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Los Angeles

High Strength and Thermally Stable

Nanostructured Magnesium Alloys and Nanocomposites

A dissertation submitted in partial satisfaction of the requirements for the
degree Doctor of Philosophy in Materials Science and Engineering

By

Yuan-Wei Chang

2015

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ABSTRACT OF THE DISSERTATION

High Strength and Thermally Stable

Nanostructured Magnesium Alloys and Nanocomposite

by

Yuan-Wei Chang

Doctor of Philosophy in Materials Science and Engineering

University of California, Los Angeles, 2015

Professor Jenn-Ming Yang, Chair

Magnesium and its alloys are currently in the spotlight of global research because of the need to limit energy consumption and reduce the environmental impact. In particular, their low densities compared to other structural metals make them a very attractive alternative in the automobile and aerospace industries. However, their low

strength compared to other structural materials (e.g. Al and steels) has limited their widespread application.

This dissertation presents the results of developing and investigation of a high strength nanostructured magnesium-aluminum alloy and composite. The nanostructured magnesium alloy is prepared by cryomilling and consolidated by spark-plasma-sintering. Focused ion beam is used to prepare micropillars with different diameters ranging from 1.5 to 8 μm and micro-compression test is conducted by nanoindenter in order to evaluate the mechanical properties. The yield strength obtained in the present study is around three times higher than conventional magnesium alloys (120 MPa vs. 370 MPa). The yield strength of the nanostructured magnesium alloy is further improved through hot extrusion, resulting in a yield strength of 550 MPa and an ultimate strength of 580 MPa. The nanostructured magnesium alloy exhibits a strong size-dependence, and a significant improvement in strength is observed when the pillar diameter is reduced to below 3.5 μm . The deformation mechanisms of the compressed pillars were characterized using transmission electron microscopy. The size-induced strengthening is attributed to a less number of dislocation sources along with a higher activity of non-basal deformation mechanisms.

We have also developed a high strength and thermally stable nanostructured magnesium composite by adding diamantane. A yield strength of 500 MPa is achieved,

moreover, excellent thermal stability is demonstrated in the magnesium alloy containing diamantanes. The strength and grain size are thermally stable after annealing at 400°C for 100 hours. In contrast, the yield strength of the alloy without diamantanes decreases significantly after annealing due to severe grain growth. These results suggest that diamantanes are pinning the grain boundaries and inhibiting grain growth at elevated temperatures. Finally, molecular dynamics simulations and finite element analysis are used to explore the deformation mechanisms of magnesium with different grain sizes at atomic resolutions and correct tapering effect on micro-compression test, respectively. The results in the dissertation show that nanostructured Mg-Al alloy and Mg-Al-Diamantane composite are promising materials for aerospace and automobile industries.

The dissertation of Yuan-Wei Chang is approved.

Suneel Kodambaka

Jiann-Wen Ju

Jenn-Ming Yang, Committee Chair

University of California, Los Angeles

2015

Dedicated to my father, mother, sister and Jean.

TABLE OF CONTENTS

LIST OF FIGURES.....	xiii
LIST OF TABLES.....	xx
ACKNOWLEDGEMENTS.....	xxi
VITA.....	xxii
PUBLICATIONS AND PRESENTATIONS.....	xxiii
Chapter 1 Introduction.....	1
1.1 Motivation.....	1
1.2 Research Problem.....	2
1.3 Scope of the Thesis.....	3
1.4 Reference.....	6
Chapter 2 Literature Review.....	7
2.1 Magnesium.....	7
2.2 Solid Solution and Precipitation Strengthening of Magnesium Alloys.....	8
2.3 Grain Size Refinement Strengthening of Magnesium Alloys.....	10
2.4 Nanostructured Materials.....	10
2.4.1 Mechanical Properties of Nanostructured Materials.....	12
2.4.2 Hall-Petch Relation: Regime I and II.....	13
2.4.3 Inverse Hall-Petch Relation: Regime III.....	15

2.5 Specimen Size Effect.....	16
2.6 Reference.....	19
Chapter 3 Characterizations of Nanostructured Magnesium-Aluminum Alloys.....	33
3.1 Introduction.....	34
3.2 Materials and Methods.....	37
3.2.1 Focused Ion Beam.....	39
3.2.2 Nanoindentation.....	40
3.3 Results and Discussion.....	42
3.3.1 SEM and TEM Analysis of Nanostructured Magnesium Alloy.....	42
3.3.2 SEM and TEM Analysis of the Extruded Nanostructured Magnesium Alloy	44
3.3.3 XRD Analysis of the Extruded Nanostructured Magnesium Alloy.....	46
3.3.4 Mechanical Behavior of the Extruded Nanostructured Magnesium Alloy	48
3.3.5 Micro-compressive Mechanical Properties of Nanostructured Magnesium Alloy.....	54
3.3.6 Strain Rate Sensitivity (SRS) of Nanostructured Magnesium Alloy.....	58
3.4 Conclusions.....	59
3.5 Reference.....	61

Chapter 4 Size-Induced Strengthening in Nanostructured Magnesium Alloy Micropillars

.....	82
4.1 Introduction.....	82
4.2 Materials and Methods.....	84
4.3 Results and Discussion.....	85
4.3.1 Characteristic of Micropillar with Different Sizes.....	85
4.3.2 Deformation Mechanism Analysis of Micropillar with Size Effect.....	87
4.4 Conclusions.....	89
4.5 Reference.....	90

Chapter 5 Characterizations of Nanostructured Magnesium Nanocomposites Reinforced by Diamantane..... 96

5.1 Introduction.....	97
5.2 Materials and Methods.....	100
5.3 Results and Discussion.....	102
5.3.1 Microstructural Characterization.....	102
5.3.2 Mechanical Characterization.....	107
5.3.3 Effect of Diamantane on the Precipitation of γ -Al ₁₂ Mg ₁₇ Phase.....	111
5.3.4 Diamantane/Mg-matrix Interaction.....	114
5.3.5 Effect of Diamantane on the Mechanical Behavior.....	114

5.4 Conclusions.....	117
5.5 Reference.....	120
Chapter 6 Thermally Stable Nanostructured Magnesium Nanocomposites Reinforced by Diamantane.....	131
6.1 Introduction.....	131
6.2 Materials and Methods.....	134
6.3 Results and Discussion.....	135
6.3.1 Grain Size Analysis After Annealing.....	135
6.3.2 Micro-Compression Analysis After Annealing.....	139
6.4 Conclusions.....	141
6.5 Reference.....	143
Chapter 7 Simulations of Mechanical Behavior in Magnesium and Micropillars.....	149
7.1 Introduction.....	149
7.2 Materials and Methods.....	151
7.2.1 Molecular Dynamic Simulation.....	151
7.2.2 Finite Element Analysis	152
7.3 Results and Discussion.....	152
7.3.1 Molecular Dynamic Simulation of Twinning in Magnesium.....	152
7.3.2 Finite Element Analysis of Micro-Compression.....	154

7.4 Conclusions.....	155
7.5 Reference.....	157
Chapter 8 Conclusions.....	167
8.1 The Current Research Accomplishments.....	167
8.2 Recommendations for Future Work.....	170

LIST OF FIGURES

Fig. 2-1 Deformation slip system of magnesium: (a) basal slip (b) prismatic slip and (c) pyramidal slip.....	24
Fig. 2-2 Rotation of basal planes due to twinning: (a) the initial material element representing the initial crystallographic directions c and a (b) lenticular represents the tensile twinning (c) contraction twinning.....	25
Fig. 2-3 modulus-normalized yield strength $\log \sigma / \mu$ vs. Burgers vector-normalized grain size $\log d / b$ for Cu, Ag and Au at 300K.....	26
Fig. 2-4 Mechanisms by which grain boundaries can affect the dislocation density (a) generation of dislocation at grain boundary ledges (b) reduction of the free slip distance and (c) geometric dislocation.....	27
Fig. 2-5 Dislocation density ρ vs. $1/d$ for the plastic deformed Cu at 300K.....	28
Fig. 2-6 Modulus normalized tensile yield strength σ / μ vs. square root of the dislocation density $\rho^{1/2}$ for Cu deformed at 300K.....	29
Fig. 2-7 TEM images of nanostructured WC with uniform grain size: (a) average grain size 11 nm and (b) average grain size 6 nm.....	30
Fig. 2-8 Hardness of WC as a function of inverse square root of the grain size.....	31
Fig. 2-9 The grain size dependence of the flow stress. (A) Stress-strain curves for 10 simulations with varying grain sizes. (B) The flow stress, defined as the average stress in the strain interval from 7 to 10% deformation. The error bars indicate the fluctuations in this strain interval. A maximum in the flow stress is seen for	

grain sizes of 10 to 15 nm, caused by a shift from grain boundary-mediated to dislocation-mediated plasticity.....	32
Fig. 3-1 The procedure of micro-pillar fabrication by using FIB.....	66
Fig. 3-2 Testing sample for nanoindentation.....	67
Fig. 3-3 A schematic representation of load vs. Indentation displacement data for an indentation experiment. The quantities shown are P_{max} : the peak indentation load; h_{max} : the indenter displacement at peak load; h_f : the final depth of the contact impression after unloading; and S : the initial unloading stiffness.....	68
Fig. 3-4 (a) Scanning electron microscopy (SEM) and electron dispersive spectroscopy (EDX) analysis of Mg-10Al after SPS consolidation. (b) EDX spectra and the quantitative analysis (insets) from the points highlighted by 1 and 2 in (a).....	69
Fig. 3-5 (a) Bright-field TEM image of the SPS'ed Mg90Al10 sample. Inset is the SAED pattern. (b) and (c) Scanning transmission electron microscopy (STEM) images of the SPS'ed Mg-10Al sample. (d) Electron dispersive spectroscopy (EDS) spectra and quantitative values (inset) from the marked points in (c).....	70
Fig. 3-6 Scanning electron microscopy (SEM) images of (a) a transverse section and (b) a longitudinal section of the extruded Mg-10Al sample.....	71
Fig. 3-7 (a) Bright-field TEM image of a cross-sectional view of the extruded Mg-10Al sample. (b) Bright-field TEM image of a coarse-grained region. (c) Bright-field TEM image of a coarse grain boundary. Inset is the SAED pattern of this grain.	

(d) HRTEM image of the grain boundary in (c). Inset is fast Fourier transform (FFT) of the image.....	72
Fig. 3-8 (a) STEM image of a parallel view of the extruded Mg-10Al sample. (b)–(d) Higher magnification STEM images from different regions of the extruded Mg-10Al sample. (e) EDS spectra and quantitative values (inset) from selected points of interest. (f) EDS line scan as a function of position along the orange arrow marked in (d).....	
	73
Fig. 3-9 (a) HRTEM image of an individual γ -Al ₁₂ Mg ₁₇ nanoprecipitate. (b) Fourier filtered HRTEM image of the nanoprecipitate. A and B are the FFT of the highlighted regions in (a) and (b). C is the color-coded indexed FFT in B for clarity.....	
	74
Fig. 3-10 X-ray diffraction spectra for the cryomilled Mg-10Al powders, and the SPS'ed and extruded samples.....	
	75
Fig. 3-11 Engineering stress–strain curves of the SPS'ed (left) and extruded (right) Mg-10Al samples obtained from compression tests.....	
	76
Fig. 3-12 (a) In-situ SEM compressive stress–strain curves for two nanostructured Mg-pillars. The blue one was stopped at 10% of strain. (b, c) SEM images of the Mg-pillar before and after compression at 10% of strain.....	
	77
Fig. 3-13 (a) SEM and (b) TEM images of the compressed pillar at $\epsilon=10\%$. (c) SAED pattern from the top of the pillar. (d) Dark-field TEM image showing nanocrystalline grains.....	
	78

Fig. 3-14 (a) TEM image of the shear band. (b) Close-up image of the shear band region highlighted in (a). Inset is the micro-diffraction pattern. (c) HRTEM images showing stacking faults (SFs). Inset is the FFT of the image. Fourier filtered HRTEM image showing SFs from the region highlighted in (c).....	79
Fig. 3-15 (a) Fourier filtered HRTEM image of contraction nanotwins. (b) FFT of the image in (a). (c) Color-coded indexed FFT for clarity.....	80
Fig. 3-16 (a) Average hardness as a function of the strain rate ranging from 0.001 to 1 of Mg-10Al alloy (b) Logarithm of the average hardness as a function of the logarithm of the strain rate.....	81
Fig. 4-1 SEM images of nanostructured Mg–10Al micropillars with different diameters (a)–(d) before and (e)–(h) after compression (2% of compressive strain).....	93
Fig. 4-2 (a) Compressive stress–strain curves of nanostructured Mg–10Al micropillars.(b) Compressive yield strength as a function of pillar diameter.....	94
Fig. 4-3 (a) Bright-field TEM image of a compressed 2.5μm micropillar. (b) HRTEM image showing extension twins in a grain oriented to the $\langle 2\bar{1}\bar{1}0 \rangle$ zone axis. Inset is its FFT. (c) HRTEM image showing prismatic dislocations terminated at SFs in a grain oriented to the $\langle 1\bar{2}1\bar{3} \rangle$ zone axis. Inset is its FFT.....	95
Fig. 5-1 Optical microscopy (a) and scanning electron microscopy (SEM) (b) images of diamantane powders.....	123
Fig. 5-2 SEM images of the bulk Mg-10Al alloy (a,b) and Mg-10Al -1 Dia nanocomposite (c,d).....	124

Fig. 5-3 X-ray diffraction (XRD) spectra for the bulk Mg-10Al and Mg-10Al-1Dia samples, and as-received diamantane powders.....	125
Fig. 5-4 Bright-field transmission electron microscopy (TEM) image of the Mg-10Al-1Dia nanocomposite. (b) Fast Fourier transform (FFT) from the region highlighted by the white rectangle in (a). Below is its indexed FFT for clarity. (c) Fourier filtered high-resolution TEM image of the region highlighted in (a)....	126
Fig. 5-5 (a) Scanning-TEM image of the Mg-10Al-1Dia sample. Inset is an enlarge image of the region highlighted by the dashed square. (b) Energy dispersive X-ray spectroscopy (EDS) spectra and quantitative values (inset) from selected points of interest in (a).....	127
Fig. 5-6 (a) Compressive stress, σ , vs. strain, ϵ , curves of nanostructured Mg-10Al and Mg-10Al-1Dia micropillars. SEM images of nanostructured Mg-10Al (b,d), Mg-10Al-1Dia (c,e) micropillars before and after 2% of compressive strain. The scale bar is 4 μm in all the images.....	128
Fig. 5-7 (a) Compressive stress, σ , vs. strain, ϵ , curves of nanostructured Mg-10Al-1Dia micropillars with different diameters. Numbers correspond to the pillars diameter in μm . (b) Compressive yield strength, σ_y , of Mg-10Al and Mg-10Al-1Dia micropillars as a function of pillar diameter, d . σ_y of the bulk Mg-10Al and Mg-10Al-1Dia samples are also included.....	129
Fig. 5-8 (a) Reduced elastic modulus, E_r , of Mg-10Al and Mg-10Al-1Dia samples as a function of indentation contact depth, h . (b) Representative force, F , vs. h curves	

of indentations made at a peak force of 1000 μN on the Mg-10Al-1Dia samples.

Hardness, H , vs. h of Mg-10Al (c) and Mg-10Al-1Dia (d) samples.....130

Fig. 6-1 XRD spectra before and after 100 hours of annealing at 400°C for (a) Mg-10Al and (b) Mg-10Al-1Dia alloy. Average grain size as a function of the annealing times at different temperature for (c) Mg-10Al and (d) Mg-10Al-1Dia alloy.....145

Fig. 6-2 EDS maps of Al atoms for (a) Mg-10Al and (c) Mg-10Al-1Dia before annealing and (a) Mg-10Al and (c) Mg-10Al-1Dia after annealing at 400°C for 100 hours.....146

Fig. 6-3 Engineering stress-strain curves of (a) Mg-10Al and (b) Mg-10Al-1Dia alloys before and after annealing at 400°C for 6 and 100 hours. Yield strength of (c) Mg-10Al and (d) Mg-10Al-1Dia alloys as a function of the annealing time at the temperature ranging from 100°C to 400°C.....147

Fig. 6-4 (a) Mg-10Al and (d) Mg-10Al-1Dia micro-pillars before compression. Before annealing, (b) Mg-10Al and (e) Mg-10Al-1Dia micro-pillars after compression. After annealing at 400°C for 100 hours, (c) Mg-10Al and (f) Mg-10Al-1Dia micro-pillars after compression.....148

Fig. 7-1 Construction of a Voronoi tessellation in 2D: a) Poisson points, b) perpendicular lines are introduced to lines connecting neighboring Poisson points and c) final Voronoi tessellation.....	158
Fig. 7-2 (a) Schematic figure of the in-situ TEM tensile test. (b) The stress-strain curve of the tensile test. (c) TEM image of the single crystal magnesium sample after tensile test.....	159
Fig. 7-3 The stress-strain curve of single crystal Mg in tensile test simulation along [0001] direction.....	160
Fig. 7-4 (a) Lateral view of the tensile test of single crystal Mg before tension (b) Lateral view after tension (c) The view faced [0001] before tensile test (d) The view faced [0001] after tensile test with twin formation as labeled by dot lines.....	161
Fig. 7-5 simulation system of polycrystalline magnesium with grain size (a) 6.4nm (b) 16nm.....	162
Fig. 7-6 (a) Stress-strain curved of polycrystalline Mg with different grain sizes (b) The relation of yield strengths with respect to different grain size.....	163
Fig. 7-7 Schematic figure of the model of pillars (a) with and (b) without tapering.....	164
Fig. 7-8 The evolution of compression for the pillar with tapering.....	165
Fig. 7-9 Stress-strain curves of the simulation and experimental pillar compression.....	166

LIST OF TABLES

Table 2-1 The grain size range and values of ρ and β determined from Fig. 2-5. Experimental and theoretical values of σ_o and K_{H-P} are also included	23
Table 3-1 Compressive properties of the SPS'ed and extruded Mg-10Al samples.....	65
Table 4-1 Compressive properties of nanostructured Mg-10Al micropillars with different diameters.....	92

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PUBLICATIONS AND PRESENTATIONS

Publications

1. **Y.W. Chang**, M. Pozuelo, J.M. Yang

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Size-induced Strengthening in Nanostructured Mg Alloy Micropillars

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4. Effect of Strain Rate and Tapering on the Compressive Strength of a
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Chapter 1

Introduction

1.1 Motivation

Weight reduction has always been an ultimate object in aerospace and automobile industries. Aluminum alloys are traditional light metal for aeronautic applications. However, aluminum alloys in aerospace applications are already optimized concerning aeronautic requirements and it is more and more difficult to further achieve weight reduction. Recently, magnesium has been of growing interest as lightweight structural materials due to their low density (1.74 g/ml) and high specific strength. Magnesium was commonly classified as the metal in airborne applications. Historically it has been used in aircraft since 1930s. In 1950s, the usage of magnesium in aircraft structures and components increased significantly. For example, Sikorsky S-56, the military helicopter made by Westland Aircraft Ltd., included around 115 kg of magnesium. Lockheed F-80C is a complete magnesium constructed aircraft. However, the amount of magnesium used in aircrafts decreased in the beginning of 1990 from hundreds to dozen kg per plane [1]. The reasons for decrease in magnesium applications are that pure magnesium is easily reactive with oxygen at room temperature. Also, magnesium suffers from poor plasticity due to their Hexagonal Closed Packed (HCP) structure with lattice constant $a=0.3202\text{nm}$ and $c=0.5199\text{ nm}$, giving Mg a c/a ratio of 1.624. The ideal c/a ratio for the close packing of sphere is 1.632 so the Mg unit cell is slightly compressed along the c

axis, resulting poor ductility compared with the materials with larger c/a ratio such as Titanium. Moreover, the tensile strength of commercial magnesium alloys is about 180 MPa, which is insufficient and limits its structural application.

1.2 Research Problem

The thesis aims to develop high strength and thermally stable magnesium alloys with nanostructure. First of all, nanostructured Mg-Al alloy will be achieved using cryomilling followed by spark-plasma-sintering (SPS) consolidation. The mechanism of cryomilling and SPS will be studied in detail. After consolidation, the relation between the microstructure and mechanical properties will be investigated. The mechanical properties will be evaluated by micro-compression test. Hot extrusion is used as the secondary processing to further strengthen Mg-Al nanostructured alloy. Incorporating diamantane into Mg alloy to form nanocomposite will be used to strengthen Mg alloy. The influence of diamantane on the microstructure, mechanical behavior and thermal stability will be investigated. The two kinds of size effects, namely, grain size effect and sample size effect on mechanical properties and deformation mechanisms of the nanocrystalline Mg alloys will be analyzed. Based on experiment and simulation result, further discussion will explore the deformation and failure mechanisms of nanocrystalline materials.

1.3 Scope of the Thesis

Chapter 2 provides a overall literature review which relates to the research background. This chapter covers several topics: 1) the crystallinity of magnesium and the deformation mechanisms, 2) the strengthening strategies of magnesium and magnesium alloys, 3) nanocrystalline materials, 4) approaches to synthesize nanocrystalline materials, 5) the mechanical properties of nanocrystalline materials, 6) specimen size effect in micro-compression.

Chapter 3 introduces the method used to synthesize Mg-10wt.% Al alloy with nanostructure using cryomilling followed by spark-plasma-sintering to consolidate. The morphology of the powders and the microstructure of powders and bulk sample are investigated by SEM, TEM. XRD not only confirms grain sizes and present phases but also the amount of Al atoms dissolved in Mg matrix, forming a solid solution. To evaluate the mechanical properties, the compressive behavior of nanostructured Mg-10wt.% alloys processed via cryomilling, spark plasma sintering and extrusion are evaluated and the deformation mechanism is analyzed with TEM. The improvement in strength is mainly attributed to the occurrence of precipitation hardening by γ -Al₁₂Mg₁₇ nanoprecipitates and basal-texture strengthening in addition to the grain size strengthening mechanism.

Chapter 4 covers specimen size effect of micro-compression. Size effects on the compressive strength of nanostructured Mg-micropillars are also investigated. Mg-10Al alloy micropillars with diameters ranging from 1.5 to 8 μ m are prepared by focused-ion-beam and tested under micro-compression. A significant improvement in strength was

found by reducing the pillar diameter $<3.5 \mu\text{m}$. The deformation mechanisms of the compressed pillars are characterized using transmission electron microscopy.

Chapter 5 introduces the diamond-reinforced nanostructured Mg-10Al nanocomposites which is processed via cryomilling and spark plasma sintering. A detailed microstructural examination using SEM, TEM and XRD reveals that diamondoids mainly located within the Mg-matrix, present a potential effect on the $\text{Al}_{12}\text{Mg}_{17}$ precipitation to stabilize grain size. Micro-compressive behavior of Mg-10 wt.% Al-1 wt.% Dia is compared with that of diamond-free nanostructured Mg-10Al alloy and the enhanced mechanical behavior of the nanocomposite will be introduced in detail.

Chapter 6 further extends the introduction of diamonds acting as grain stabilizer. Diamonds not only can enhance compressive strength but also can improve the thermal stability of nanostructured Mg nanocomposites. Diamond-reinforced nanostructured Mg-10Al nanocomposites processed by cryomilling and spark plasma sintering shows excellent thermal stability after annealing at 400°C for up to 100 hours. Micro-compression tests were carried out to study the mechanical properties before and after annealing. The effect of incorporating diamonds on the thermal stability will also be discussed in detail in this chapter.

Chapter 7 shows the simulation works using molecular dynamics and finite element simulations. Molecular dynamics simulation (LAMMPS) is used to study the deformation mechanism of pure magnesium. Single crystal magnesium tensile behavior

is compared with the experimental result in the literature. The yield strengths of pure magnesium with different grain sizes are simulated to study the mechanical properties of nanocrystalline magnesium. Inversed Hall-Petch relation is founded when the grain size is smaller than ~ 20 nm. Finite element analysis (Abaqus) is used to study the tapering effect on the micro-compression test. Tapering is inevitable in micro-pillar fabrication and causes inaccuracy in determining yield strength. The finite element simulation shows that the yield strength of a tap-free pillar is similar to the yield strength calculated from the cross-section at middle height in experiment. Moreover, strain hardening in micro-compression can be corrected with FEA.

Chapter 8 summerises the results and main conclusion of the thesis. Further opportunities for future research is also outlined.

