 7075 Al and AZ91 Mg alloys by acting on the starting powders (by grain refinement) as well as optimization of the cold pressing and sintering process and/or the joint application of pressure and temperature (FAHP or hot extrusion). This main conclusion can be divided and motivated into the following partial conclusions:

1. The grain refinement approach was selected to enhance the mechanical properties of starting materials. Considering that the starting materials were in powder form, the mechanical alloying technique seemed to be the best choice for the manufacturing of nanocrystalline alloy powders with desired characteristics in high quantity. The main challenge was to optimize this technique for the safe production of high-quality nanostructured products from the starting powders. The nanostructured alloys processed by mechanical alloying were found to be resistant to crystalline growth at high temperatures, allowing them to be consolidated by conventional PM routes without losing significantly their superior properties.

2. Cold compaction and sintering is widely regarded as the most convenient PM route for consolidating metallic powders. However, the main challenge remains optimizing the processing parameters such as sintering temperature, time, and atmosphere for obtaining the best sintered properties. The nanocrystalline powders processed by mechanical alloying did not show good response to sintering and suffered from crystalline growth during the sintering process, confirming that these powders cannot effectively be consolidated by this route. Thanks to its chemical composition specifically designed for sintering, Alumix 431D was highly responsive to sintering and reached high sintered densities through liquid phase sintering. By contrast, liquid phase sintering was found to have detrimental effects on the sintering of the AZ91 alloy powders produced by mechanical grinding and atomization. The systematic sintering studies of AZ91 powders exhibit that the main barrier to successful sintering remains improving the wettability of the liquid phase which forms during the sintering process.

3. In contrast to sintering, field-assisted hot pressing (FAHP) was capable of processing full-density bulk materials from the mechanically alloyed powders. Thanks to the low

pressing temperature and short processing time used, the bulk alloys consolidated from nanocrystalline 7075 Al and AZ91 Mg alloy powders exhibited ultra-fine grain structures and very high hardness values. Fully dense products were also consolidated from the AZ91 powders produced by mechanical grinding and atomization, confirming that FAHP has great potential for Mg PM.

4. Pores present in the microstructure of porous materials act as stress concentration points, increasing the sensitivity to cracking and limiting the amount of deformation to fracture. Nevertheless, uniaxial hot compression provides useful information on the hot deformation behavior and workability characteristics of powder compacts. The data obtainable through hot compression testing can be analyzed to develop processing maps, which determine the optimum hot deformation window for each powder compact. Different powder compacts exhibited good workability within their optimized hot deformation window and produced crack-free, uniformly deformed specimens, suggesting that the developed processing maps successfully identified the safe domain for the hot deformation of each powder compact.

5. Hot extrusion without canning and degassing was used to produce full density alloys from the as-received and mechanically alloyed powders. The microstructures and mechanical properties of the extrusion products were carefully studied. The obtained results confirmed that the hot extrusion without canning and degassing can be considered as an advantageous technique for consolidation of the Al-based and Mg-based powders.

6. Through the characterization techniques employed for this thesis, it has been shown that the bulk alloys consolidated from the nanocrystalline 7075 Al and AZ91 Mg alloy powders exhibit as-fabricated mechanical properties which are superior to those of their wrought counterparts after heat treatment.