1.4 Reference

- [1] L. Ostrovsky, Y. Henn, in: Int. Conf. "New Challenges Aeronaut. ASTEC 07, 2007, pp. 1–5.

Chapter 2

Literature Review

Abstract

This literature review begins with a brief introduction of crystallinity and slip deformation and twinning systems of magnesium. The up-to-dated strengthening strategies are also covered. After that, a general overview of nanostructured metals and the mechanical properties will be presented. The current understanding of specimen size effect on yield metals will be reviewed next.

2.1 Magnesium

Magnesium and its alloys are currently in the spotlight of global research because of the need of limiting energy consumption and reduce the environmental impact of human processes. In particular, their low density compared to other structural metals makes them a very attractive alternative for the automobile and aerospace industry. However, their low strength and poor ductility compared to other structural materials (e.g. Al and steels) has limited their widespread applications. Poor ductility is due to only three possible Burgers vectors can be active on basal, prismatic and pyramidal planes while in polycrystalline metals, at least five independent slip systems are required to sustain a general homogeneous deformation without forming cracks [1]. The main slip plane in magnesium is basal slip, i.e., slip on the (0001) plane with a $\langle 11\bar{2}0 \rangle$ Burgers

vector. Although prismatic slip $\{1\bar{1}00\}\langle 11\bar{2}0\rangle$ and pyramidal slip $\{1\bar{1}01\}\langle 1120\rangle$ have also been observed, their critical resolved shear stress (CRSS) is about 100 times greater than the CRSS of basal slip at room temperature [2]. The illustration of three slip systems of magnesium is shown in Fig.2-1. Additionally, for hexagonal closed-packed (hcp) metals, twinning is one of the main deformation mechanisms for plasticity since the Burgers vectors lie on the basal plane and no plastic strain parallel to the c-axis can be accommodated by any of the $\langle a\rangle$ slip systems. When a grain is in tension along the $\langle c\rangle$ axis, $\{10\bar{1}2\}$ twin is expected to occur (extension twin) and this leads to 86.3 degrees rotations of the basal plane. Under compression loading, $\{10\bar{1}1\}$ twin is expected and it has a 56 degrees angular difference with the basal planes of the initial crystal (contraction twin) [3]. The two main twin modes are as depicted in Fig. 2-2. Recently, it has been demonstrated that the introduction of nanotwins in nanostructured face-centered cubic (fcc) can result in extraordinarily high strength with concurrent ductility [4]. However, size-scale effects i.e. grain size [5–7] and specimen dimensions [8–13] seem to be critical on the deformation mechanism by twinning in hcp materials.

2.2 Solid Solution and Precipitation Strengthening of Magnesium Alloys

In order to improve the strength of Mg alloys, several approaches have lately been developed in terms of optimizing their composition, texture and grain size. Among all these approaches, alloying Mg with different solute atoms, in particular with rare earth (RE) elements also have received considerable attention. It has been proven that RE

elements can contribute to enhance the strength of Mg alloys not only by solid solution strengthening [14,15] but also by texture strengthening [16,17]. Moreover, it has recently been reported that RE elements can reduce the stacking fault energy of the Mg matrix, which enables the formation of high density of stacking faults (SFs). A yield strength of around 575 MPa is reported for a Mg–Gd–Y–Ag–Zr alloy by introducing high density of SFs with nanoscale spacing [18]. In addition, RE elements can rise to different precipitated phases [19–24] and dispersoids [25] that can also contribute to the strength of the Mg alloy by precipitation hardening. However, the main drawback of all the above approaches is the cost of the alloy. RE elements are relatively expensive and the amount of RE required to improve the strength of Mg is significant that will definitely increase the alloy cost. In addition to RE elements, zinc, zirconium, cerium, silver and aluminum are also widely used to stabilize the chemical property and enhance the mechanical property of magnesium and Mg alloys are widely used in aircraft, missiles, machinery, tools, materials-handling equipment, automobiles and computer parts. In lightweight magnesium alloys, aluminium constitutes the main alloying element, chiefly because of its low price, availability, low density and the advantageous effects on corrosion and strength properties [26]. The AZ91 alloy (contains about 9 wt.% Al and 1 wt.% Zn, with addition of about 0.4 wt.% Mn) is the most widely used magnesium alloy exhibiting a good combination of high strength at room temperature, good castability and excellent corrosion resistance.

2.3 Grain Size Refinement Strengthening of Magnesium Alloys

Besides solid solution strengthening, one of the most effective and well studied is grain size refinement. Grain refinement has been proved to be an effective method to enhance the strength and alter the ductility of the materials. Several methods have been proposed to produce materials with nanostructured grain structures. So far, most of the research work on nanostructured materials has been carried out on face-centered cubic and body-centered cubic metals. However, there has been little investigation of nanostructured Mg alloys. Recently, it was reported that grain refinement can help to improve the strength and ductility of Mg alloys. The effect of grain size on the elongation of Mg-0.9% Al alloy was reported by Yamashita et al. [27]. Elongation to failure increases to 15% when the grain size is reduced from 400 to 17 μm . Mukai et al. also reported that the ductility in WE43 magnesium alloy could be enhanced by the grain refinement (1.5 μm) [28]. Kubota et al. reported a good combination of high strength and high ductility of fine-grained Mg alloys at room temperature as a result of grain refinement [29]. Over the past two decades, great strides have been made in the development of nanostructured bulk materials and the properties of nanostructured bulk materials will be introduced in detail in the following.

2.4 Nanostructured Materials

Nanostructured materials have gained a lot of attention as a result of their unique microstructure, which leads to outstanding physical and mechanical properties [30,31]. A

number of methods have been developed to achieve a bulk material with nanometer-scale grains. These include rapid solidification [32], plasma processing [33], electrodeposition [34], sputtering [35], torsion straining under high pressure[36], equal channel angular pressing [37], and mechanical attrition—ball milling [38–41]. Cryomilling is basically a mechanical milling process conducted in a liquid nitrogen atmosphere, which results in much shorter milling times to reach the desired fine particle size. There are several advantages of cryomilling over milling at room temperature. First, powder agglomeration and welding to the milling media are suppressed, resulting in a more efficient milling outcome [42]. Recently, cryomilling i.e., mechanical milling in liquid nitrogen atmosphere has also been used as a potential SPD technique to attain nanocrystalline grains in a number of alloys, such as Al [43,44], Ni [45], Fe–Al [46], and particularly in Mg-alloys [42,47]. The milling time required to attain nanocrystalline grains is significantly reduced due to the extremely low temperatures during cryomilling, which suppress dynamic recovery and recrystallization [47]. As a consolidation technique, the spark-plasma- sintering (SPS) method has demonstrated to synthesize cryomilled Mg-powders into a bulk nanostructured material without a significant grain growth [42]. Recently, it has been reported that it is possible to attain high strength nanostructured Mg–Al–Zn alloy with a compressive yield strength of 442 MPa by using cryomilling followed by SPS [47]. To synthesize the cryomilled powders into a bulk material, a number of conventional consolidation methods, such as hot-isostatic-pressing (HIPing) [22] and cold-isostatic- pressing (CIP) [23], exist, which are generally accompanied by

extrusion [24], as a secondary process to remove any remaining porosity and to enhance the mechanical properties. However, a significant grain growth has been observed using HIPing or after secondary process. To preserve the initial fine grain size after consolidation, it has been demonstrated that spark-plasma-sintering (SPS) can successfully consolidate nanostructured powders into a bulk material form with shorter time and lower temperature than those required in the conventional methods and without any secondary process [25,27]. SPS is basically a modified hot pressing technique in which a pulsed DC current and an uniaxial pressure are applied simultaneously. Traditionally, the current passes through an electrically conductive graphite die and heats the sample. The localized high temperature at powder particle contacts can further lead to the densification of the powders. After SPS consolidation, bimodal grain size distribution was founded. nanostructured materials are well known for their high-strength, but frequently suffer significant losses in ductility. Recently, it has been reported that by combining nanocrystalline grains with coarse-grained regions in a bimodal grain size distribution the mechanical properties of nanostructured materials can be significantly improved [48–50].

2.4.1 Mechanical Properties of Nanostructured Materials

Dislocation structure with three regimes is in effect of grain size on the yield stress at low homologous temperatures. Regime I, II and III were discovered in Cu, Ag, Au under transmission microscopy observations [51]. Regime I (grain size $\geq 0.5 \mu\text{m}$) is

defined by the presence of well-defined dislocation cells, regime II (grain size ≈ 10 -500 nm) is characterized by the absence of well-defined cell and dislocations is more uniformly dispersed. There is no dislocation observed in Regime III (grain size $< \sim 10$ nm). The relation between grain size and yield strength of Cu, Ag and Au at 300K is illustrated in Fig.2-3 [51]. It is worth to note that grain size hardening occurs in regimes I and II and grain size softening occurs in regime III.

2.4.2 Hall-Petch Relation: Regime I and II

The effect of grain size on the yield strength σ is usually expressed in terms of the Hall-Petch relation [52,53].

$$\sigma = \sigma_0 + K_{H-P} d^{-1/2}$$

Where σ_0 is the intrinsic friction stress of a given material, K_{H-P} the H-P constant and d is grain size. In the past, a single Hall-Petch equation was considered covering the entire grain size range from nanometer to micrometers. However, the face center cubic (FCC) metals such as Cu, Ag, Au and Ni were reported that there are two separate Hall-Petch relations: one for $d > \sim 200$ nm and the other one for $d < \sim 200$ nm. The latter one have a larger σ_0 and a smaller K_{H-P} than the former one [54]. There are three mechanisms proposed to explain the phenomena: (a) grain boundary ledges provide sources for dislocations (b) grain boundaries reduce the average free slip distance of dislocation movement and (c) additional “geometric” dislocations are required to accommodate the inhomogeneity of strain which occurs in the transfer of slip from one

grain to its neighbor [55]. Fig. 2-4 illustrates the three mechanisms and those three mechanisms follow the relation:

$$\rho = \frac{\beta}{bd}$$

Where ρ is dislocation density, b is Burgers vector and d is grain size. $\beta \approx 0.05$ for mechanism (a), ~ 1 for (b) and 0.25 for (c). Fig. 2-5 shows the relation of ρ and d^{-1} for copper. The data lie on three regions that correspond to mechanism (a), (b) and (c), whose slope decreases in this order [56]. Also, it is well studied that the relation between tensile yield strength σ and dislocation density ρ can be described as the following equation:

$$\sigma = \mu b \rho^{1/2}$$

Where μ is shear modulus. The relation of σ / μ vs. $\rho^{1/2}$ for the grain size ranging from 10 nm to 150 μm in Cu is plotted in Fig. 2-6. These results show that at a fixed plastic deformation condition, the density of dislocation increases with decreasing grain size. Therefore, the so-called dislocation density model can explain Hall-Petch relation. In addition, grain size can affect the mechanism by which the dislocations are generated and also influence on the form and arrangement of the dislocations so that Hall-Petch relation parameters for nanostructured metals can be different from their micro grain size counterpart. In FCC metals, σ_o is larger and K_{H-P} is smaller in nanocrystalline grain size than the ones in micrometer grain size. This can be attributed to the different mechanism by which grain boundaries affect the dislocation density and structure [56].

The values calculated from Fig. 2-5 (experimental) and from dislocation density model (theoretical) are summarized in table 2-1.

2.4.3 Inverse Hall-Petch Relation: Regime III

In the past, it was difficult to achieve high quality, impurities and imperfection free sample with grain size below 20 nm so that the mechanical behavior of the materials in regime III was not well studied. Narayan et. al. used pulsed laser deposition to synthesize WC and successfully controlled the grain sizes with high degree of uniformity as shown in Fig. 2-7 [56]. The sample is hereafter tested with hardness tester. The results of the hardness vs. the reciprocal square root of the grain size in WC are shown in Fig. 2-8. It is interesting to point out that the hardness increases linearly with decreasing grain size shown to a certain grain size, and below the critical grain size, the hardness decreases. It is attributed that intragrain deformation dominates above the critical grain size and below the critical grain size, intergrain deformation dominates, for example, grain boundary shear [57]. This phenomenon leads to softening, i.e., hardness decreases with a decrease in grain size. In fact, there has been a fair amount of controversy results regarding the softening characteristics below the critical grain size. Most of the controversial data is due to the samples with nonuniform grain size distribution or impurities within grain boundaries. Although the grain size is uniform in WC case, defect content within the grains is varied and not characterized. Therefore, simulation is sought as the tool to study regime III nanostructured materials with ideal conditions. Schiøtz et al. used molecular

dynamics simulation to create pure copper system with grain size ranging from 5 nm to 50 nm. The simulations indicate that the deformation mechanism is different in regime III. The plastic deformation is no longer dominated by dislocation motion but is instead carried by atomic sliding in the grain boundaries, which for very small grains constitute a substantial fraction of the material. When the grain size is reduced, the fraction of grain boundary atoms increases, leading to the observed softening. During the elongation of the simulated copper samples, the stress is calculated, and the resulting stress-strain curves from 10 simulations with different grain sizes are shown in Fig. 2-9A. In the systems with the smallest grain size, grain boundary sliding gradually sets in as the stress builds up, but only very limited dislocation activity is seen in the grains. In the coarser grain systems, grain boundary sliding is less important, and numerous dislocations are observed [58].

2.5 Specimen Size Effect

Studies on size-scale effects i.e. grain size and specimen dimension have attracted considerable attention in recent years because of their influence on the mechanical behavior of materials [13]. In general, it is well accepted that the strength of metals can be improved through refinement of the grain size by the Hall-Petch mechanism. Interestingly, it has also been demonstrated that the strength of the material can be improved by reducing the specimen dimensions, as first reported by Uchic et al. in Ni based superalloys [59] and by Greer et al. in single crystal Au [60]. Nowadays, the

optimization of the mechanical properties of materials at the micron and submicron scales is crucial for the design of high performance micro-electrical-mechanical (MEMS) devices. Consequently, researchers have focused on investigating both grain size and specimen size effects on the mechanical behavior of micron/submicron-pillars of polycrystalline materials such as Ni [61,62], Ag [63], TiAl [50], Cu [64] and Pt [65].

In the case of Mg, many efforts have been dedicated to study the compressive behavior of single-crystal Mg micron/submicron-pillars [8,9,11,12,66,67]. These studies have shown that the compressive strength of single crystal Mg-micropillars mainly depends on the initial dislocation density [66] and the orientation of the basal planes with respect to the loading direction [8,9,66]. Byer and Ramesh [66] reported a size effect on the yield strength by decreasing the initial dislocation density. Lilleodden [9] observed a remarkable increase in compressive strength along the c-axis for single crystal Mg-micropillars with diameters $<10\text{ }\mu\text{m}$. It is well known that when the c-axis is nearly parallel or perpendicular to the loading direction, alternative deformation mechanisms such as non-basal slip and/or twinning can be activated since the Schmid factor for basal plane sliding is very small. For instance, a significant hardening was found on single crystal Mg-micropillars loaded in compression along the c-axis by the activation of multiple slip systems on pyramidal planes [8,9]. However, it is interesting to note that no sign of twinning is found in those works. It appears that a size effect is also associated with the deformation by twinning. As reported by Yu et al. [12], the deformation by twinning becomes unfavorable when the specimen size decreases. Ye et al. [11]

demonstrated a strong size effect associated with basal plane sliding and extension twinning in single crystal Mg nano- and micro-pillars. In fact, it has recently been demonstrated by Prasad et al. [67] that the required stress to nucleate twins in single crystal Mg-micropillars is higher than that in single crystal Mg bulk samples.

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Table 2-1 The grain size range and values of ρ and β determined from Fig. 2-5.

Experimental and theoretical values of σ_o and K_{H-P} are also included.

Line	GS Range (μm)	ρ_i (10^{14}m^{-2})	β	$\sigma_i(\text{MPa})$		$K_{H-P}(\text{MPa}\cdot\text{m}^{1/2})$	
				Calc.	Expt. ^a	Calc.	Expt. ^a
A	>16	2.0	1.1	177	26-223	0.67	0.16-0.14
B	0.2-16	1.0	0.10	108	26-223	0.21	0.16-0.14
C	<0.2	18.0	0.013	457	320	0.07	0.07

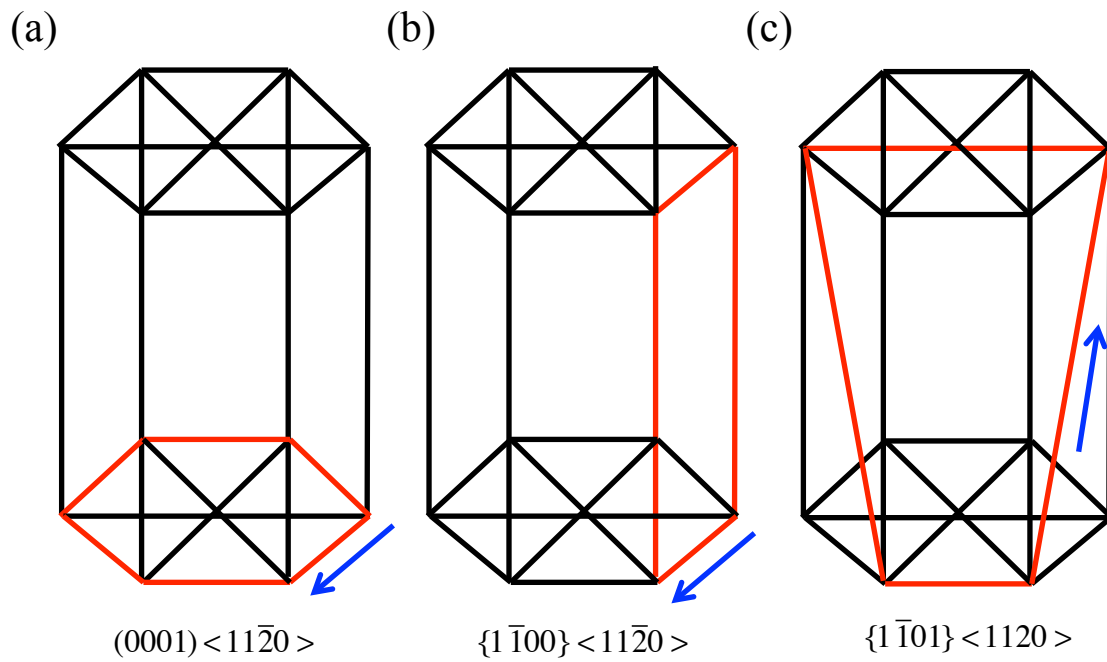


Fig. 2-1 Deformation slip system of magnesium: (a) basal slip (b) prismatic slip and (c) pyramidal slip.

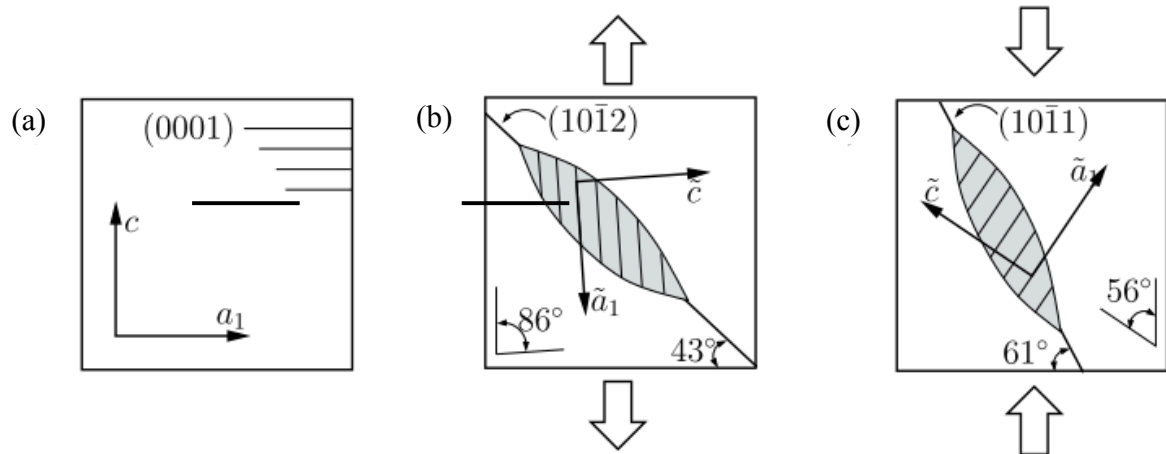


Fig. 2-2 Rotation of basal planes due to twinning: (a) the initial material element representing the initial crystallographic directions c and a (b) lenticular represents the tensile twinning (c) contraction twinning [3].

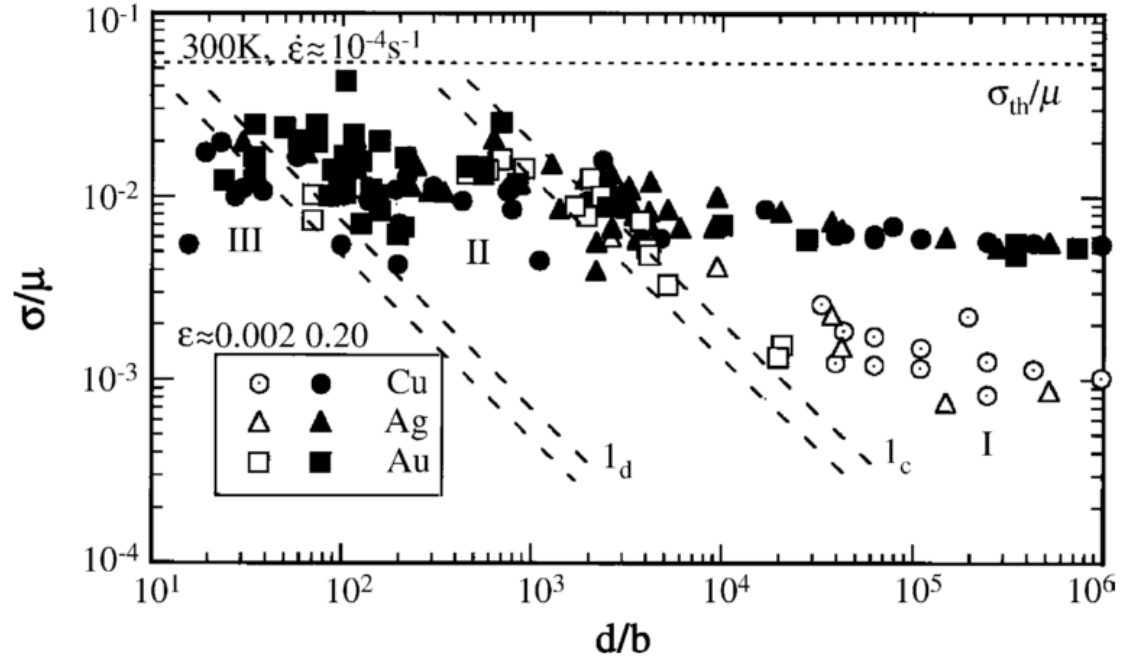


Fig. 2-3 modulus-normalized yield strength $\log \sigma / \mu$ vs. Burgers vector-normalized grain size $\log(d / b)$ for Cu, Ag and Au at 300K [51].

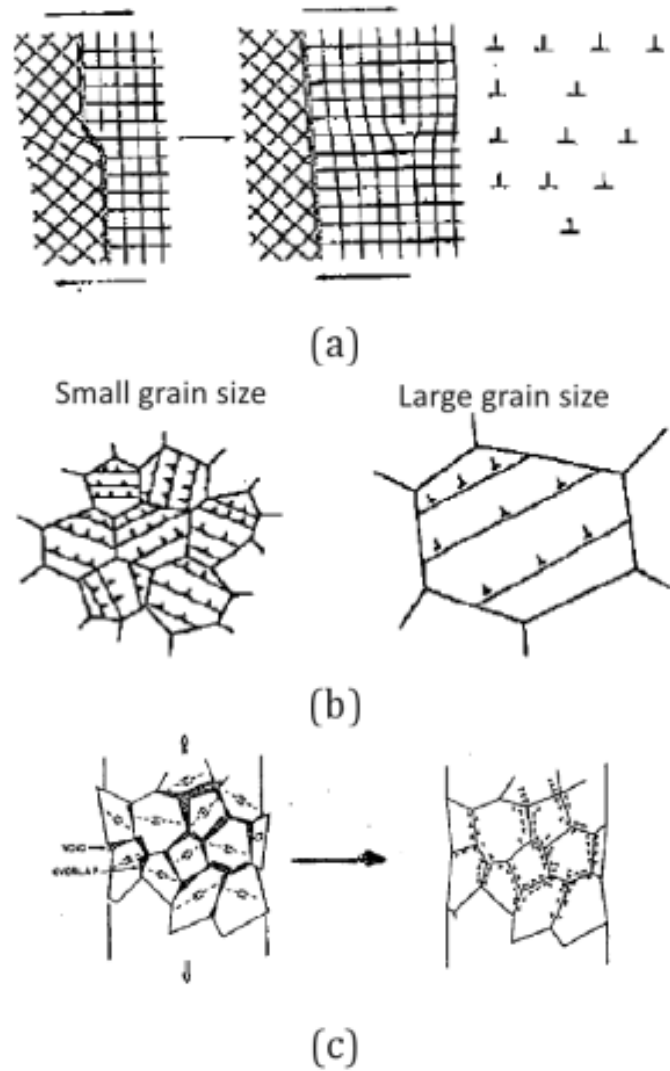


Fig.2-4 Mechanisms by which grain boundaries can affect the dislocation density (a) generation of dislocation at grain boundary ledges (b) reduction of the free slip distance and (c) geometric dislocation [55].

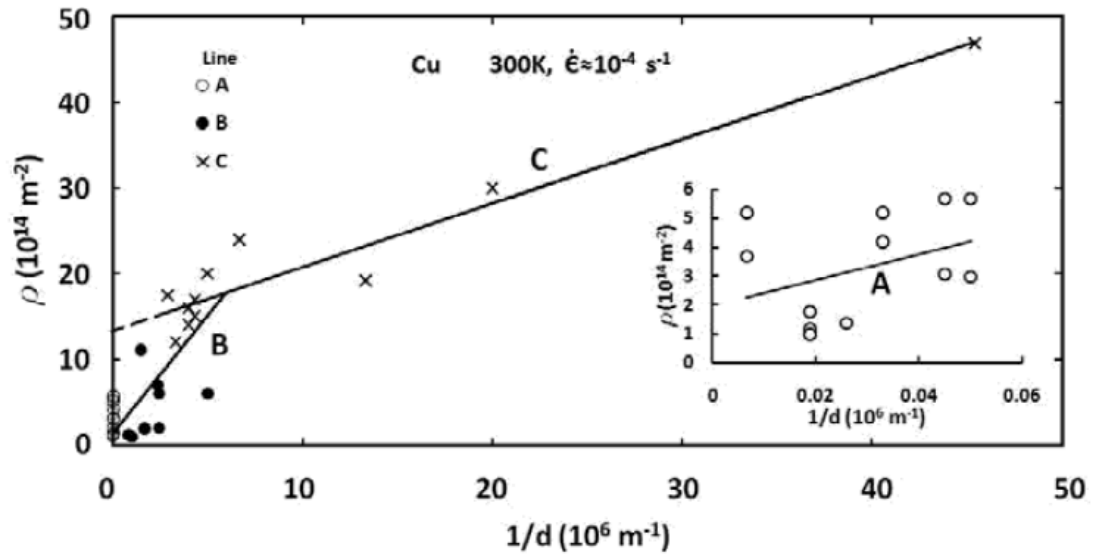


Fig. 2-5 Dislocation density ρ vs. $1/d$ for the plastic deformed Cu at 300K [56].

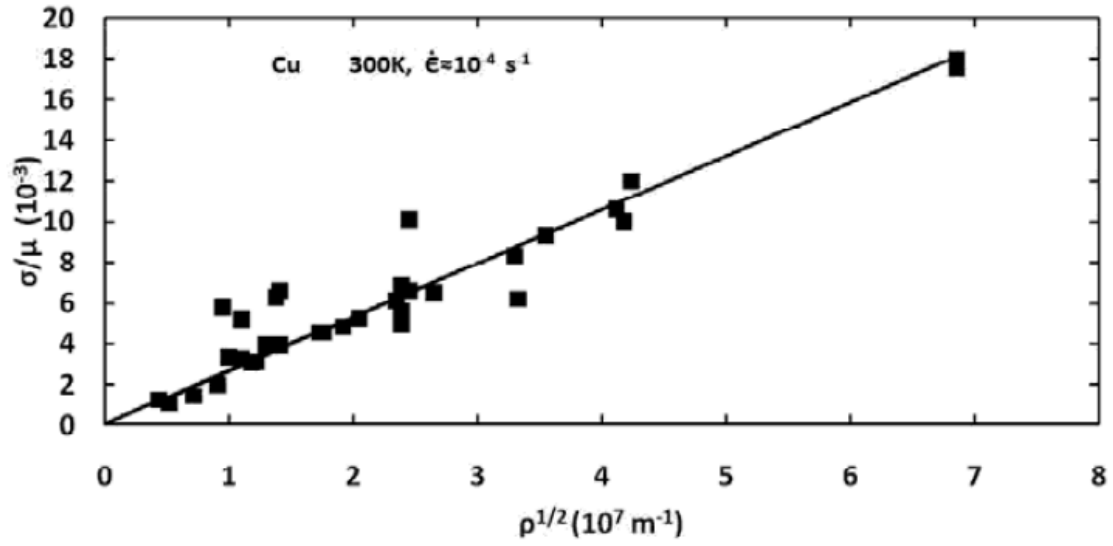


Fig. 2-6 Modulus normalized tensile yield strength σ / μ vs. square root of the dislocation density $\rho^{1/2}$ for Cu deformed at 300K [56].

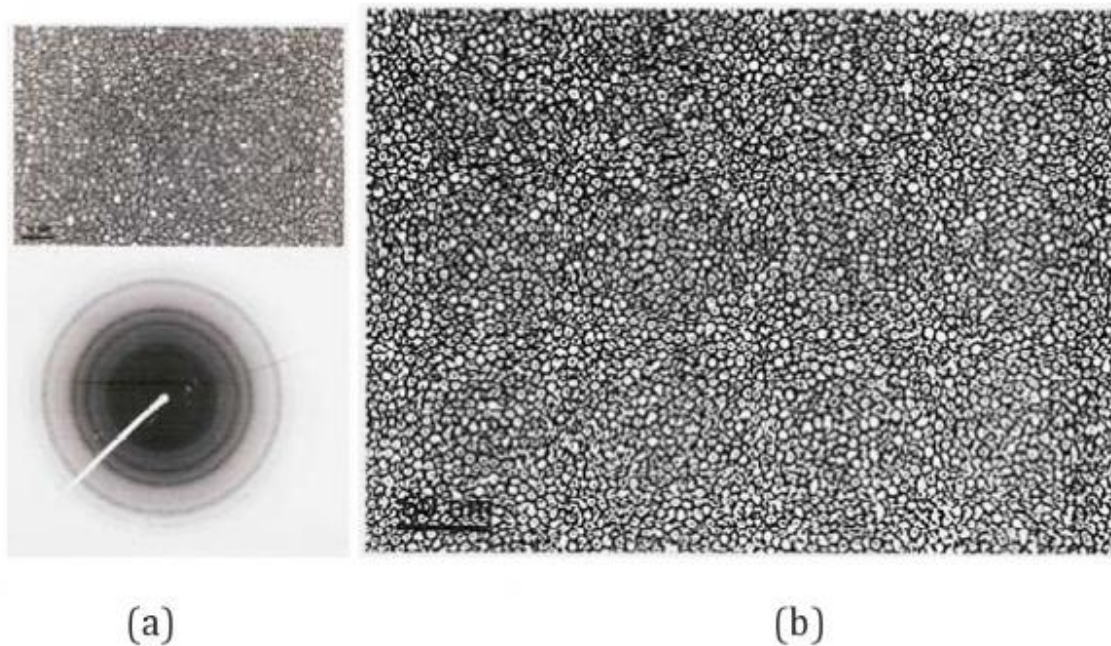


Fig. 2-7 TEM images of nanostructured WC with uniform grain size: (a) average grain size 11 nm and (b) average grain size 6 nm [56].

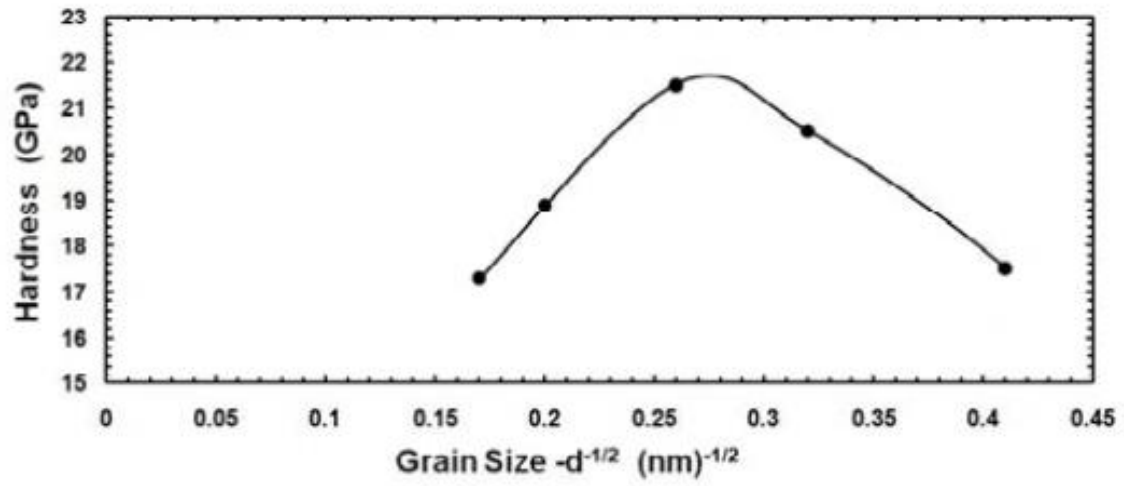


Fig. 2-8 Hardness of WC as a function of inverse square root of the grain size [56].

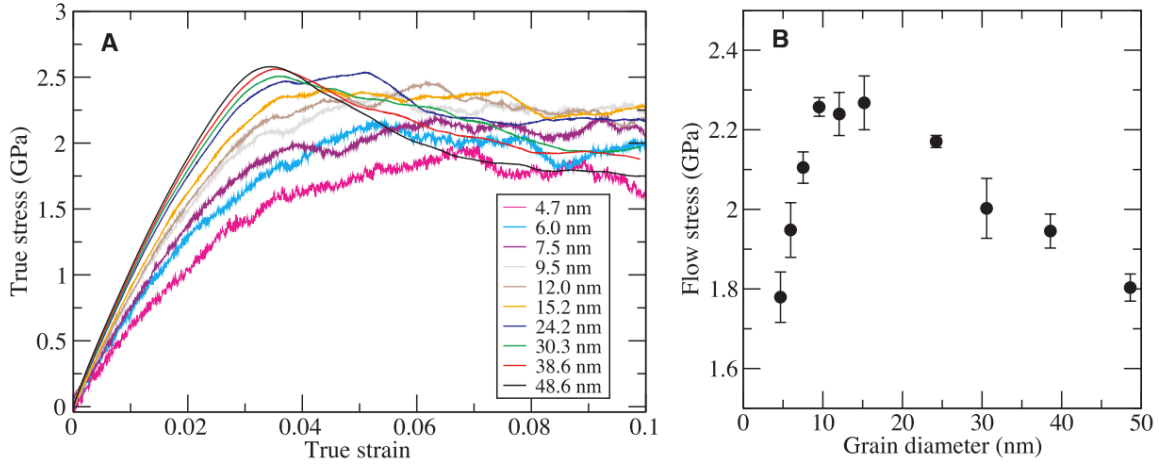


Fig. 2-9 The grain size dependence of the flow stress. (A) Stress-strain curves for 10 simulations with varying grain sizes. (B) The flow stress, defined as the average stress in the strain interval from 7 to 10% deformation. The error bars indicate the fluctuations in this strain interval. A maximum in the flow stress is seen for grain sizes of 10 to 15 nm, caused by a shift from grain boundary-mediated to dislocation mediated plasticity [58].

Chapter 3

Characterizations of Nanostructured Magnesium-Aluminum Alloys

Abstract

In this chapter, the microstructural characterization and compressive behavior of nanostructured Mg–10Al alloys processed via cryomilling, spark plasma sintering and extrusion are investigated. The compressive results of nanostructured Mg micropillars is also discussed. Using in-situ scanning electron microscopy microcompression tests, we directly study the mechanical behavior of nanostructured Mg–10Al (wt%) alloys that have been processed by cryomilling and spark plasma sintering. Compressive yield strength of 320 MPa and an elongation at failure higher than 12% was achieved. Using high-resolution transmission electron microscopy, we demonstrate that basal plane sliding and contraction twins are the deformation mechanisms involved in the shear band that occurs at 10% of strain. The warm extrusion is used to further enhance the strength of Mg–10Al alloys. It leads to ~40% improvement in compressive strength of nanostructured Mg–10Al alloys. A yield strength of 550 MPa, and an ultimate strength of 580 MPa are measured. The improvement in strength is mainly attributed to the occurrence of precipitation hardening by γ -Al₁₂Mg₁₇ nanoprecipitates and basal-texture strengthening in addition to the grain size strengthening mechanism. Our results suggest a successful approach for the design of high strength nanostructured Mg–Al alloys.

3.1 Introduction

Nanostructured materials have gained a lot of attention as a result of their unique microstructure, which leads to outstanding physical and mechanical properties.[1,2] A number of methods have been developed to achieve a bulk material with nanometer-scale grains. These include rapid solidification,[3] plasma processing,[4] electrodeposition,[5] sputtering,[6] torsion straining under high pressure,[7] equal channel angular pressing,[9] and mechanical attrition—ball milling.[8–11] In terms of cost and productivity, mechanical milling is an effective method to synthesize a large quantity of nanostructured material in powder form. This method induces severe plastic deformation, which consists of repeated welding, fracturing, and rewelding of the powders. Cryomilling is basically a mechanical milling process conducted in a liquid nitrogen atmosphere, which results in much shorter milling times to reach the desired fine particle size. There are several advantages of cryomilling over milling at room temperature. First, powder agglomeration and welding to the milling media are suppressed, resulting in a more efficient milling outcome [12]. Second, oxidation reactions during milling are reduced under nitrogen atmosphere. Third, the milling time required to attain a nanostructure is significantly reduced due to the extremely low temperatures during cryomilling, which suppress dynamic recovery and recrystallization [13]. The drawback of this processing technique is that small amounts of impurity elements may be introduced during cryomilling and form nanoscale dispersions. However, it is well accepted that the existence of second phases such as oxides, nitrides, and carbides enhances the retarding force on grain-

boundary migration, which plays a significant role in stabilizing the microstructure. [14] Extensive experiments have been performed to achieve nanostructured Al-based alloys, [14–20] Zn–Al alloys,[21] Mg–Fe mixtures,[22] and Ti alloys[23] by cryomilling. However, nanostructured Mg-based alloys fabricated by cryomilling have not been reported yet. As of today, grain refinement of Mg and Mg-based alloys to nanometer scale by conventional processing techniques continues to be a challenging task mainly due to the dynamic recovery and recrystallization that cannot be suppressed.[24] In addition, it is well known that the hexagonal crystal structure of Mg provides only a limited number of active slip systems. Therefore, factors such as shear planes, grain rotation, and texture seem to play an important role in assisting grain refinement by conventional techniques.[25–27] In this work, we demonstrate that nanostructured Mg-based alloy powders with an average grain size of 30 nm can be successfully processed by cryomilling. To synthesize the cryomilled powders into a bulk material, a number of conventional consolidation methods, such as hot-isostatic-pressing (HIPing)[17] and cold-isostatic-pressing (CIP),[18] exist, which are generally accompanied by extrusion,[16–19] as a secondary process to remove any remaining porosity and to enhance the mechanical properties. However, a significant grain growth has been observed using HIPing or after secondary process. To preserve the initial fine grain size after consolidation, it has been demonstrated that spark-plasma-sintering (SPS) can successfully consolidate nanostructured powders into a bulk material form with shorter time and lower temperature than those required in the conventional methods and without

any secondary process.[28,29] SPS is basically a modified hot pressing technique in which a pulsed DC current and an uniaxial pressure are applied simultaneously. Traditionally, the current passes through an electrically conductive graphite die and heats the sample. The localized high temperature at powder particle contacts can further lead to the densification of the powders. In addition to bottom up approaches, concurrently, many alternatives based on severe plastic deformation (SPD) techniques (top down approaches) are used to enhance the strength of Mg and its alloys via grain size refinement. These SPD methods include the conventional equal channel angular pressing (ECAP) [30–33], accumulative roll bonding (ARB) [34], high-pressure torsion (HPT) [35], hot extrusion [36], alternate biaxial reverse corrugation (ABRC) [37] and high-ratio differential speed rolling [38]. As an example, using multi-directionally forging at room temperature [39], it is possible to attain a yield strength of 480 MPa for a Mg–Al–Zn alloy with an average grain size around 0.6 μm . As for the specimen size effect, while many efforts have been devoted to study the size effect on single crystal Mg micropillars, the effect of specimen size on polycrystalline Mg micropillars has not been reported yet. In this work, we report the influence of specimen size (diameter) on the compressive strength of nanostructured Mg-10Al micropillars with a bimodal grain size distribution. Our approach involves the study of several nano/micro-crystalline grains simultaneously, which allows us to study the important role that the grain orientation plays in the activity of the deformation mechanisms in nanostructured Mg-micropillars. In addition, a secondary process via warm extrusion are performed to moderately modify the

microstructure of the sintered material and attain superior mechanical properties. The cryomilled powders, as well as the SPS sintered material before and after extrusion are characterized by SEM, TEM, EDX and XRD. The mechanical behavior of the nanostructured Mg–Al alloys before and after extrusion is investigated by bulk compression tests at room temperature. The underlying strengthening mechanisms are also discussed.

3.2 Materials and Methods

Commercially available gas-atomized Mg and Al powders were blended to formulate a composition of Mg90Al10 (wt%) (referred as Mg-10Al in the following). Half of a kilogram of the blended powder was cryogenically-milled for 8 h under liquid nitrogen atmosphere in a Union Process, Szegvari mill (Akron, OH) extensively modified at California Nanotechnologies for safe light alloy processing. Hardened stainless steel balls (6-mm diameter) were used as milling media at a particular ball-to-charge ratio for a given material. A 30:1 ball-to-powder mass ratio is common for milling metallic powders. Powder consolidation was performed using an SPS system (Syntex Inc., Dr. Sinter Lab TM, model SPS-515S, Kanagawa, Japan). The processed powder was placed in a graphite die lined with graphite foil. The sintering process was performed in a vacuum and under a maximum uniaxial pressure of 100 MPa. A K-type thermocouple inserted into the outer wall of the die was used to control the ramp rate (75 °C/min) and hold temperature (for 5 min at 360 °C) as a pulsed electric current was applied through

graphite punches. The SPS-consolidated specimen resulted in pucks with 25 mm and 15mm of diameter and thickness, respectively. Cylinders with 10 and 20 mm of diameter and length, respectively, were machined from SPS pucks and subsequently extruded at 260 °C. The extrusion ratio was 2:1 giving an effective strain of $\epsilon = 1.6$. The morphologies of the cryomilled powders, SPS specimen and extruded specimen were investigated with scanning electron microscopy (SEM). A FEI Nova 230 Variable Pressure SEM (VP-SEM) was used for this purpose. High-resolution microstructural characterization was carried out using a FEI Titan 300-kV scanning transmission electron microscope (STEM). The composition was determined using energy dispersive X-ray spectroscopy (EDS) in the STEM equipped with an Oxford Instruments EDS system. TEM samples were prepared by spreading of an ultrasonicated suspension of the powders in ethanol onto a regular Cu-grid. A FEI Nova 600 Nanolab DualBeam focused ion beam (FIB)-SEM was used to prepare thin film TEM samples from the bulk material. X-ray diffraction (XRD) was performed using a Panalytical X'Pert Pro X-ray Powder Diffractometer using Cu K α ($\lambda = 0.1542$ nm) radiation to determine the phases present and crystalline size. In order to evaluate the bulk mechanical behavior of the sintered material, compression tests were performed at displacement rate of 0.011 mm/s using an Instron machine with a load cell of 60 klb. Compression samples of 5.6 and 6.2mm in diameter and length, respectively, were machined from SPS pucks and extruded bars. In-situ scanning-electron-microscopy (SEM) microcompression tests are conducted to study the mechanical behavior of nanostructured hcp Mg-micropillars with a bimodal grain

structure. High-resolution transmission-electron-microscopy (HRTEM) analysis has been accomplished in order to study the deformation mechanisms at atomic scale and the underlying deformation mechanisms.

3.2.1 Focused Ion Beam

Focused ion beam, also known as FIB, is a technique used particularly in the semiconductor industry, materials science and increasingly in the biological field for site-specific analysis, deposition, and ablation of materials. An FIB setup is a scientific instrument that resembles a scanning electron microscope (SEM). However, while the SEM uses a focused beam of electrons to image the sample in the chamber, FIB uses a focused beam of ions instead. FIB can also be incorporated in a system with both electron and ion beam columns, allowing the same feature to be investigated using either of the beams [40]. Unlike an electron microscope, FIB is inherently destructive to the specimen. When the high-energy gallium ions strike the sample, they will sputter atoms on the surface. Gallium atoms will also be implanted into the top few nanometers of the surface, and the surface will be made amorphous. Because of the sputtering capability, the FIB is used as a micro- and nano-machining tool, to modify or machine materials at the micro- and nanoscale. Commonly the smallest beam size for imaging is 2.5–6 nm. The smallest milled features are somewhat larger (10–15 nm) as this is dependent on the total beam size and interactions with the sample being milled. In this research study, FIB will be intensely used to prepare micro-pillars and TEM samples. The procedure of making a

pillar with 3.5 μm diameter is shown in Fig. 3-1. The milling pattern with 35 μm outer diameter and 5 μm inner diameter is used to create a crater to avoid the touch between the indentation tip and substrate. The milling pattern with 5.5 μm outer diameter and 3.5 μm inner diameter is used to tailor the pillar into the desired shape.

3.2.2 Nanoindentation

In the following, nanoindenter technics will be paid more attention to be introduced. Nanoindenter has been widely used as a powerful advanced technique for providing quantitative information of mechanical properties including elastic moduli, hardness, micro-compression and wear resistance of a variety of materials [41,42]. The advantages of nanoindenter over conventional hardness micro-indenter lie in the continuous measurements of force and displacement as an indentation is made. With the precise load and displacement resolutions, mechanical properties can be determined even when the indentations are too small to be imaged conventionally [43]. Measuring hardness and elastic moduli of thin films can be realized. With equipping Berkovich tips, measurements of hardness, elastic moduli and scratches can be achieved. Micro-compression tests and impressive creep tests can be carried out by flat-ended punch tip. In order to measure accurate results, the samples were grinded and polished until a mirror-finish surface was obtained. (Figure 3-2) The polished samples were glued by crystal wax (melting point $\sim 70\text{ }^{\circ}\text{C}$) if the sample is not sensitive to heat. Otherwise, silver paste can act as a glue agent if the sample is sensitive to heat. Those glue agents can

stabilize the testing samples during performing indentation.

A complete load-displacement cycle of an indentation is shown in Fig. 3-3. It is analyzed according to the equation:

$$S = \frac{dP}{dh} = \frac{2}{\sqrt{\pi}} E_r \sqrt{A}$$

Where $S = dP / dh$ is the experimetically measured stiffness of the unloading data, A is the projected area of the elastic contact and E_r is the reduced modulus defined as:

$$\frac{1}{E_r} = \frac{1 - \nu^2}{E} + \frac{1 - \nu_i^2}{E_i}$$

where E and ν are Young's modulus and Poisson's ratio of the tested specimen and E_i and ν_i are the same paramters for the indenter. By measuring the unloading stiffness and the projected area, the modulus can thus be obtained [43]. In addition to the Young's modulus, the indentation result can be used to dtermine the hardness, H . The hardness is defined as the mean pressure the materials support under load. With this definition, the hardness is calculated as:

$$H = \frac{P_{\max}}{A}$$

It is worth to point out that the hardness measured from nanoindenter is different from that obtained from the conventional hardness tester where the area is defined by direct measurement of the residual hardness impression. The primary distinctions between depth sensing indentation and conventional microhardness testing is the manner in which

the contact area is established from an analysis of the load-displacement data rather than by imaging of the indentation after the load is removed and measuring the diagonal lengths [44]. As the indenter is driven into the material, an impression conforming to the shape of the indenter to some contact depth appears. The depth h and the projected A have the relation expressed as:

$$A(h) = 24.5h^2 + C_1h + C_2h^{1/2} + C_3h^{1/4} + \dots + C_8h^{1/128}$$

where C_1 through C_8 are constants. The lead term describes a perfect Berkovich indenter; the others describe deviations from the Berkovich geometry due to the blunt of the tip. The micro-compression is carried out by the nanoindenter coupled with flat-ended punch tip. Using in-situ SEM microcompression test, we can directly observe the stress-strain behavior along with morphological, size and shape changes in micropillars. One of the advantages of in-situ SEM mechanical testing is the continuous monitoring of the alignment, which is known to affect the test's accuracy [45].

3.3 Results and Discussion

3.3.1 SEM and TEM Analysis of Nanostructured Magnesium Alloy

The microstructural characteristic of the cryomilled Mg-10 wt.% Al powders has been reported by Pozuelo et al. [46]. This result indicates that the cryomilling reduces the crystallite size ($\sim 3:1$) of the as-received powders and an average grain size of 30 nm was achieved after 8 hours cryomilling. After cryomilling, the cryomilled powders were consolidated by SPS to produce a disk-shaped specimen, referred to as the SPS sample.

Figure 3-4 (a) shows the SEM image of the microstructure of the SPS sample after polishing and etching with Nital 2%. The composition of the Mg-10Al sample, confirmed by the EDX analysis as shown in Fig. 3-4(b). Figure 3-4 (a) reveals interdendritic network morphology of a second phase that corresponds to $\text{Al}_{12}\text{Mg}_{17}$. Figure 3-4(a) shows the interdendritic $\text{Al}_{12}\text{Mg}_{17}$ in bright contrast (highlighted by position 1). In dark contrast appear the Mg-rich regions (highlighted by position 2) as revealed by the EDX analysis shown in Fig. 3-4(b). The EDX quantitative analysis of position 1 reveals a composition $\text{Al}_{12}\text{Mg}_{17}$, i.e., around 52.4 wt.% Mg and 39.3 wt.% Al, whereas position 2 gives a rich Mg composition of 85.4 wt.% Mg and 3.7 wt.% Al. Fig. 3-5 shows the TEM analysis of the sample after SPS (referred as SPS'ed sample). Fig. 3-5(a) is a bright-field TEM image showing the characteristic bimodal grain size distribution commonly obtained after SPS [29,46] Fine-grains with an average grain size around 35 ± 17 nm along with coarse-grains around 400 ± 164 nm can be observed. The SAED pattern (inset) from the image shows a typical rings pattern from nanostructured Mg grains and also some strongest spots from coarse-grains. The bimodal grain distribution can be also indentified in the high-angle annular dark-field (HAADF) STEM images (Fig. 3-5b and c). It is interesting to note that in addition to equiaxed coarse-grains (Fig. 3-5b) some grains have grown along preferential directions resulting in elongated coarse-grains (Fig. 3-5c). HAADF-STEM images allow us to determine differences in composition given by the Z-contrast. In fact, Al-rich areas are distinguished by the brightest contrast in the STEM image (Fig. 3-5b) as confirmed by the EDS results (Fig. 3-5d). From the quantitative

EDS analysis, we found the precipitation of the intermetallic $\text{Al}_{12}\text{Mg}_{17}$ (γ -phase) in Al-rich areas. Note that the γ -precipitate highlighted in Fig. 3-5c exhibits an elongated shape and size longer than 800 nm. On the contrary, α -Mg matrix is clearly identified in the darkest areas as shown by the EDS analysis in Fig. 3-5c.

3.3.2 SEM and TEM Analysis of the Extruded Nanostructured Magnesium Alloy

Figure 3-6 shows the SEM image of the microstructure of the extruded SPS sample after polishing and etching with Nital 2%. Figure 3-6 (a) reveals interdendritic network morphology of a $\text{Al}_{12}\text{Mg}_{17}$ phase at the transverse section. The amount of $\text{Al}_{12}\text{Mg}_{17}$ is more and $\text{Al}_{12}\text{Mg}_{17}$ is more closely packed compared to the sample without extrusion. Figure 3-6(b) shows the longitudinal section. It is interesting to note that the interdendritic $\text{Al}_{12}\text{Mg}_{17}$ with bright contrast is aligned along the extrusion direction. The characteristic bimodal grain size distribution obtained after SPS also remains after extrusion. Bright-field TEM image of a cross-sectional view of the extruded sample (Fig. 3-7a) clearly shows a fine-grain region with an average grain size around 38 ± 18 nm (top part of the image) along with a coarse-grained region with grains around 500 ± 290 nm (bottom part of the image). No sign of recrystallization was found. From the TEM analysis of coarse-grained regions (Fig. 3-7b and c), we found dislocations array at grain boundaries of grains bigger than 200 nm (marked by arrows in Fig. 3-7b). Fig. 3-7c displays dislocations array at a grain boundary of a coarse grain oriented to the $[0001]$ zone axis as shown its SAED pattern (inset). HRTEM image of the grain boundary in Fig.

3-7c reveals the presence of prismatic dislocations (highlighted by $\perp$) terminated at stacking faults (Fig. 3-7d). Inset is the indexed FFT of the image indicating the $\{1\bar{1}00\}$ planes where dislocations occur. STEM analysis of a parallel view of the extruded sample is shown in Fig. 3-8. Elongated α -Mg grains parallel to the extruded direction (highlighted by ED) are clearly observed (Fig. 3-8a). The intermetallic γ -Al₁₂Mg₁₇ phase appears in the form of small precipitates also aligned along the extrusion direction that can be identified by the brightest contrast in the HAADF-STEM images. These small precipitates can be better seen at higher magnification in Fig. 3-8b and c and confirmed by the EDS data obtained from selected points of interest (Fig. 3-8e). We provide further evidence using EDS line scan as a function of position (Fig. 3-8f), which shows the variation in Al and Mg content along the orange arrow marked in Fig. 3-8d. The blue and black curves in Fig. 3-8f correspond to Al-K and Mg-K line intensities, respectively. We can easily correlate Al-hills and Mg-valleys with the position where γ -precipitates are located. We would like to point out the small size of these precipitates with more spherical shape after extrusion. From a total of 40 intermetallic precipitates collected from different regions of the extruded sample, we determine an average size of 28 ± 15 nm, which is ~ 30 times smaller than that before extrusion. This result suggests that γ -precipitates are deformed and fractured during the extrusion process, which leads to nm size intermetallic precipitates. HRTEM was used in order to better characterize these γ -Al₁₂Mg₁₇ nanoprecipitates. Fig. 3-9a is a HRTEM image showing an individual γ -Al₁₂Mg₁₇ nanoprecipitate of 25 nm size. Moiré fringes can be observed due to the

superposition of the lattices of both the α -Mg matrix and γ -Al₁₂Mg₁₇ nanoprecipitate. Labels A and B highlight areas from the Mg matrix and nanoprecipitate, respectively. Fig. 3-9A and B are fast Fourier transforms (FFT) of these two areas. The indexed FFT in A reveals a hcp-Mg grain oriented to the $[1\bar{2}1\bar{3}]$ zone axis. From the indexed FFT of B color code for clarity (Fig. 3-9C), we identify at least three reciprocal lattices. In addition to the Mg lattice $[31]$ oriented to the $[1\bar{2}1\bar{3}]$ zone axis (highlighted in red), we also indentify the bcc-Al₁₂Mg₁₇ lattices $[32]$ oriented to the $[\bar{1}13]$ and $[001]$ zone axes that are highlighted in green and blue, respectively. In fact, the blue one oriented to the $[001]$ zone axis is obtained from the region enclosed by the blue rectangle in the Fourier filtered image of Fig. 3-9b. This observation indicates that another γ -Al₁₂Mg₁₇ nanoprecipitate is underneath. The orientation relationships between the matrix and nanoprecipitates are $[1\bar{2}1\bar{3}]_{\alpha} \parallel [\bar{1}13]_{\gamma} \parallel [001]_{\gamma}$.

3.3.3 XRD Analysis of the Extruded Nanostructured Magnesium Alloy

XRD analysis was performed in order to confirm the presence of the main α -Mg and γ -Al₁₂Mg₁₇ phases. X-ray spectra of the cryomilled powders, SPS'ed and extruded samples are included in the plot of Fig. 3-10. XRD data of the cryomilled powders reveal the characteristic peaks of Mg and Al. The crystallite size determined by the peak broadening according to the Scherrer equation is ~ 33 nm after cryomilling, which is in good agreement with the TEM results (30 nm). After SPS, it is interesting to note the peaks corresponding to the intermetallic γ -Al₁₂Mg₁₇ phase as expected from the phase

diagram. As acquired from the TEM analysis, the crystallite size from the fine-grain region remains stable after SPS. However, it can be seen that Mg peaks are slightly shifted to lower angles comparing with those from the cryomilled powders spectrum. This observation suggests an increase in the Mg lattice parameter after SPS that might be due to the reduction of Al atoms in solid solution by the precipitation of the intermetallic phase. Considering that the size of the Al solute atom is smaller than Mg atom, the effective lattice parameters for the Mg rich alloy will be higher based on Lubarda's theory [47]. The XRD spectrum from a parallel view of the extruded sample clearly reveals a deformation texture on the basal (0002) planes, which is commonly observed in extruded rods of hexagonal materials. This is termed as the “cylindrical texture” where the basal planes are parallel to the extrusion axis [48]. The same main phases are also observed in the sample after extrusion and no changes in the peak broadening are noticeable. In fact, a crystallite size ~ 35 nm is measured by the peak broadening, which is also in good agreement with the TEM data (38 nm). It is interesting to note that the spectrum of the extruded sample is slightly shifted to higher angles comparing with the spectra of the cryomilled and SPS'ed samples, which is indicative of some shrinkage in the lattice parameters. From the same relative peak height between α -Mg and γ -Al₁₂Mg₁₇ in the SPS'ed and extruded spectra, we can consider that the volume fraction of the intermetallic phase has not changed after extrusion, which in turn indicates that the same amount of Al atoms is in solid solution. Therefore, we believe that this shrinkage in lattice parameters might be due to the strain introduced by the plastic deformation during extrusion.

3.3.4 Mechanical Behavior of the Extruded Nanostructured Magnesium Alloy

In order to evaluate the mechanical behavior of the sintered material, compression tests on the SPS'ed and extruded samples were performed at room temperature. Their representative engineering stress–strain curves are shown in Fig. 3-11 and the relevant mechanical properties are summarized in Table 1. At least 5 samples were tested per condition, although only two are shown here to demonstrate the reproducibility on the results. The plots show clearly the same tendency in both samples. SPS'ed samples (left plot) exhibit a classic elastic regime with a compressive yield strength (YS) of around 398 MPa and an ultimate compressive strength (UCS) of 464 and 468 MPa, respectively before failure at ~2.4% of strain. A compressive YS of 550 MPa and an UCS of 580 MPa are achieved after extrusion without reducing the elongation to failure (right plot). These are remarkable compressive results obtained on the extruded samples tested along the extrusion direction with a substantially improvement in strength around 40% (Table 1). The compressive strength (YS of 550 MPa, UCS of 580 MPa) for a nanostructured Mg–Al alloy (without any additional alloying elements) after extrusion are comparable to the highest strength values recently reported under tension for a Mg–Gd–Y–Ag–Zr alloy (YS of 575 MPa, UTS of 600 MPa) [49]. Comparing with the values reported in the literature for commercial Mg–Al–Zn alloys, the compressive YS values of extruded nanostructured Mg–10Al alloys are ~5 and 3 times higher than those for the extruded AZ61 (120 MPa) [50] and AZ31 (160 MPa) [51], respectively. In the case of a nanostructured AZ80 alloy processed by cryomilling and SPS a compressive YS of 442 MPa is reported [52]. The

compressive strength values obtained in this investigation are striking results for a conventional Mg–Al alloy (without any additional alloy elements). These remarkable results obtained from the compression tests that were conducted in the longitudinal direction of the extruded Mg–10Al samples are discussed in terms of: (1) grain size, (2) γ -Al₁₂Mg₁₇ nanoprecipitates and (3) texture. The aim to perform a secondary process via extrusion was mainly to introduce some plastic deformation to the sintered material in order to moderately modify its microstructure and attain superior mechanical properties. For this purpose, the extrusion parameters (extrusion ratio, ER, and temperature) were carefully chosen mostly to prevent significant changes in the grain size. We used ER=2:1 and T=260 °C, which are actually very low values comparing with the regular extrusion parameters reported in the literature. For instance, ER between 25:1 and 66:1 and extrusion temperatures between 250 and 400 °C have been reported for the commercial extruded AZ31 and AZ91 Mg alloys [51,53]. For a Mg–Al–Ca–Mn alloy the extrusion parameters were ER=20:1 and temperature of 350 °C [54]. And for a Mg–Zn–Y–Zr alloy the ER and temperature range was 10:1 and 300–400 °C, respectively [55]. No significant changes in the grain size and no sign of recrystallization have been found after extrusion in the present study. In fact, the characteristic bimodal grain size distribution obtained after SPS (Fig. 3-5) also remains after extrusion (Figs. 3-7 and 3-8). We only found a slightly growth of the mean grain size in both fine-grained (from 35±17 nm to 38±18 nm) and in coarse-grained (from 400±164 nm to 500±290 nm) regions after extrusion. The formation of a bimodal grain structure has previously been reported [29,46,56] and

mainly attributed to a local heterogeneous grain growth during SPS consolidation. It is theorized that during initial stages of SPS, small surface contact areas are formed where the current density is highly localized. As a result of this localized current density, contact areas are heated up due to the Joule effect, which favors grain growth in these localized regions. Therefore, the growth of some grains along preferential directions resulting in elongated coarse-grains (Fig. 3-5c) can be explained by a temperature gradient in the sample, which is indeed an intrinsic characteristic of the SPS process. It has also been reported that bimodal grain size distribution can contribute to enhance not only the strength but also the ductility [42,57]. Coarse-grains may facilitate the mobility of dislocations and contribute to the ductility, while nanocrystalline grains contribute to the strengthening by the Hall–Petch mechanism. However, additional factors should be considered in addition to the grain size strengthening in order to explain a 40% improvement in compressive strength for the extruded sample. This will be addressed in detail in the following sections.

In addition, it is well known that grain size has a significant influence on work hardening, i.e. a decrease in grain size leads to a strong reduction in work hardening. As shown in Fig. 3-11, the compressive stress–strain curves of both SPS'ed and extruded samples exhibited a very low work hardening. In general, the strain hardening effect is higher under compression than under tension because twinning is mostly activated under compression. However, the flow curve shape in compression may become similar to that in tension by decreasing grain size. This effect has been observed in ultrafine-grained

materials and attributed to a decrease in twinning activity with decreasing grain size [58]. In particular for nc materials, the lack of work hardening has mainly been explained because of the limited dislocation storage inside nc grains [59], a decrease in twinning activity [58] and also due to a contribution of the grain boundary sliding (GBS) mechanism [60]. In the case of nc Mg, it has been reported that deformation twinning is suppressed due to the high stress required for a twin to nucleate [36], which increases drastically with decreasing grain size to the nm scale [58,61]. However, we have recently provided evidence of nanotwins in nanostructured Mg–Al alloys processed by cryomilling. We demonstrate that the thermo-mechanical conditions during cryomilling (high strain rate and cryogenic temperatures) provide the required critical stress to facilitate nanotwins-generation in nanostructured Mg–Al alloys. Using high-resolution TEM studies and molecular dynamic (MD) simulations, we prove that the two common twinning systems in coarse-grained Mg prevail in nanocrystalline grains. Moreover, from in-situ SEM micro-compression studies [42], we found that basal plane sliding and contraction twins are the mechanisms involved in the deformation under compression of nanostructured Mg–10Al micropillars.

Furthermore, a strong decrease in the hardening rate has been observed in fine-grained Mg alloys and attributed to a contribution of the GBS mechanism [60]. It appears that GBS plays an important role in the plastic deformation of very fine-grained Mg-based alloys at room temperature and its tendency increases with decreasing grain size [60,62–64]. Under high stress conditions, GBS becomes the major deformation

mechanism at room temperature in nanostructured Ni [65] as well as in nanostructured Mg [64]. In the present study, we provide evidence of GB containing dislocations arrays as a consequence of straining under extrusion (Fig. 3-7). The high density of dislocations at GB might induce GBS at room temperature in nanostructured Mg–Al alloys. However, further investigation is needed to fully understand the lack of work hardening in nanostructured Mg–Al alloys with a bimodal grain structure where the dislocations mediated and/or twinning mechanisms cannot be negligible.

We have noticed that extruded samples mainly exhibit a deformed microstructure with coarse-grains elongated along the extrusion direction and no sign of recrystallization. However, a strong extrusion effect was observed on the intermetallic γ -Al₁₂Mg₁₇ phase that is discussed as follows. During the cross-section reduction of the SPS'ed sample in the extrusion die, the Mg-matrix is plastically deformed leading to the characteristic elongated grains along the extrusion direction (Fig. 3-8). At the same time, we have evidence that the γ -Al₁₂Mg₁₇ second phase already present after SPS, transforms into more spherical and smaller precipitates with nm sizes (28 ± 15 nm) after extrusion. This observation suggests that the preexisting γ -Al₁₂Mg₁₇ phase can be deformed and fractured during the secondary process. As a matter of fact, it has been reported that the intermetallic Al₁₂Mg₁₇ becomes soft and deformable at temperatures above 150 °C. Therefore, it is reasonable to think that γ -Al₁₂Mg₁₇ deforms with the Mg-matrix during hot extrusion at 260 °C. However, due to the differences in plasticity between the Mg matrix and intermetallic compound, the brittle intermetallic γ -Al₁₂Mg₁₇ is breaking up

into nanoprecipitates under the plastic deformation during extrusion (Figs. 3-8 and 3-9). We believe that this microstructural feature is a key factor that plays an important role in the enhancement of strength. The intermetallic compound in the form of nanoprecipitates can serve as obstacles for dislocation movement that will increase the stress necessary for the motion of dislocations. Therefore, in addition to the grain size strengthening the contribution of the precipitation hardening attributed to the dislocation-nanoprecipitates interaction should be considered.

XRD analysis after extrusion has demonstrated the typical deformation texture consisting of a basal fiber with $[10\bar{1}0]$ directions parallel to the compression axis. That means that the c-axis is constrained under compression along the extrusion direction. When deformation occurs in the condition of c-axis constraint, it is well known that no basal $\langle a \rangle$ slip can support deformation along the extrusion direction, because the Schmid factor for basal $\langle a \rangle$ slip is equal to zero. Then, other deformation mechanism such as prismatic $\langle a \rangle$ slip or twinning can be activated. However, the critical resolved shear stresses for non-basal slips and twinning are much higher than that for the basal slip near room temperature [48]. Therefore, a basal texture oriented in the compression direction can contribute to the improvement in strength and also be responsible to the low strain hardening observed. This is mainly because the deformation mechanism by basal slip is not favored under this texture condition [34,59]. Our previous results from in-situ SEM microcompression tests on nanostructured Mg-10Al alloys [42] have demonstrated the important role that the grain orientation plays in the activation of certain deformation

mechanisms. In particular, for grains oriented with the c-axis almost parallel to the loading direction, the Schmid factor was very low for basal plane sliding. Instead, grains turned to deform by twinning. In fact, contraction nanotwins of $\sim 2\text{nm}$ width were identified

3.3.5 Micro-compressive Mechanical Properties of Nanostructured Magnesium Alloy

Mg-10Al micropillars with diameters $\sim 3.5\ \mu\text{m}$ and aspect ratio of 1:3 were machined by focused-ion-beam (FIB) in order to perform in-situ SEM microcompression tests. A FEI Nova600 Nanolab DualBeam FIB-SEM is used for this purpose. Microcompression tests were performed using a PI-85 PicoIndenter instrument (Hysitron Inc.) installed on a FEI Nova230 Variable Pressure SEM (VP-SEM). We used a conventional diamond indenter with a flat- end tip of $\sim 8\ \mu\text{m}$ in diameter at $20\ \text{nm/s}$ displacement-rate control. TEM samples of the compressed pillars were prepared by FIB. TEM analysis was carried out using a FEI-Titan TEM operating at $300\ \text{kV}$. Using in-situ SEM microcompression test, we directly observe the stress–strain behavior along with morphological, size and shape changes in Mg-micropillars. One of the advantages of in-situ SEM mechanical testing is the continuous monitoring of the alignment, which is known to affect the test's accuracy [66]. Five Mg-10Al alloy micropillars were tested under the same conditions. In order to avoid any overestimation of the measured stress due to the tapering (1.5°), the diameter is considered at half-height of the pillar ($\sim 4\ \mu\text{m}$).

A typical compressive stress–strain curve (black color) is shown in Fig. 3-12a. A yield strength of 310 MPa is measured resulting two times higher than that reported for single-crystal Mg-micropillars $\sim 6\text{ }\mu\text{m}$ in diameter ($\sim 170\text{ MPa}$) [67]. Based on our results, no size effect in strength is observed for nanostructured Mg-micropillars with diameters $\geq 3.5\text{ }\mu\text{m}$. Note that the maximum strength of 630 MPa is reached with 13% elongation at failure. From the video , we can correlate SEM images with stress–strain curves. Interestingly, the formation of shear bands is detected at 10% of deformation. Next test was then stopped at 10% of strain (blue curve) in order to study the deformation mechanisms activated at this particular deformation. Similar results are obtained with yield strength of 320 MPa and a maximum strength of 534 MPa at 10% of strain. It is interesting to note, two stress drops just after the transition from elastic to plastic flow that might be associated with the nucleation and propagation of twins [68]. 20° tilted-view SEM images acquired from the video of a typical Mg-micropillar before and after compression ($\epsilon=10\%$) are shown in Fig. 3-12b and c, respectively. Initial height and diameter are ~ 17 and $\sim 4\text{ }\mu\text{m}$, respectively (Fig. 3-12b). During compressive loading, plastic deformation is mainly concentrated on the top of the pillar that leads to a slightly bigger diameter ($\sim 4.5\text{ }\mu\text{m}$) after compression. Shear bands are clearly observed at 10% of deformation (Fig. 3-12c). Fig. 3-13a shows 52° tilted-view high-resolution SEM image of the compressed pillar at $\epsilon=10\%$. Shear bands are better observed on the pillar surface formed $\sim 60^\circ$ with respect to the loading direction. In order to characterize the microstructure and study the deformation mechanism at this particular strain, a TEM

sample of the compressed pillar was prepared by FIB. Fig. 3-13b is a bright-field TEM image showing a polycrystalline Mg-pillar as confirmed by the selective- area-electron-diffraction (SAED) pattern (Fig. 3-13c) taken from the top of the pillar. From Fig. 3-13b, we can identify the bimodal grain size distribution characteristic after SPS consolidation [46]. In addition to grain sizes ~ 500 nm, we also observe some regions with grains smaller than 20 nm as shown by the dark-field TEM image (Fig. 3-13d) obtained by setting the objective aperture in the Mg (10-11) ring. Fig. 3-13a is a bright-field TEM image showing the shear band (highlighted by a white arrow in Fig. 3-13b) that forms an angle $\sim 60^\circ$ with respect to the loading direction. Fig. 3-14b shows a close-up image of the region enclosed by a white rectangle in Fig. 3-14a. Its micro-diffraction pattern (inset) reveals that the shear band occurs on the basal planes for a grain oriented to the $[2\bar{1}\bar{1}0]$ zone axis. In addition, HRTEM image shown in Fig. 3-14c reveals the presence of basal stacking faults (SFs) defects (highlighted by white arrows) as confirmed by the FFT of the image (inset). Characteristic streaks parallel to the (0001) direction as a result of basal SFs can be observed. The atomic-resolved TEM image (Fig. 3-14d) shows better the SFs enclosed by the white rectangle in Fig. 3-14c. In general, basal slip will be the main deformation mechanism for a system with basal planes at particular angles that result in the largest Schmid factor [68]. The Schmid factor for basal sliding in this grain is 0.433 where basal planes have an angle $\sim 30^\circ$ with respect to the loading direction. Interestingly, we have found that twinning is also involved in the deformation of the nanostructured Mg-micropillar (Fig. 3-15). In fact, nanotwins ~ 2 nm widths have been

identified in a neighboring nanocrystalline Mg-grain oriented to the $[1\bar{2}1\bar{3}]$ zone axis as shown by Fourier filtered HRTEM image in Fig. 3-15a. Basal planes in this grain are almost parallel to the loading direction and that results in a low Schmid factor (0.053) for basal plane sliding. Twin boundaries (TB) giving a mirror relationship between the parent and twin planes are highlighted by solid white lines in Fig. 3-15a. FFT of the image (Fig. 3-15b) clearly reveals splitting spots due to the presence of twins. From the analysis as shown by its color-coded indexed FFT (Fig. 3-15c), we indentify contraction twins on the characteristic $\{10\bar{1}1\}$ planes with the misorientation relation between the parent (blue) and the twin (red) $\sim 58^\circ$ [69,70]. It is interesting to observe that TBs can propagate by the motion of atomic steps with a step height of two-atomic $\{10\bar{1}1\}$ planes (highlighted by two arrows parallel to the $\{10\bar{1}1\}$ planes). Molecular-dynamics simulations have demonstrated that contraction twins can be activated in Mg-grains and controlled by two-layer zonal twinning dislocations [70,71]. We believe that the introduction of nanotwins along with the bimodal grain size structure explain the remarkable compressive strength and ductility of nanostructured Mg-micropillars. While nanocrystalline grains contribute to the strengthening by the Hall–Petch mechanism, coarse-grains and nanotwins facilitate the mobility of dislocations that results in an enhanced ductility. In particular, nanotwins can create more local sites for nucleating and accommodating dislocations [72], which is beneficial for the improvement in strain hardening and ductility.

3.3.6 Strain Rate Sensitivity (SRS) of Nanostructured Magnesium Alloy

The strain rate sensitivity on the mechanical properties is an important factor for structural applications and can be expressed as [73]:

$$m = \frac{\sqrt{3}kT}{V^*}$$

where k is the Boltzmann constant, T is the temperature, H is the hardness and V^* is the activation volume for plastic deformation, in the relation [74]:

$$V^* = \sqrt{3}kT \frac{\partial \ln \dot{\epsilon}}{\partial \ln H}$$

where $\dot{\epsilon}$ is strain rate. By substitute the expression of V^* to the expression of m , the relation between SRS and strain rate can be obtained as:

$$m = \frac{\partial \ln H}{\partial \ln \dot{\epsilon}}$$

Fig. 3-16 (a) shows the hardness with different strain rates ranging from 0.001 to 1. The results show that with increasing strain rate, the yield strength increases significantly from 1.34 to 2.66 GPa. Fig. 3-16 (b) shows the relation between $\ln H$ vs. $\ln \dot{\epsilon}$. The linear relation is shown and the slope is m . In this case, $m=0.0881$ is measured. There are a limit number of literatures reporting the SRS of nanostructured magnesium or magnesium alloy. The SRS obtained by Dorn et al. of single crystal magnesium is around 0.041 [75]. It is worth to point out that this is based on the basal slip system for magnesium. Creep test on single crystal magnesium at room temperature conducted by Conrad et al. shows an SRS of ~ 0.19 [76]. Trojanova et al. measured the SRS for NC-Mg ($d = 100$ nm) to be ~ 0.31 at room temperature [77]. Hwang et al., measured the SRS for

nanostructured magnesium (grain size = 45 nm) to be 0.6 at room temperature [64]. It then suggests that the SRS of Mg may be increased by reduced grain size.

3.4 Conclusions

High strength nanostructured Mg–10Al alloys are successfully processed via cryomilling and SPS followed by warm extrusion. Remarkable compressive strength (YS of 550 MPa, UCS of 580 MPa) are measured at room temperature for conventional Mg–Al alloys (without any additional alloy elements). The high strength achieved is attributed to a combination of grain size strengthening, precipitation hardening and texture strengthening mechanisms. TEM data, in good agreement with the XRD analysis, reveal nanocrystalline grains of the cryomilled powders with an average size of 30 nm. In the SPS consolidated Mg alloy, we found a bimodal grain size distribution with coarse grains around 400 nm and nanocrystalline grains with an average grain size of 35 nm. After extrusion, no significant changes in the grain size and no sign of recrystallization are found. In fact, the characteristic bimodal grain size distribution after SPS also remains after extrusion. We found that the preexisting γ -Al₁₂Mg₁₇ phase can be deformed and fractured during the extrusion process, which leads to the formation of γ -Al₁₂Mg₁₇ nanoprecipitates. We believe that these nanoprecipitates play an important role in the enhancement of strength as obstacles for dislocation movement. Finally, from XRD analysis we identified a basal texture oriented in the compression direction that also contributes to the improvement in strength by the activation of non-basal slip systems

and/or twinning. In addition, by using in-situ SEM microcompression tests we have demonstrated high strength with concurrent ductility for Mg-micropillars with a bimodal grain size structure. The orientation effect of two neighboring grains on the deformation mechanism at 10% of strain has been studied by HRTEM. One grain oriented to the $[2\bar{1}\bar{1}0]$ zone axis with the basal planes at $\sim 60^\circ$ with respect to the loading direction mainly deforms by basal plane sliding. Basal SFs defects have also been observed. And another grain oriented to the $[1\bar{2}1\bar{3}]$ zone axis with the basal planes almost parallel to the loading direction deforms by twinning. In fact, contraction nanotwins of ~ 2 nm width have been identified. These results indicate that basal plane sliding and contraction twinning mechanisms are involved in the deformation under compression of high strength and ductile nanostructured Mg-micropillars.

3.5 Reference

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Table 3-1. Compressive properties of the SPS'ed and extruded Mg-10Al samples.

Samples	No.	Yield strength (MPa)	Ultimate strength (MPa)	Strain at failure (%)
SPS'ed	1	398.3	464.2	2.2
	2	396.8	467.5	2.4
Extruded	1	547.6	572.0	2.1
	2	550.1	579.7	2.4

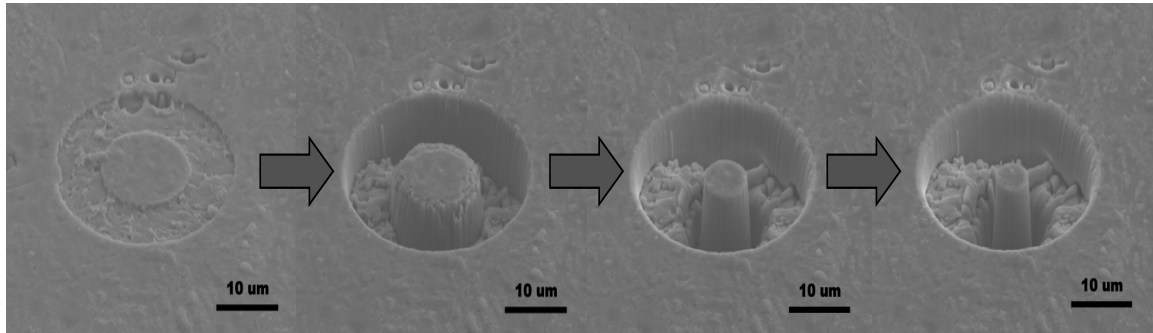


Fig. 3-1 The procedure of micro-pillar fabrication by using FIB.



Fig.3-2 Testing sample for nanoindentation

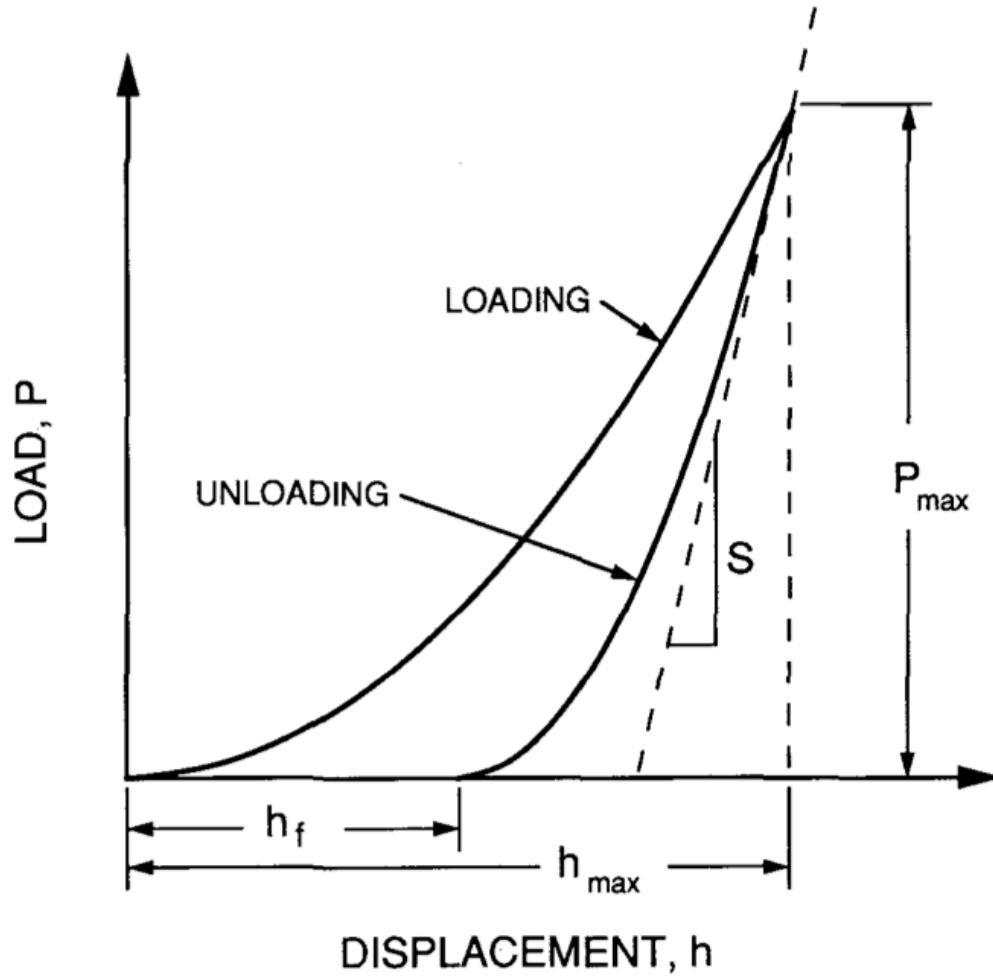


Fig. 3-3 A schematic representation of load vs. Indentation displacement data for an indentation experiment. The quantities shown are P_{max} : the peak indentation load; h_{max} : the indenter displacement at peak load; h_f : the final depth of the contact impression after unloading; and S : the initial unloading stiffness [43].

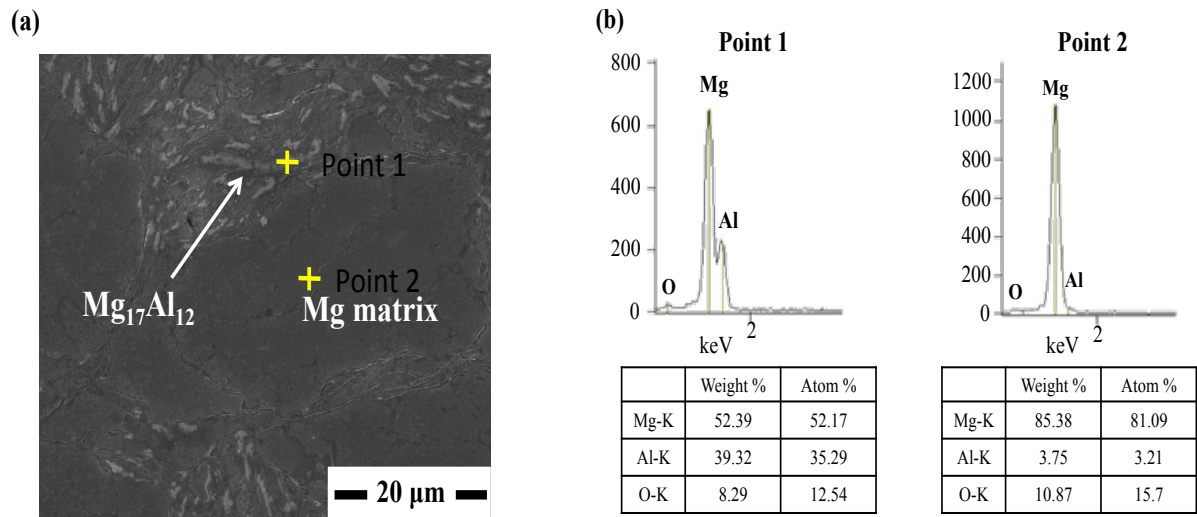


Fig. 3-4 (a) Scanning electron microscopy (SEM) and electron dispersive spectroscopy (EDX) analysis of Mg-10Al after SPS consolidation. (b) EDX spectra and the quantitative analysis (insets) from the points highlighted by 1 and 2 in (a).

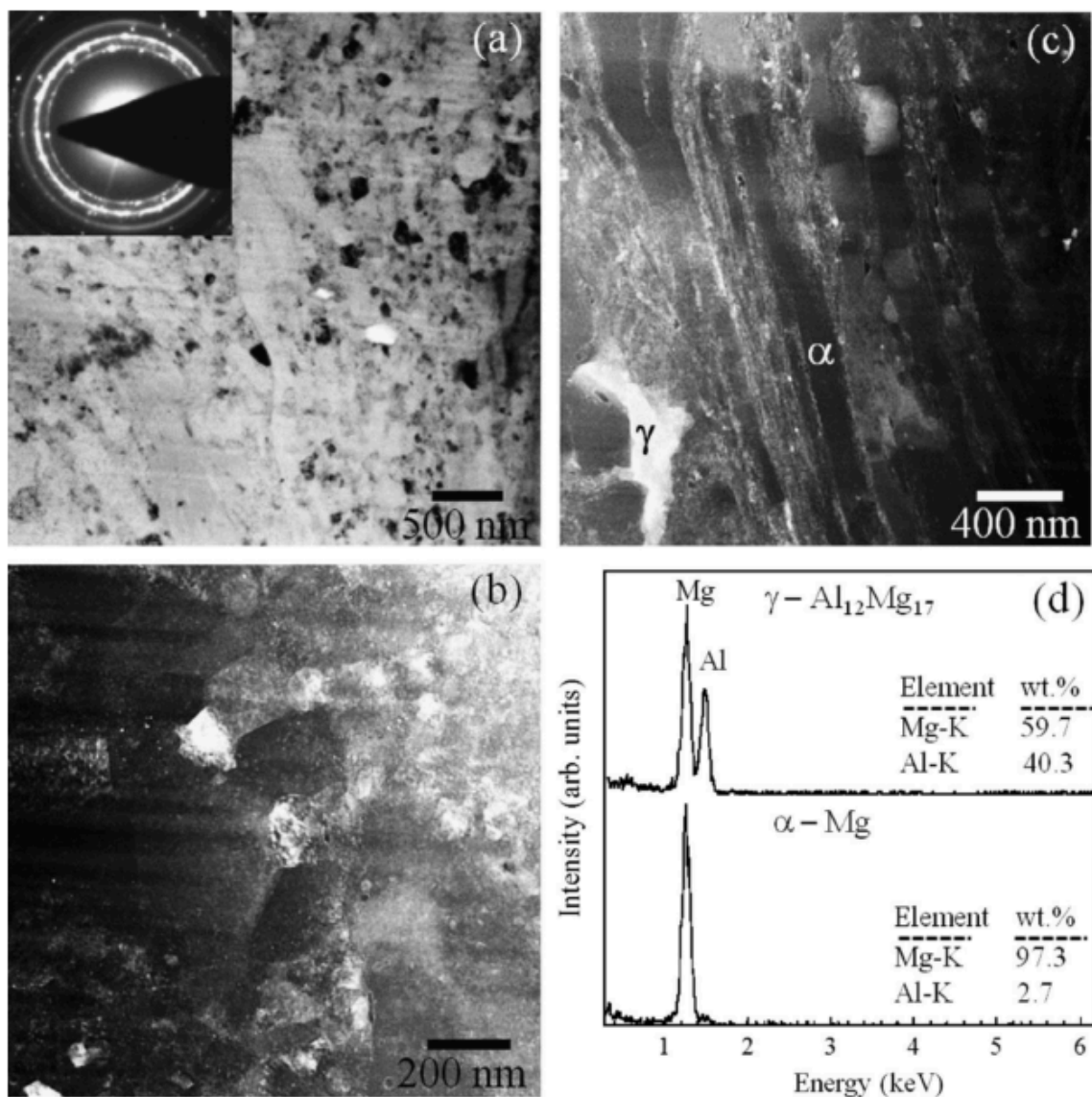


Fig. 3-5. (a) Bright-field TEM image of the SPS'ed Mg₉₀Al₁₀ sample. Inset is the SAED pattern. (b) and (c) Scanning transmission electron microscopy (STEM) images of the SPS'ed Mg-10Al sample. (d) Electron dispersive spectroscopy (EDS) spectra and quantitative values (inset) from the marked points in (c).

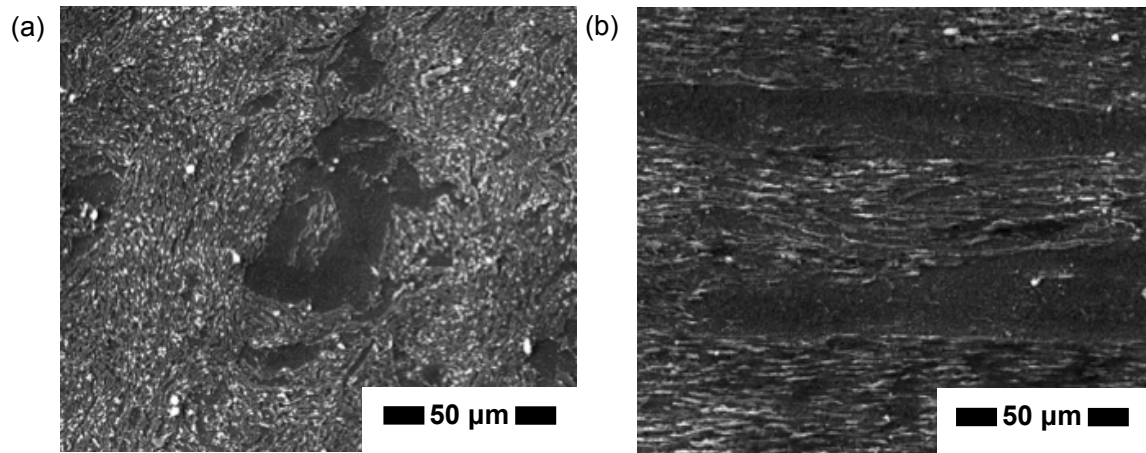


Fig. 3-6 Scanning electron microscopy (SEM) images of (a) a transverse section and (b) a longitudinal section of the extruded Mg-10Al sample.

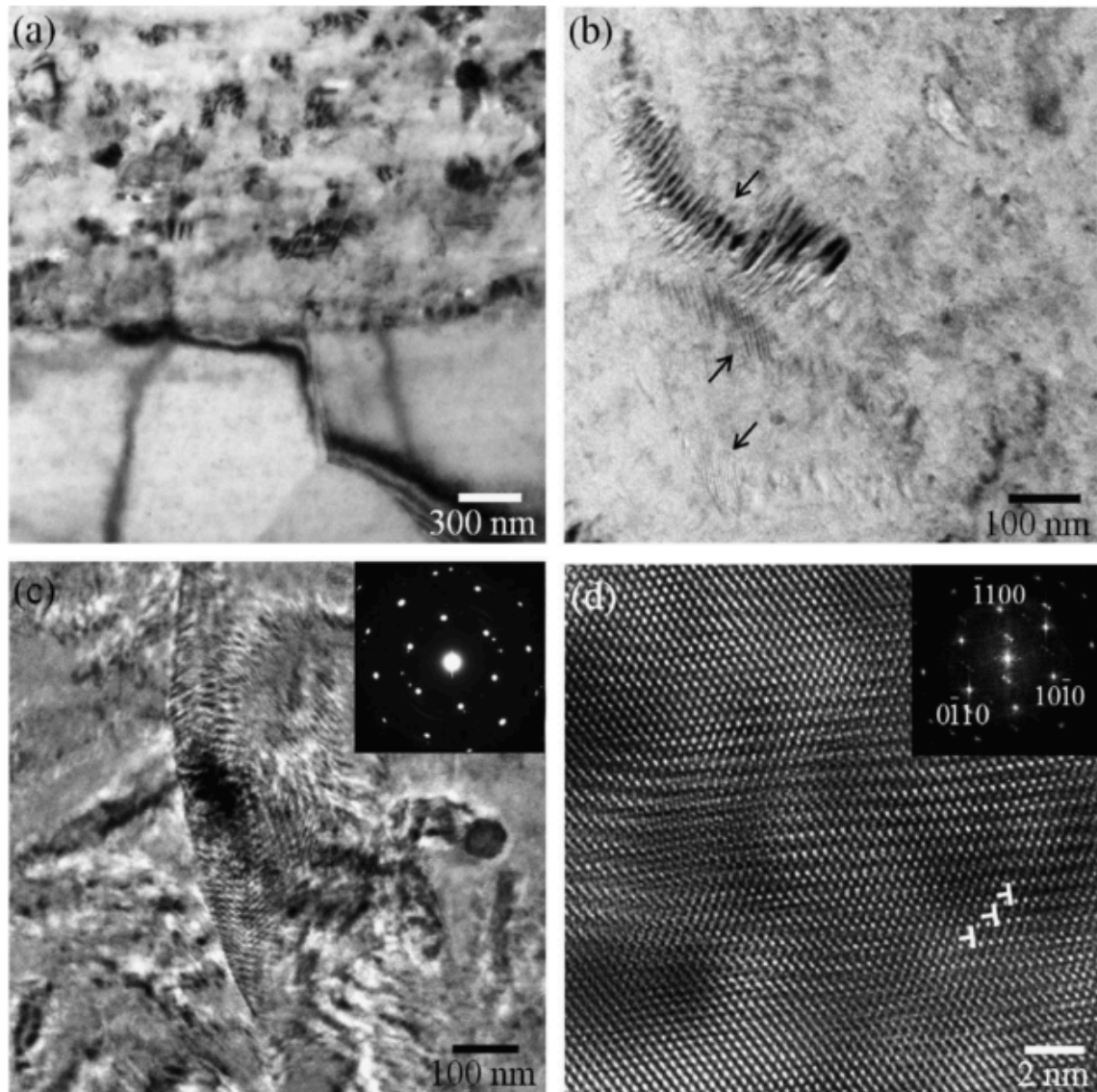


Fig. 3-7. (a) Bright-field TEM image of a cross-sectional view of the extruded Mg-10Al sample. (b) Bright-field TEM image of a coarse-grained region. (c) Bright-field TEM image of a coarse grain boundary. Inset is the SAED pattern of this grain. (d) HRTEM image of the grain boundary in (c). Inset is fast Fourier transform (FFT) of the image.

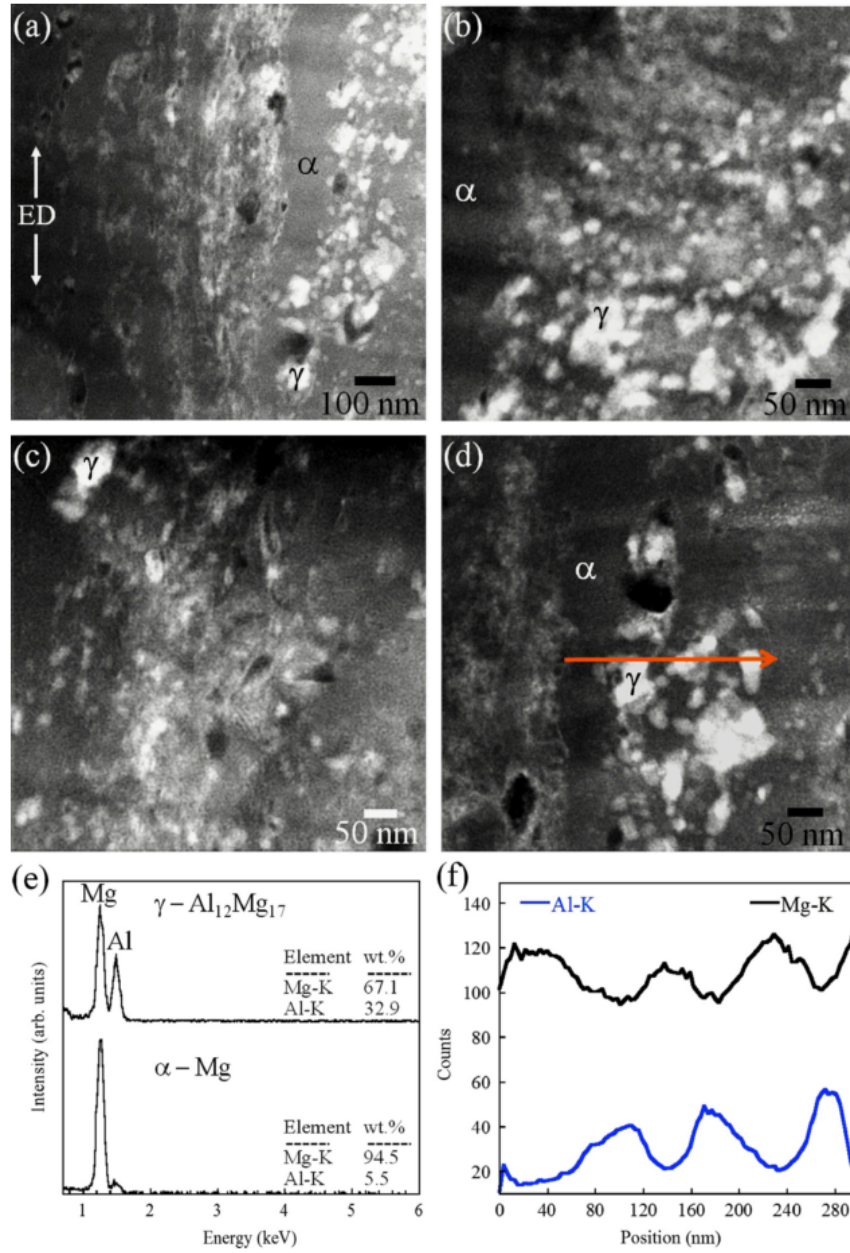


Fig. 3-8. (a) STEM image of a parallel view of the extruded Mg-10Al sample. (b)–(d) Higher magnification STEM images from different regions of the extruded Mg-10Al sample. (e) EDS spectra and quantitative values (inset) from selected points of interest. (f) EDS line scan as a function of position along the orange arrow marked in (d).

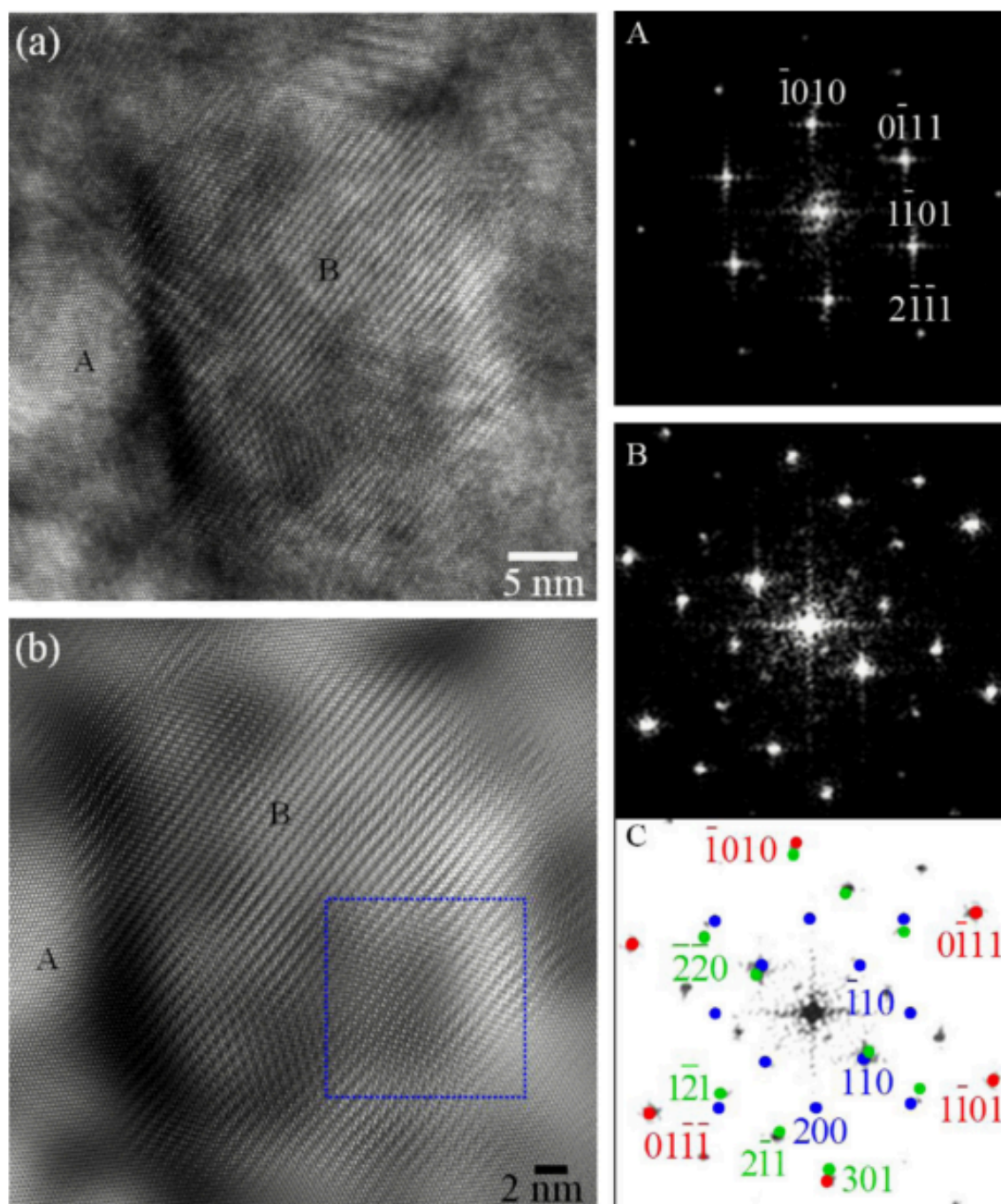


Fig. 3-9. (a) HRTEM image of an individual $\gamma\text{-Al}_{12}\text{Mg}_{17}$ nanoprecipitate. (b) Fourier filtered HRTEM image of the nanoprecipitate. A and B are the FFT of the highlighted regions in (a) and (b). C is the color-coded indexed FFT in B for clarity.

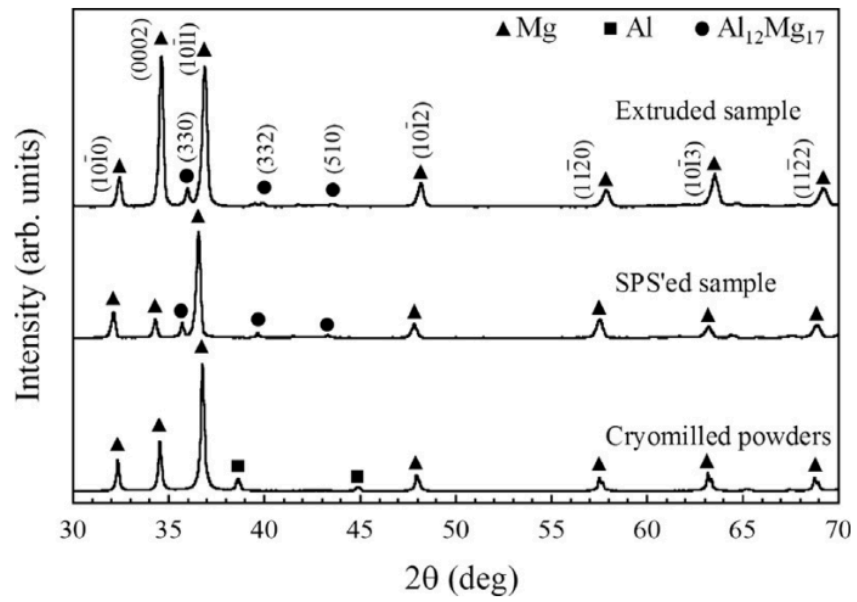


Fig. 3-10. X-ray diffraction spectra for the cryomilled Mg-10Al powders, and the SPS'ed and extruded samples.

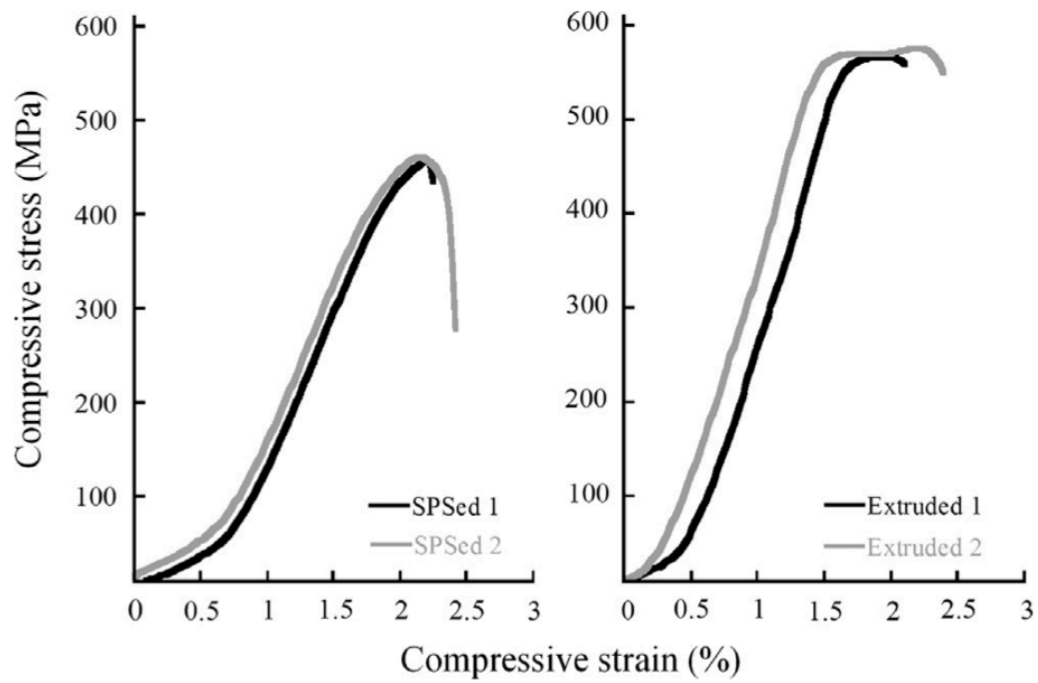


Fig. 3-11. Engineering stress–strain curves of the SPS'ed (left) and extruded (right) Mg-10Al samples obtained from compression tests.

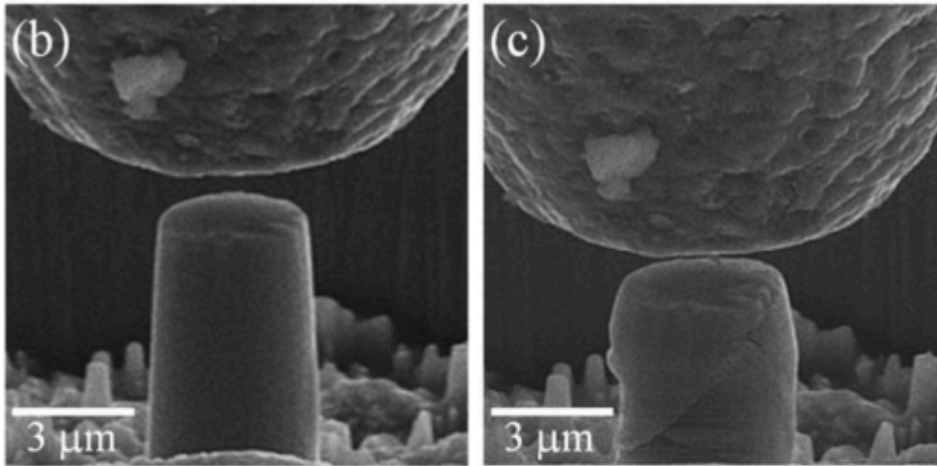
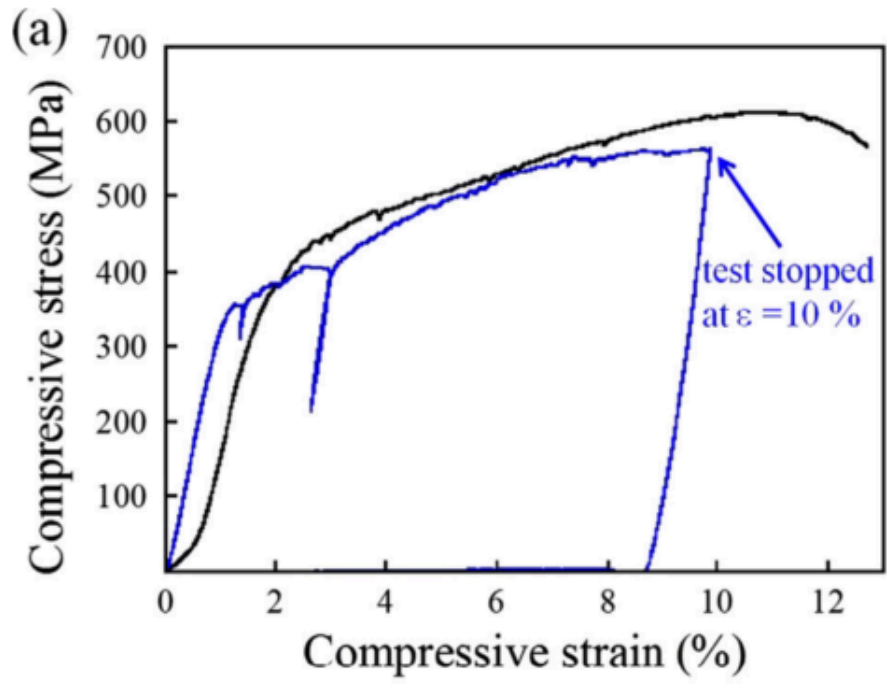


Fig. 3-12. (a) In-situ SEM compressive stress–strain curves for two nanostructured Mg-pillars. The blue one was stopped at 10% of strain. (b, c) SEM images of the Mg-pillar before and after compression at 10% of strain.

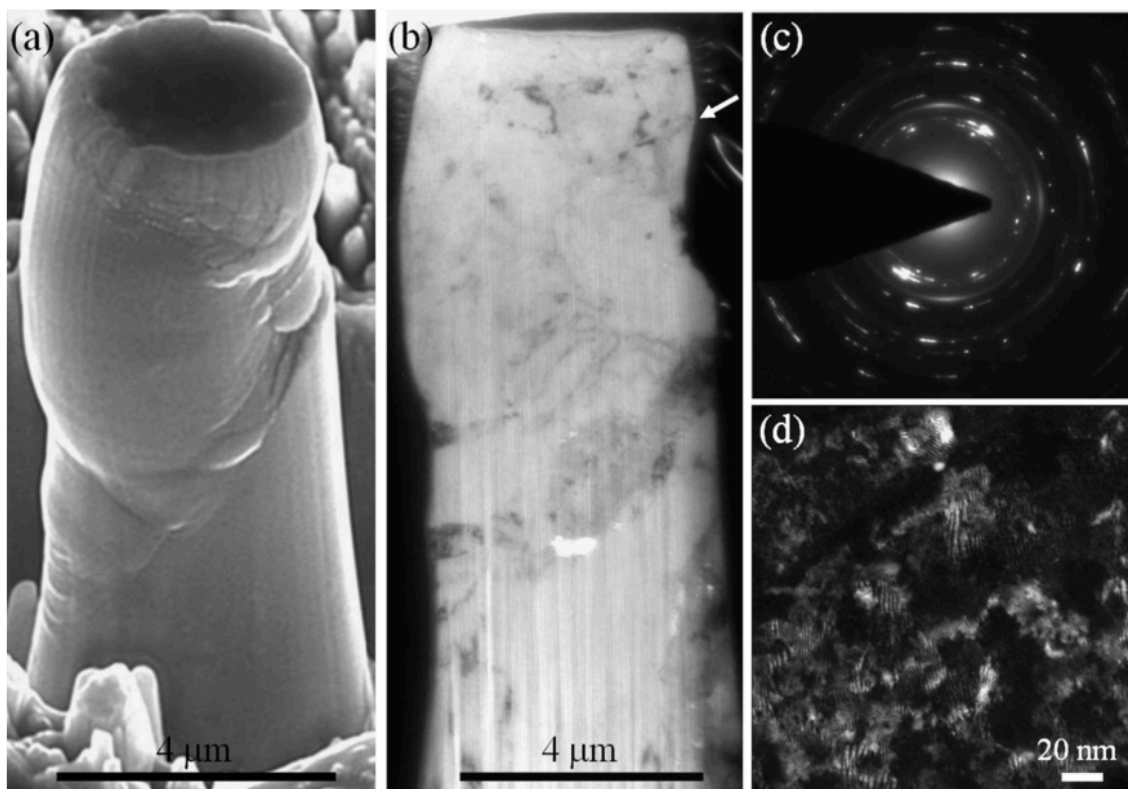


Fig. 3-13. (a) SEM and (b) TEM images of the compressed pillar at $\epsilon=10\%$. (c) SAED pattern from the top of the pillar. (d) Dark-field TEM image showing nanocrystalline grains.

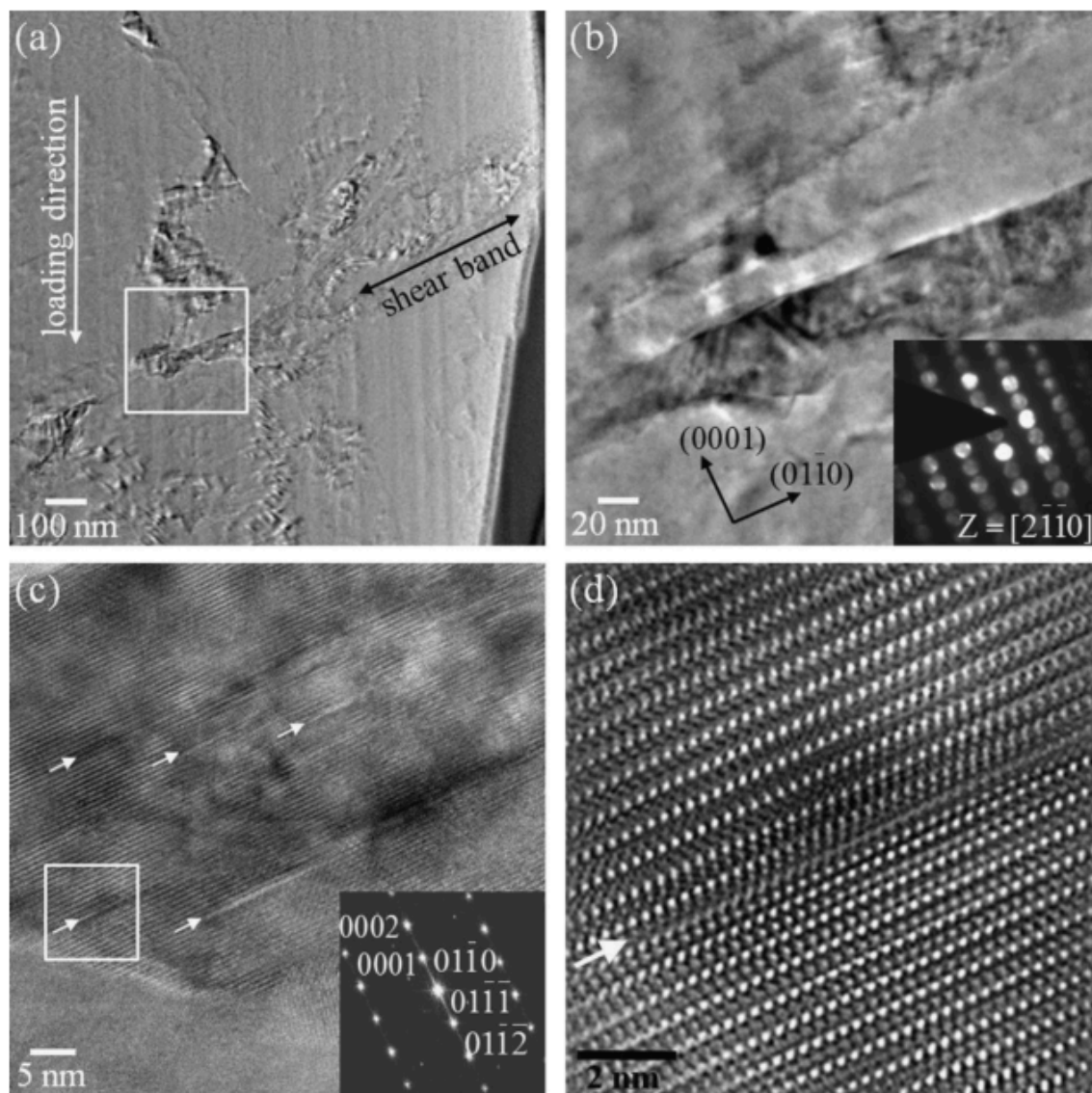


Fig. 3-14. (a) TEM image of the shear band. (b) Close-up image of the shear band region highlighted in (a). Inset is the micro-diffraction pattern. (c) HRTEM images showing stacking faults (SFs). Inset is the FFT of the image. Fourier filtered HRTEM image showing SFs from the region highlighted in (c).

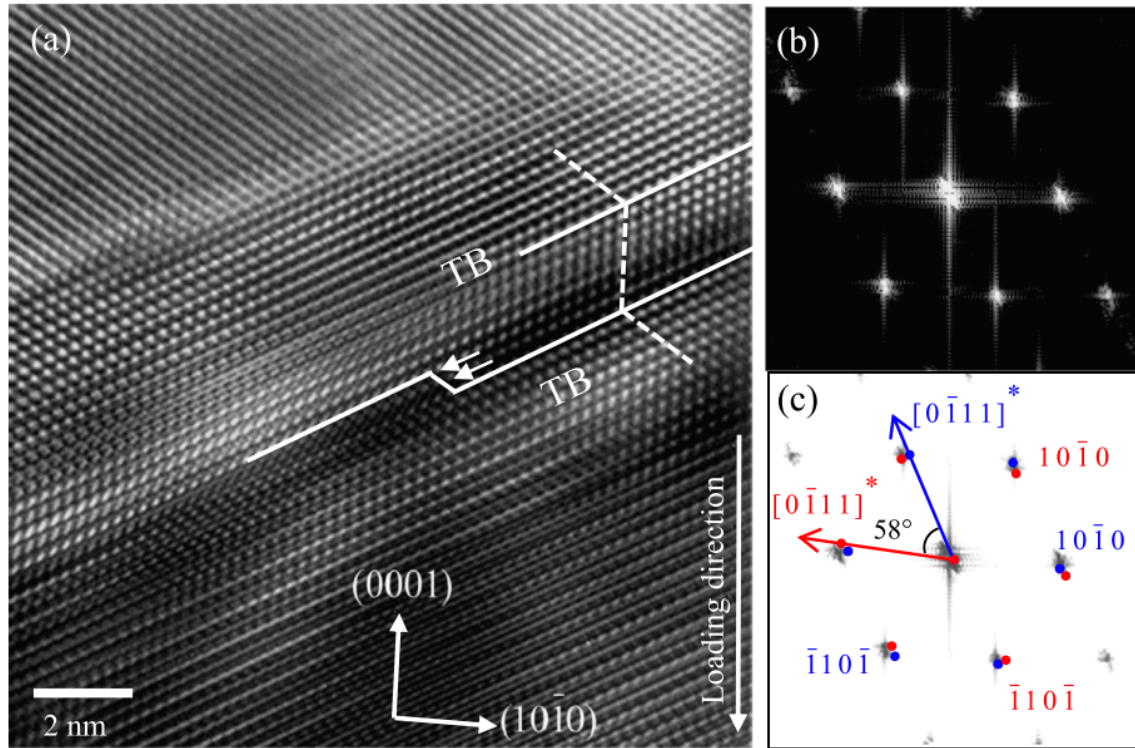


Fig. 3-15. (a) Fourier filtered HRTEM image of contraction nanotwins. (b) FFT of the image in (a). (c) Color-coded indexed FFT for clarity.

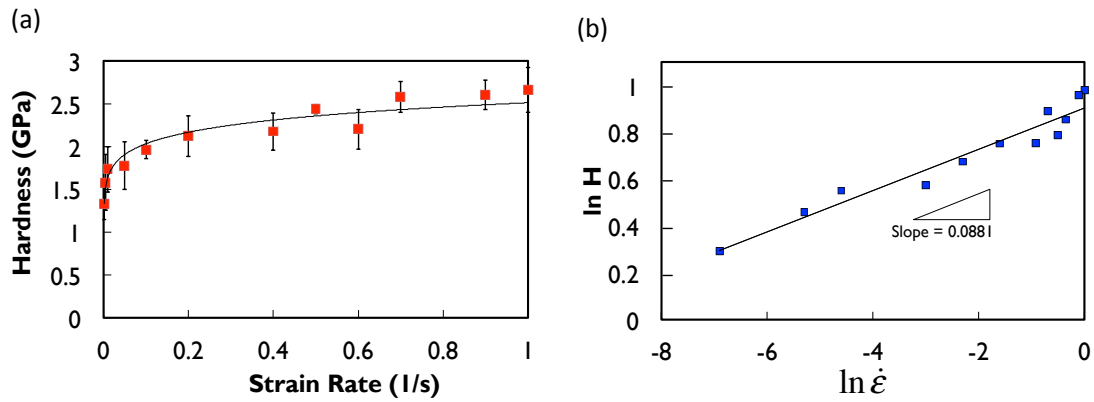


Fig. 3-16 (a) Average hardness as a function of the strain rate ranging from 0.001 to 1 of Mg-10Al alloy (b) Logarithm of the average hardness as a function of the logarithm of the strain rate.

Chapter 4

Size-Induced Strengthening in Nanostructured Magnesium Alloy Micropillars

Abstract

Size effects on the compressive strength of nanostructured Mg-micropillars are investigated. Mg–10Al alloy micropillars with diameters ranging from 1.5 to 8 μm are prepared by focused-ion-beam and tested under micro-compression. A significant improvement in strength was found by reducing the pillar diameter $<3.5 \mu\text{m}$. The deformation mechanisms of the compressed pillars are characterized using transmission electron microscopy. We attribute the size-induced strengthening to a less number of dislocation sources along with a higher activity of non-basal deformation mechanisms.

4.1 Introduction

Studies on size-scale effects i.e. grain size and specimen dimension have attracted considerable attention in recent years because of their influence on the mechanical behavior of materials [1]. In general, it is well accepted that the strength of metals can be improved through refinement of the grain size by the Hall-Petch mechanism. Interestingly, it has also been demonstrated that the strength of the material can be improved by reducing the specimen dimensions, as first reported by Uchic et al. in Ni based superalloys [2] and by Greer et al. in single crystal Au [3]. Nowadays, the

optimization of the mechanical properties of materials at the micron and submicron scales is crucial for the design of high performance micro-electrical-mechanical (MEMS) devices. Consequently, researchers have focused on investigating both grain size and specimen size effects on the mechanical behavior of micron/submicron-pillars of polycrystalline materials such as Ni [4,5], Ag [6], TiAl [7], Cu [8] and Pt [9]. In the case of Mg, many efforts have been dedicated to study the compressive behavior of single-crystal Mg micron/submicron-pillars [10–15]. These studies have shown that the compressive strength of single crystal Mg-micropillars mainly depends on the initial dislocation density [11] and the orientation of the basal planes with respect to the loading direction [10–12]. Byer and Ramesh [11] reported a size effect on the yield strength by decreasing the initial dislocation density. Lilleodden [12] observed a remarkable increase in compressive strength along the c-axis for single crystal Mg-micropillars with diameters $<10\text{ }\mu\text{m}$. It is well known that when the c-axis is nearly parallel or perpendicular to the loading direction, alternative deformation mechanisms such as non-basal slip and/or twinning can be activated since the Schmid factor for basal plane sliding is very small. For instance, a significant hardening was found on single crystal Mg-micropillars loaded in compression along the c-axis by the activation of multiple slip systems on pyramidal planes [10,12]. However, it is interesting to note that no sign of twinning is found in those works. It appears that a size effect is also associated with the deformation by twinning. As reported by Yu et al. [15], the deformation by twinning becomes unfavorable when the specimen size decreases. Ye et al. [13] demonstrated a

strong size effect associated with basal plane sliding and extension twinning in single crystal Mg nano- and micro-pillars. In fact, it has recently been demonstrated by Prasad et al. [14] that the required stress to nucleate twins in single crystal Mg-micropillars is higher than that in single crystal Mg bulk samples. While many efforts have been devoted to study the size effect on single-crystal Mg micropillars, the effect of specimen size on polycrystalline Mg micropillars has not been reported yet. In this chapter, we report the influence of specimen size (diameter) on the compressive strength of nanostructured Mg–10Al micropillars with a bimodal grain size distribution. Using transmission electron microscopy (TEM) we investigate the underlying deformation mechanisms.

4.2 Materials and Methods

Nanocrystalline Mg-10Al (wt.%) powders were prepared by cryomilling for 8 h under liquid nitrogen atmosphere in a Union Process, Szegvari mill at California Nanotechnologies. Cryomilled powders were consolidated using a spark plasma sintering (SPS) system (Syntex Inc., Dr. Sinter Lab TM, model SPS-515S). The sintering process was carried out in vacuum for 5 min at 400°C and under uniaxial pressure of 100 MPa. More details about the material processing can be found in Refs. [16,17] Mg–10Al micropillars with diameters ranging from 1.5 to 8µm and aspect ratio of 1:3 were fabricated by FIB. A series of concentric annular milling patterns with different currents were applied. In order to tailor the pillars into the desired shape and minimize the tapering, [18,19] a low beam current (<1 nA) was used as final milling step. Uniaxial

micro-compression tests were performed using a MTS Nanoindenter XP. A diamond indenter with a flat-end tip of 10 μm in diameter was used. The strain rate was controlled in the range of 3×10^{-3} and 5×10^{-4} (s^{-1}). TEM samples of the compressed pillars were prepared by FIB and examined using a FEI-Titan TEM operating at 300kV.

4.3 Results and Discussion

4.3.1 Characteristic of Micropillar with Different Sizes

Four characteristic Mg–10Al micropillars before and after compression are shown in Figure 4-1. Figure 4-1(a)–(d) show 52° tilted-view SEM images of those micropillars with top diameters of 8, 3.5, 2.5 and 1.5 μm , respectively, before compression. It is evident to observe that all pillars are slightly tapered as a result of the annular cutting method by FIB. The sidewall taper angle and pillar length are indicated in all images. We measure taper angles $\leq 1.5^\circ$, which are smaller than the values reported in the literature ($2\text{--}5^\circ$) for typical micropillars machined by FIB [20,21]. Figure 4-1 (e)–(h) show 52° tilted-view SEM images of the compressed pillars up to 2% of strain. Shear bands are apparent on the pillars surface, especially for pillars with diameters $\leq 3.5\mu\text{m}$. In contrast, 8 μm pillars plastically deform showing a barreling shape similar to the bulk samples under compression. This observation suggests that a transition from homogeneous-like to shear-band deformation occurs by reducing the pillar diameter. The results of the micro-compression tests are shown in Figure 4-2 and presented in Table 4-1. At least five samples were tested for each pillar diameter as shown in Table 4-1. The average yield

strength and the standard deviation have also been included. In order to avoid any overestimation of the measured stress due to the tapering, the stress was obtained using the load divided by the middle cross-section area of the pillars. Figure 4-2 (a) shows representative engineering stress vs. strain curves for nanostructured Mg–10Al pillars with different diameters. From the linear slope of the stress–strain curve, we estimate the elastic modulus, E , ~ 50 GPa, which is in good agreement with that measured by nanoindentation with a Berkovich tip (52 GPa). The yield strength, which is determined as the end of the proportional limit of each curve is highlighted by an arrow. Pillars with 8 and $3.5\mu\text{m}$ diameters present similar yield strength values i.e. 373 and 374 MPa, respectively. It is interesting to note that the yield strength increases significantly when decreasing the pillar diameter. In particular, the yield strength values for 2.5 and $1.5\mu\text{m}$ pillars are 549 and 746 MPa, respectively. Therefore, an increase of around 50% and 100% is obtained when decreasing the pillar size to 2.5 and $1.5\mu\text{m}$, respectively. Additionally, the stress–strain curves of Figure 4-2 (a) indicate a less ductile behavior for the smallest pillars as confirmed by their values of strain at failure in Table 4-1. Thus, in addition to a significant increase in strength, a reduction in ductility is observed for pillars with smaller diameter. The trend of the yield strength as a function of pillar diameter can be better seen in Figure 4-2 (b). These results suggest a strong size effect on the strength of nanostructured Mg micropillars with diameters smaller than $3.5\mu\text{m}$. In contrast, no size effect was observed when the diameters are higher than $3.5\mu\text{m}$. In fact,

the compressive strength of micropillars with diameters higher than $3.5\mu\text{m}$ is similar to that of the bulk sample (397 MPa) [17].

4.3.2 Deformation Mechanism Analysis of Micropillar with Size Effect

TEM analysis was performed in order to study the underlying deformation mechanisms during micro-compression. Figure 4-3 (a) is a bright-field TEM image of a compressed $2.5\mu\text{m}$ micropillar showing the characteristic bimodal grain size distribution after SPS sintering. As described in our previous work, [17] the bimodal grain size distribution consists of fine-grains $\sim 35\text{ nm}$ and coarse-grains $\sim 400\text{ nm}$. No apparent texture was found. See Ref. [17] for more microstructural details. We identify at least three shear bands forming an angle with respect to the LD of $\sim 70^\circ$ (labeled 1 and 2 at the top of the pillar) and $\sim 60^\circ$ (labeled 3 at the bottom of the pillar). High-resolution TEM (HRTEM) image from the shear band 1 (Figure 4-3(b)) reveals extension twins on the characteristic $\{10\bar{1}2\}$ planes (highlighted by yellow solid lines) in a grain with the c-axis almost perpendicular to the LD. In fact, nanotwins of $<1\text{ nm}$ widths can be observed. This has been confirmed by indexing its fast Fourier transform (FFT) (inset). Interplanar distances measurements indicate the misorientation relation between the parent (solid lines) and the twin (dashed lines) close to the expected angle of 86° for a grain oriented to the $<2\bar{1}\bar{1}0>$ zone axis. Note that $\pm(0002)_T$ (basal planes from the twin) and $\pm(0002)_P$ (basal planes from the parent) are almost perpendicular to each other. In addition to the twinning mechanism, we find prismatic dislocations (highlighted by $\perp$) terminated at

stacking faults (SFs) in a grain close to the shear band 2 (Figure 4-3c). Inset is the indexed FFT of the image indicating the $\{1\bar{1}00\}$ planes where dislocations occur for a grain oriented to the $\langle 1\bar{2}1\bar{3} \rangle$ one axis. The characteristic streaks parallel to the $\langle 1\bar{1}00 \rangle$ direction as a result of prismatic SFs are also apparent. From the TEM analysis, we find that extension twinning and prismatic slip can be activated during compression of 2.5 μm nanostructured micropillars. While extension twinning is a common deformation mechanism seen in Mg bulk samples, higher stress is required to nucleate extension twins in micropillars [14]. In addition, it is well known that the critical resolved shear stress for prismatic slip and twinning is always higher than that for the basal slip [22]. Therefore, we believe that the enhanced strength observed in nanostructured Mg–10Al micropillars with 2.5 μm diameter is mainly due to the activation of the aforementioned deformation mechanisms. From our previous work based on in situ SEM micro-compression studies of nanostructured Mg–10Al micropillars with 4 μm diameter, [23] we found in addition to basal plane sliding, contraction twins in a grain oriented with the c-axis almost parallel to the LD. These results highlight the important role that the grain orientation plays in the strengthening of nanostructured Mg micropillars. As demonstrated by the TEM analysis of 2.5 μm micropillars, alternative deformation mechanisms such as non-basal slip and/or twinning can be activated in grains with the c-axis nearly parallel or perpendicular to the LD, since the Schmid factor for basal plane sliding is very small. These observations suggest that the contribution from grains favorably oriented for basal slip (within a bimodal grain distribution

randomly oriented without any preferential texture [17]) to the pillar strength decreases with decreasing pillar diameter. Additionally, by reducing pillar diameter the number of grain boundaries also decreases,[24] which significantly reduces the number of potential dislocation sources.[4] Hence, the applied stress required for nucleation or activation of dislocations, i.e. yield strength also increases. Based on this, we conclude that the size-induced strengthening is due to a smaller number of dislocation sources along with a higher activity of non-basal dislocation sliding and twinning.

4.4 Conclusions

A strong specimen size effect on the compressive strength of nanostructured Mg–10Al alloy micropillars is observed. We find that the yield strength increases significantly when the pillar diameter is $<3.5\mu\text{m}$. An increase of around 50% and 100% is obtained when the pillar diameter decreases to 2.5 and $1.5\mu\text{m}$, respectively. In contrast, no size effect is observed for pillar diameter $\geq 3.5\mu\text{m}$. We attribute the size-induced strengthening to a less number of dislocation sources along with a higher activity of non-basal dislocation sliding and twinning.

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Table 4-1 Compressive properties of nanostructured Mg–10Al micropillars with different diameters.

Pillar diameter (μm)	Yield strength (MPa)	Strain at failure (%)	Average yield strength (MPa)	Average strain at failure (%)
1.5	742	2.4	746 ± 19	2.6 ± 0.2
	729	2.7		
	778	2.7		
	746	2.8		
	734	2.5		
2.5	577	3.6	554 ± 21	3.9 ± 0.3
	536	3.7		
	549	4.4		
	575	3.9		
	533	3.7		
3.5	347	4.2	364 ± 15	4.5 ± 0.2
	374	4.6		
	373	4.8		
	379	4.3		
	349	4.7		
8.0	373	4.8	362 ± 12	4.7 ± 0.3
	362	5.5		
	350	4.1		
	373	4.3		
	350	4.7		

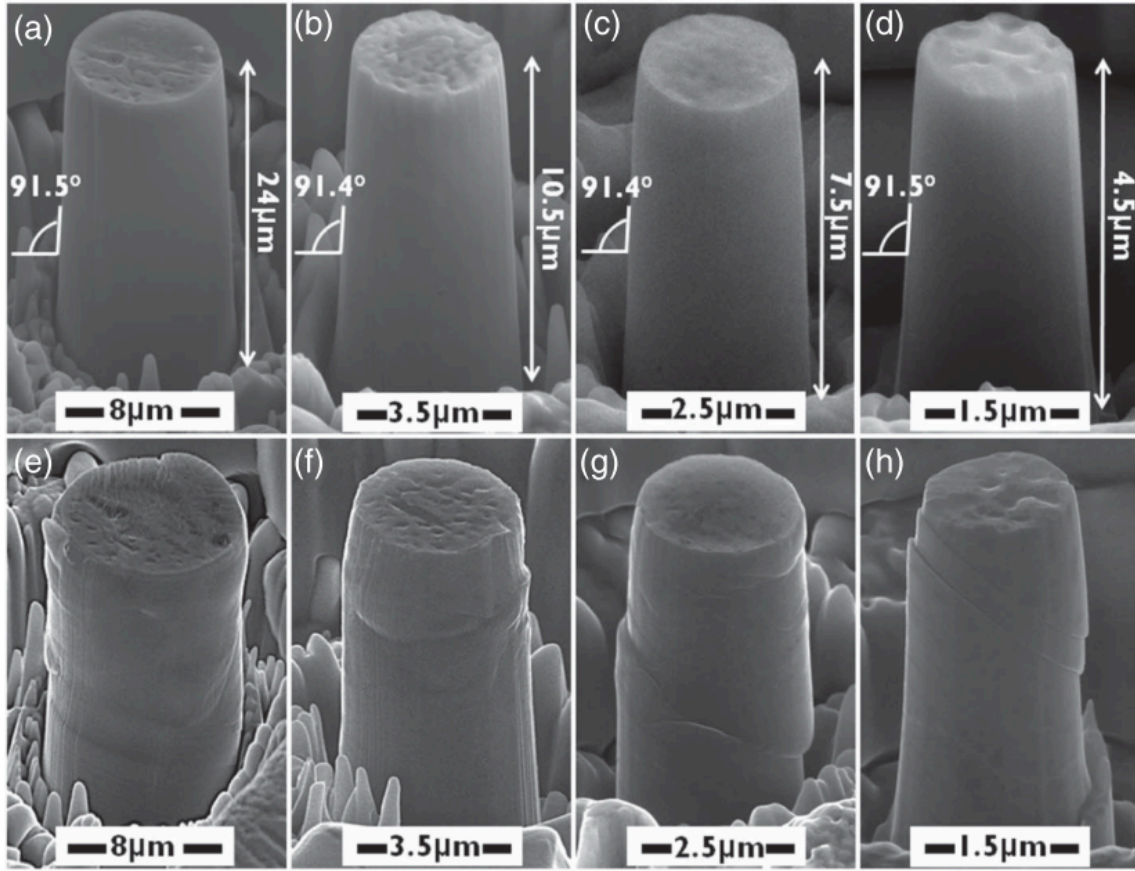


Fig. 4-1 SEM images of nanostructured Mg-10Al micropillars with different diameters

(a)–(d) before and (e)–(h) after compression (2% of compressive strain).

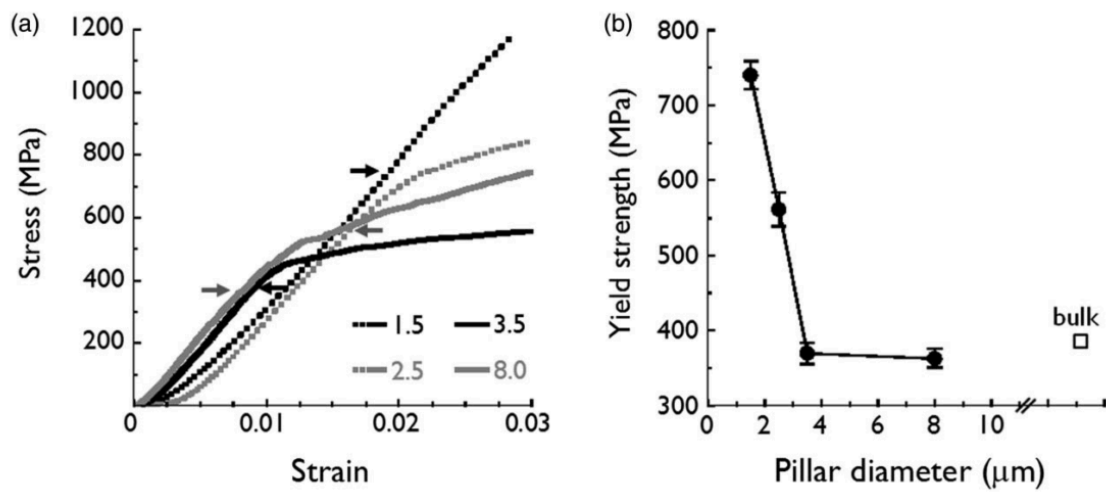


Fig. 4-2 (a) Compressive stress–strain curves of nanostructured Mg–10Al micropillars.

(b) Compressive yield strength as a function of pillar diameter.

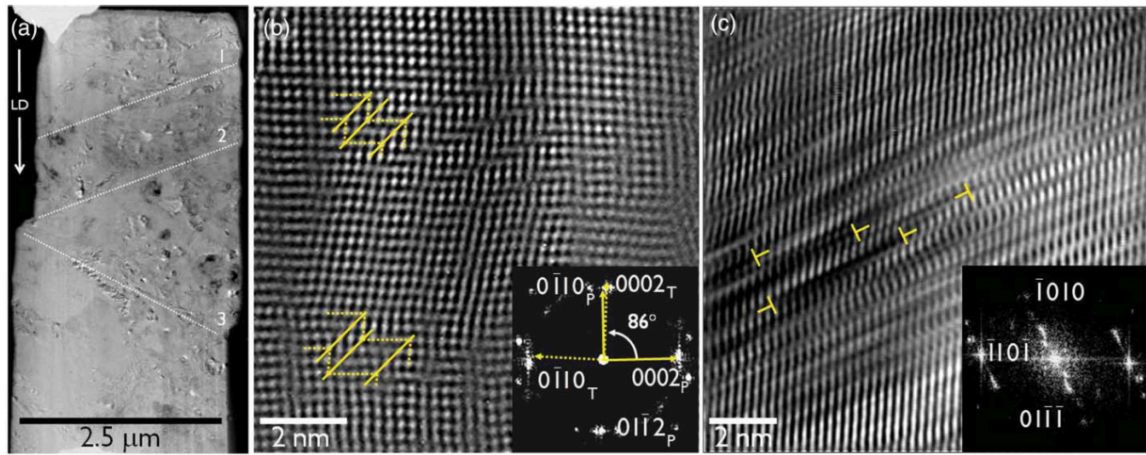


Fig. 4-3 (a) Bright-field TEM image of a compressed 2.5μm micropillar. (b) HRTEM image showing extension twins in a grain oriented to the $\langle 2\bar{1}\bar{1}0 \rangle$ zone axis. Inset is its FFT. (c) HRTEM image showing prismatic dislocations terminated at SFs in a grain oriented to the $\langle 1\bar{2}1\bar{3} \rangle$ zone axis. Inset is its FFT.

Chapter 5

Characterizations of Nanostructured Magnesium Nanocomposites Reinforced by Diamantane

Abstract

Nanostructured Mg–10Al nanocomposites reinforced by diamondoids were processed via cryomilling and spark plasma sintering. The effect of 1 wt% of diamantane on the microstructure of the nanostructured Mg–10Al nanocomposites was studied using scanning and transmission electron microscopies, electron dispersive spectroscopy and X-ray diffraction. A detailed microstructural examination revealed that diamondoids mainly located within the Mg-matrix induce a lattice strain along the *c*-direction and a potential effect on the γ -Al₁₂Mg₁₇ precipitation. The mechanical behavior of the nanostructured Mg-based nanocomposites was investigated by micro- and macro-compression tests along with in-situ SEM nanoindentation experiments at room temperature. The compressive strength, elastic modulus and hardness of the nanocomposites were found to be significantly improved as compared with the mechanical behavior of diamondoids-free nanostructured Mg–10Al alloys. Since no change in the grain size has been found after adding diamantane, we attribute the enhanced mechanical behavior of the nanocomposites to a combined effect of precipitation hardening and the microscopic residual stress generated by diamantane–Mg

matrix mismatch. Our results provide new insights into the mechanisms involved in the development of high-performance Mg-nanocomposites.

5.1 Introduction

Nanocomposites are defined as multi-phase solid materials wherein at least one of the phases (typically the reinforcement) has dimensions <100 nm [1]. Over the last decade, several approaches have been developed to reinforce the Mg-matrix using different reinforcements in the nm scale such as carbon nanotubes (CNTs) [2,3], B_4C [4], Al_2O_3 [5–7], Y_2O_3 [8], ZrO_2 [9], SiO_2 [10], Cu [11] and SiC [12–14] nanoparticles among others. Additionally, nanocomposites can be also developed by reducing matrix grain sizes to the nm scale [1]. In fact, nanostructured Mg- based alloys have shown enhanced compressive strength over the conventional Mg-alloys [15,16] mainly because of the grain size strengthening mechanism by Hall-Petch [17,18]. Therefore, the addition of nano-reinforcements to nanostructured Mg-based matrix can be a promising approach in improving the mechanical properties of Mg beyond what can be achieved through alloying and grain refinement.

In general, the interface between the matrix and reinforcements plays a key role in the mechanical performance of nanocomposites. It has been reported that the presence of second phases at the interfaces may cause embrittlement [19], resulting in a detrimental

effect on the mechanical behavior of the composite. For instance, a decrease in the tensile strength of Mg matrix has been reported by the addition of AlN because of an excessive chemical reaction at the interfaces [20]. Using SiC nanoparticles/whiskers as reinforcements in Mg-matrix composites may lead to the formation of several reaction products such as oxides [21,22], Mg_2Si [13,23,24] and Al-C-O ternary compounds [24]. Since chemical reactions at the interfaces can significantly influence the mechanical properties of the composite, interfaces should be properly tailored in order to minimize any undesirable reaction products. In particular for Mg-based nanocomposites this is a challenging task because of the high reactivity of the Mg-matrix. Therefore, proper selection of reinforcements is a necessary step on the design of high-performance nanocomposites.

Diamondoids are hydrogen-terminated nanodiamonds with a basic repetitive unit of ten-carbon tetracyclic cage system called “adamantane” ($\text{C}_{10}\text{H}_{16}$) [25]. Their sp^3 carbon framework is completely superimposable on the diamond lattice. Diamondoids are derived from petroleum and can be produced in large volumes at a low cost [25,26]. Because of their exciting properties, diamondoids are being used in a wide range of applications such as templates and molecular building blocks in nanotechnology, drug delivery and targeting, in DNA directed assembly, tissue engineering among others (See ref. [27] and references therein). In particular, their diamond-like properties, e.g. strength,

rigidity and thermal stability [26] make them a potential filler material for nanocomposites.

In this chapter, we use diamantane ($C_{14}H_{20}$) containing two cages of adamantane in order to reinforce the nanostructured Mg-matrix. Prior work on using diamantane as reinforcement material is a study by Ghosh et al. [28] on polymer-based nanocomposites. They reported that diamondoids are capable of enhancing the thermo-mechanical properties of polymers. In the case of metal-matrix nanocomposites, Maung et al. [29] reported high thermal stability in cryomilled nanocrystalline Al powders by adding diamantane. However, they also found an inverse Hall- Petch behavior, i.e. softening with decreasing grain size in bulk nanocrystalline Al containing diamantane [30]. Here, we present results from a detailed microstructural and mechanical characterization of a diamantane reinforced nanostructured Mg-10Al nanocomposite that is compared with the diamantane-free nanostructured Mg-10Al alloy. The microstructural characterization of the as-received diamantane and the bulk nanostructured Mg-samples processed via cryomilling and spark plasma sintering (SPS) are determined by digital optical microscopy (OM), scanning and transmission electron microscopies (SEM, TEM), electron dispersive spectroscopy (EDX) and X-ray diffraction (XRD). The mechanical behavior of the nanostructured Mg-based alloy and nanocomposite is investigated by micro- and macro-compression tests along with in-situ SEM nanoindentation experiments

at room temperature. We show that 1 wt.% of diamantane enhances the compressive strength of the bulk nanostructured Mg-10Al alloy by 30%.

5.2 Materials and Methods

Pure Mg and Al powders were blended to formulate the final composition Mg-10Al (wt.%) alloy. After blending the powders were cryomilling for 8 hours under liquid nitrogen environment to produce nanocrystalline grains. We successfully incorporated 1 wt. % of diamantane during cryomilling to produce Mg-10Al-1Dia (wt.%) alloy powders. After cryomilling, the powders were degassed and densified using a spark plasma sintering (SPS) system (Syntex Inc., Dr. Sinter Lab TM, model SPS-515S). The SPS sintering process was carried out in vacuum for 5 min at 400 °C and under uniaxial pressure of 100 MPa. More details about the material processing can be found in ref. [16,31]. The morphology of the as-received diamantane powders was investigated using digital optical and scanning electron microscopies. A Keyence VHX-5000 Digital Microscope and a FEI Nova 230 Variable Pressure SEM (VP-SEM) at 10 kV accelerating voltage were used for this purpose. The microstructural characterization of bulk Mg-samples and their composition was determined using the VP-SEM equipped with an Oxford Instruments energy dispersive X-ray spectroscopy (EDS) system at 15 kV accelerating voltage. X-ray diffraction (XRD) was performed using a Panalytical X'Pert

ProX-ray Powder Diffractometer using Cu K α ($\lambda = 0.1542$ nm) radiation in order to determine the crystalline size and different phases. High-resolution microstructural characterization of the diamondoids embedded into the Mg-matrix was carried out using a FEI Titan 300-kV scanning transmission electron microscope (STEM). The composition of the Mg-matrix nanocomposite was determined using energy dispersive X-ray spectroscopy (EDS) in the STEM equipped with an Oxford Instruments EDS system. A FEI Nova600 Nanolab DualBeam focused ion beam (FIB)-SEM was used to prepare thin film TEM samples from the Mg-nanocomposite.

In order to evaluate the mechanical behavior of nanostructured Mg-matrix nanocomposites, micro- and macro-compression tests along with in-situ SEM nanoindentation experiments were performed at room temperature. Uniaxial micro-compression tests were performed using a MTS Nanoindenter XP. A diamond indenter with a flat-end tip of 10 μm in diameter was used. The strain rate was controlled in the range of 3×10^{-3} and 5×10^{-4} (s^{-1}). Micro-pillars of Mg-10Al and Mg-10Al-1Dia samples with different diameters and aspect ratio of 1:3 were machined by FIB operated at 30 kV. A series of concentric annular milling patterns with different currents were applied. In order to tailor the pillars into the desired shape and minimize the tapering [32,33], a low beam current (<1 nA) was used as final milling step. Macro-compression tests from the bulk samples were performed in order to compare with the micro-compression results.

Macro-compression tests were conducted at displacement rate of 0.011 mm/s using an Instron machine with a load cell of 60 Klb. Compression samples of 5.6 and 6.2 mm in diameter and length, respectively, were machined from both Mg-10Al and Mg-10Al-1Dia samples. Finally, in-situ SEM nanoindentation experiments were accomplished using a PI- 85 PicoIndenter instrument (Hysitron Inc.) installed on the FEI Nova600 Nanolab DualBeam FIB-SEM. A cubed-corner diamond indenter with of ~200 nm tip was used for all measurements performed at load-rate control with a peak force of 1000 μN .

5.3 Results and Discussion

5.3.1 Microstructural Characterization

Figure 1(a) shows an optical microscopy image of as-received diamantane powders in the form of aggregates around 50 μm in size. We find that diamantane particles are transparent, with cubic shapes as a result of its cubic crystal structure [27]. Diamantane surface morphology can be better seen in the SEM image of Fig. 1(b). It is interesting to observe the surface roughness with multiple craters-like holes that might facilitate their interface bonding with the Mg-matrix during processing. The SEM characterization of the bulk Mg-10Al and Mg-10Al-1Dia samples processed by cryomilling and SPS is shown in Fig.2. Consistent with the results published in our

previous study [16], the characteristic microstructures reveal in addition to the α -Mg matrix, a second phase network of the intermetallic $\text{Al}_{12}\text{Mg}_{17}$ (γ -phase) in Al-rich areas. It is interesting to note that the precipitation of γ - $\text{Al}_{12}\text{Mg}_{17}$ phase exhibits different morphologies as clearly shown by higher magnification SEM images (Fig. 2b and 2d). First of all, discontinuous and continuous precipitation of $\text{Al}_{12}\text{Mg}_{17}$ from the supersaturated α -Mg phase can be observed in the Mg-10Al microstructure (Fig. 2b). On one hand, discontinuous precipitation (labeled as γ_D) involves the formation of a lamellar aggregate of $\text{Al}_{12}\text{Mg}_{17}$ phase and an Al-depleted α -Mg phase. On the other hand, continuous precipitation of $\text{Al}_{12}\text{Mg}_{17}$ phase presents a lath-shaped morphology distributed through the α -Mg matrix. Note that large γ -precipitates bigger than 50 μm can be found in the Mg-10Al sample (Fig. 2b). In contrast, the precipitation of γ - $\text{Al}_{12}\text{Mg}_{17}$ phase in the Mg-10Al-1Dia nanocomposite (Fig. 2d) is quite different showing a particular dendritic morphology with the Mg-matrix visible in the interdendritic space. No presence of large precipitates and discontinuous precipitation has been found in the sample with diamantane. As a matter of fact, this particular morphology is similar to that found in an Al-rich Mg-Al alloy (Mg-30Al wt.%) [31]. These observations suggest a potential effect of diamantane on the precipitation process of γ - $\text{Al}_{12}\text{Mg}_{17}$ phase in the nanocomposite.

In order to confirm the phases present in the Mg-10Al alloy and the Mg-10Al-1Dia nanocomposite, we use XRD. Figure 3 shows in addition to the XRD spectra for the Mg-10Al and Mg-10Al-1Dia samples, the spectrum for the as-received diamantane powders. The characteristic peaks of Mg and $\text{Al}_{12}\text{Mg}_{17}$ intermetallic phases are clearly observed in both Mg-10Al and Mg-10Al-1Dia samples. In addition, no sign of secondary phases has been found in the Mg-10Al-1Dia spectrum indicating that there is no reaction between diamantane and the Mg-10Al alloy. The average crystallite size determined by the peak broadening is ~ 35 and ~ 36 nm for the Mg-10Al and Mg-10Al-1Dia samples, respectively. These results indicate that there is no change of the nanocrystalline grain size after adding diamondoids to the Mg-10Al alloy.

From the diamantane spectrum, we determine the lattice parameter of diamantane with a face-centered cubic crystal structure of $a = 9.826 \pm 0.312 \text{ \AA}$, which is slightly higher than the lattice parameter of adamantane ($a = 9.441 \text{ \AA}$). Because of the small volume fraction of diamantane in the nanocomposite, their characteristic peaks are imperceptible in the Mg-10Al-1Dia spectrum. This is consistent with the results previously reported for the same amount of diamantane (1 wt. %) in an Al-matrix [29].

Using high-resolution TEM (HRTEM) and STEM analyses, we were able to identify diamantane in the Mg-matrix. Fig.4 (a) is a typical bright-field TEM image showing a few nanocrystalline Mg grains. Fig. 4 (b) is the fast Fourier transform (FFT)

from the region highlighted by the white rectangle in Fig. 4 (a). In addition to the diffraction spots due to the hcp Mg lattice oriented to the $[2\bar{1}\bar{1}0]$ zone axis (see the indexed pattern below), we also find additional spots that are identified as fcc diamantane oriented to the $[\bar{1}12]$ zone axis. The orientation relationships between the diamantane and Mg-matrix results to be $[\bar{1}12]_{\text{Dia}} // [2\bar{1}\bar{1}0]_{\text{Mg}}$ and $[1\bar{1}1]_{\text{Dia}} // [0002]_{\text{Mg}}$.

The lattice constants of Mg-matrix obtained from the measured interplanar distances between $\{0002\}$ and $\{10\bar{1}0\}$ planes from the FFT result $a = 3.2 \text{ \AA}$ and $c = 5.4 \text{ \AA}$. As compared with the theoretical values of lattice parameters, we measure a lattice strain of $\sim 1\%$ and 4% in a and c , respectively. In contrast, the measured lattice constants for Mg-matrix in the diamantane-free sample ($a = 3.2 \text{ \AA}$ and $c = 5.4 \text{ \AA}$) yield a lattice strain of $\sim 1\%$ and 0.2% in a and c , respectively. These results suggest a lattice distortion along the c -direction in the Mg-matrix for the sample with diamantane. Fig. 4 (c) is a Fourier filtered HRTEM image of the region highlighted by the white rectangle showing the distortion of the atomic arrangements due to the overlapped lattices. Partial dislocations (highlighted by $\perp$) terminated stacking faults are also identified on the basal planes, which confirm a local inhomogeneous lattice distortion along the c -direction as a result of the insertion of diamantane in the Mg-matrix.

Using STEM and EDS performed in the TEM (Fig. 5), we determine differences in composition in the Mg-10Al-1Dia sample given by the Z-contrast. As expected from our previous work [16], γ -Al₁₂Mg₁₇ phase (Al-rich areas) is distinguished by the bright contrast (highlighted by 1) while Mg matrix is clearly identified in the dark zones (highlighted by 2) in the STEM image (Fig. 5a) and confirmed by the EDS analysis (Fig. 5b). Inset is an enlarge image of the region highlighted by the dashed square. Black spots are clearly visible inside the Mg grain that correspond to C-rich areas as confirmed by the EDS results (Fig. 5b). In fact, the EDS spectrum from point 2 reveals a big peak of carbon that is even higher than the Mg peak. We are aware of the limitations to quantitatively determine by EDS the concentration of light elements like carbon. However, the relative amount of carbon found in point 2 (90 wt.%) compared with that in point 1 (37 wt.%) is very significant. These results point out that not only the black spots correspond to diamantane but also that diamantane is mainly located within the Mg-matrix.

5.3.2 Mechanical Characterization

In order to evaluate the effect of diamantane on the mechanical behavior of the nanostructured Mg nanocomposite, we first performed micro-compression tests at room temperature on Mg-10Al and Mg-10Al-1Dia micropillars. Representative engineering compressive stress, σ , vs. strain, ϵ , curves for these samples are shown in Fig. 5-6. At least 5 pillars were tested per composition, although only one is shown here as a comparison. In order to avoid any overestimation of the measured stress due to the tapering, the stress was obtained using the load divided by the middle cross-section area of the pillars. The average yield strength value for the Mg-10Al was around 364 MPa, while a remarkable yield strength of 474 MPa was obtained for Mg-10Al-1Dia micropillars. Thus, a 30% improvement in strength of the Mg-10Al alloy can be attained by adding diamantane. It is interesting to note that the slope of the elastic region for the Mg-10Al-1Dia curve is also higher than that for the sample without diamondoids, which suggests a higher elastic modulus for the Mg-10Al-1 Dia sample. This will be study in more detail by means of in-situ SEM nanoindentation experiments in the next section. An example of the characteristic Mg-10Al and Mg-10Al-1Dia micropillars before and after compression can be seen in Fig. 5-6(b-e). Fig. 5-6(b) and (c) show 52° tilted-view SEM images of the two micropillars with diameters at half-height $\sim 4 \mu\text{m}$ and aspect ratio of 1:3 before compression. Fig. 6 (d-e) show 52° tilted-view SEM images of the compressed

pillars up to 2% of strain. Shear bands are apparent on the surface of both pillars. However, it is clearly observed that the compressed Mg-10Al pillar is much shorter and wider than the pillar with diamondoids, which indicates a higher plastic deformation occurred on the Mg-10Al pillar. In other words, the Mg-10Al-1Dia micropillar is more resistant to the compression loading.

Motivated by these results, we decided to further study the mechanical behavior of diamondane-reinforced micropillars with different diameters. Interestingly, we found a remarkable size effect when the pillar diameter, d , decreases below 3.5 μm as previously observed in nanostructured Mg-10Al micropillars [34]. Fig. 5-7(a) shows representative engineering stress, σ , vs. strain, ϵ , curves for nanostructured Mg-10Al-1Dia micropillars with different diameters (between 1.5 and 8 μm). The compressive σ_y of the bulk Mg-10Al and Mg-10Al-1Dia samples are also included. Pillars with 8 and 3.5 μm diameters present similar yield strength, σ_y values i.e. 500 MPa and 495 MPa, respectively. In fact, the compressive strength of micropillars with diameters bigger than 3.5 μm is similar to that of the bulk sample (519 MPa). However, σ_y increases significantly when decreasing d . In particular, σ_y values for 2.5 and 1.5 μm micropillars are 650 MPa and 860 MPa, respectively. Therefore, an increase of around 30 % and 70 % is obtained when decreasing the pillar size to 2.5 and 1.5 μm , respectively. The trend of σ_y as a function of d can be better seen in Fig. 5-7(b). The results of the Mg-10Al micropillars [34] have

been added as a comparison. It is interesting to note that both samples present the same trend of σ_y as a function d , although the σ_y values of Mg-10Al-1Dia micropillars are always higher than those for the Mg-10Al micropillars for all pillar diameters. These results suggest a strong size effect on the strength of nanostructured Mg micropillars with diameters smaller than 3.5 μm . In contrast, no size effect was observed when the diameters are bigger than 3.5 μm . In fact, the compressive strength of micropillars with diameters bigger than 3.5 μm is similar to that of the bulk samples, i.e. 397 and 519 MPa for the Mg-10Al and Mg-10Al-1Dia samples, respectively.

In order to further investigate the reinforcement effect by diamondoids in the Mg- matrix, in-situ SEM nanoindentation tests were performed under load control mode with a peak force of 1000 μN . Fig. 5-8(a) shows the results of reduced elastic modulus, E_r , of bulk Mg-10Al and Mg-10Al-1Dia samples as a function of indentation contact depth, h . As expected, E_r decreases with increasing h in both samples. For lower h , E_r of the Mg-10Al sample increases up to ~ 75 GPa, which corresponds to the reported elastic modulus for the intermetallic $\text{Al}_{12}\text{Mg}_{17}$ compound [35]. In contrast, for higher h the average E_r is ~ 50 GPa, which is in good agreement with the elastic modulus of Mg-10Al alloy measured by nanoindentation with a Berkovich tip (52 GPa) [34]. It is interesting to note that E_r of the sample with diamantane is always higher than that of the sample without diamantane as a result of a strong reinforcement by diamantane. In particular for

lower h , a maximum value of $E_r \sim 120$ GPa is reached, which is roughly a 2-fold increase of E_r compared to the sample without diamantane. Fig. 5-8(b) displays the representative force, F , vs. h curves of indentations made at a peak force of $1000 \mu\text{N}$ on the Mg-10Al-1Dia sample. The shape of the loading curves and their different dependence on penetration depth are also indicative of differences in hardness of the Mg-10Al-1Dia sample. The shift in the curves toward lower penetration depth indicates the effective reduction in the displacement accounting to the strengthening of the Mg-matrix by diamantane. Fig. 5-8(c) and 8(d) display the hardness, H , versus h of Mg-10Al and Mg-10Al-1Dia samples, respectively. As expected, the hardness increases with decreasing contact depth in both samples. For the Mg-10Al sample (Fig. 8c), the highest and the lowest values of hardness tend to be ~ 4 and ~ 1 GPa, respectively. These results are in good agreement with the hardness values reported for the intermetallic $\text{Al}_{12}\text{Mg}_{17}$ phase (4.3 GPa) and Mg-matrix (1.35 GPa). Similar behavior is observed for the Mg-10Al-1Dia sample (Fig. 8d), although the diamantane contribution can lead to a maximum hardness value (at lower contact depth) ~ 7 GPa. In the present study, we demonstrate that the compressive strength, elastic modulus and hardness of the Mg-10Al alloy can be significantly enhanced by adding diamantane. Considering that diamantane does not introduce any change in the grain size, the overall improved mechanical properties of the

Mg-10Al-1Dia nanocomposite are mainly attributed to the diamantane reinforcement itself and its effect on the precipitation of γ -Al₁₂Mg₁₇ phase.

5.3.3 Effect of Diamantane on the Precipitation of γ -Al₁₂Mg₁₇ Phase

The precipitation of the intermetallic Al₁₂Mg₁₇ occurs in Mg-10Al alloys in which the Al solid solubility increases with increasing temperature during SPS consolidation process at 400 °C. Thereby, during cooling down a new phase (γ -Al₁₂Mg₁₇) is formed by precipitation from an initially supersaturated solid solution. In general for Mg-Al alloys, both continuous and discontinuous precipitation occur competitively [36,37]. While discontinuous precipitation is favored when the grain boundary (GB) diffusion process is dominant, the continuous precipitation takes place during cooling down when the volume diffusion becomes faster [38].

From the SEM characterization of both Mg-10Al and Mg-10Al-1Dia samples processed under the same cryomilling and SPS conditions, we found significant differences in the morphology of the γ -Al₁₂Mg₁₇ phase precipitation (Fig. 5-2). First of all, discontinuous precipitation (γ_D) by which lamellar aggregates of Al₁₂Mg₁₇ phase are formed at GBs with a posterior growth into the α -Mg phase behind a migrating GB was not observed in the nanocomposite. The absence of this kind of precipitation involving GB mobility suggests that diamantane constrains the GB motion in the nanocomposite by

the Zener mechanism. Second, the large γ -precipitates ($\sim 50 \mu\text{m}$) found in the Mg-10Al were not present in the Mg- 10Al-1Dia nanocomposite. These large γ -precipitates were also observed in the same Mg-10Al alloy processed by SPS at 360°C [16]. However, since the SPS process is performed at higher temperature (400°C) in this work, the precipitates are bigger as a result of Al diffusion processes following the kinetics of precipitation coarsening [39]. Assuming that GB diffusion processes are significant in nanostructured Mg-matrix with a high volume fraction of GBs [40], the absence of these large precipitates indicates that diamondoids are also restricting diffusion processes along GBs in the Mg-10Al-1Dia nanocomposite. Finally, we observed that $\gamma\text{-Al}_{12}\text{Mg}_{17}$ morphology in the nanocomposite was similar to that in an Al-rich Mg-Al alloy (Mg-30Al wt.%) [31]. This observation could be explained by an effect of diamantane on the precipitation kinetics in the Mg matrix. From the TEM and STEM analysis (Fig. 5-4 and 5-5), we inferred that diamantane is mainly located in the Mg-matrix. In theory, the hcp crystal structure of the Mg-matrix is more capable of accommodating diamantane than the bcc crystal structure of the intermetallic $\text{Al}_{12}\text{Mg}_{17}$. Therefore, we believe that the incorporation of diamantane into the Mg lattice might accelerate the decomposition of the supersaturated Al solid solution, promoting the precipitation of $\gamma\text{-Al}_{12}\text{Mg}_{17}$ in these Al-rich zones with an Al-depleted $\alpha\text{-Mg}$ phase behind. This hypothesis is based on the nanoscale regulated intermetallic precipitation previously reported by De Cicco et al. and

Paramsothy et al. for Mg-Al-Zn alloys reinforced by SiC [41] and Si₃N₄ [42] nanoparticles. They concluded that Al segregation occurred on the nanoparticles/Mg-matrix interface promoting the Al₁₂Mg₁₇ formation. We believe that these morphological changes in the γ -Al₁₂Mg₁₇ phase promoted by diamantane, play a key role in the strengthening of the nanocomposite by reducing the inter-precipitate spacing for dislocation glide [37,43]. Non-deformable Al₁₂Mg₁₇ precipitates act as a barrier for dislocation movement contributing to the strength by the Orowan mechanism. As reported by Clark [36] for a Mg-9Al (wt %) alloy no slip dislocations shear the Al₁₂Mg₁₇ precipitates on the basal planes. Moreover, as reported by Nie [44] the shape and orientation of shear-resistant precipitates can lead to a different contribution on the strengthening in Mg alloys. In fact, Nie demonstrated that larger prismatic precipitates lead to a higher contribution to the strength than the basal precipitates plates. Recently, Liao et al. [45] have reported by MD simulations the interaction between basal slip and a Al₁₂Mg₁₇ precipitate. They concluded that the precipitate is not plastically sheared by a basal dislocation mainly because the matrix/precipitate interface is weak. As a result, the basal dislocation can glide through the interface without plastically shearing the precipitate.

5.3.4 Diamantane/Mg-matrix Interaction

Diamantane with its characteristic diamond-like properties, e.g. strength and rigidity [26] may also act as obstacles for dislocation movement. From HRTEM analysis, we determined that the insertion of diamantane in the Mg-matrix induced a lattice distortion mainly along the c- direction (Fig. 5-4), generating a microscopic residual stress (RS). Such a RS might arise due to a temperature change during processing because of a different thermal expansion coefficient of diamantane and the Mg-matrix or/and during mechanical loading because of their differences in stiffness [46][50]. As reported by Fernandez et al. [47], there is a correlation between RS and a yield stress in compression that results to be higher than that in tension (the strength differential effect) in reinforced metal matrix composites. We believe that the microscopic-RS due to the thermal/elastic mismatch between diamantane and the Mg-matrix might also contribute to the enhancement of compressive strength in the nanocomposite.

5.3.5 Effect of Diamantane on the Mechanical Behavior

From micro- and macro-compression tests, compressive yield strengths of 470 and 519 MPa were measured for the Mg–10Al–1Dia nanocomposite, which resulted to be 30% higher than those for the Mg–10Al alloy. In addition, we have demonstrated that the strength of the nanocomposite can be improved by reducing the specimen dimensions,

which has important implications for the design of high-performance micro-mechanical devices. A remarkable size effect on the compressive strength of diamantane-reinforced nanostructured Mg micropillars with diameters smaller than 3.5 microns was found (Fig. 5-7). In contrast, no size effect was observed when the diameters are bigger than 3.5 μm . In fact, the compressive strength of micropillars with diameters bigger than 3.5 μm was similar to that of the bulk nanocomposite sample. These results are consistent with the size-induced strengthening in nanostructured Mg-10Al alloy micropillars [34]. Although the yield strength values for the nanocomposite are always higher than those for the diamantane-free sample. It is important to note that the size effect found on the samples with diamondoids is similar to that of the samples without diamondoids, suggesting that similar deformation mechanisms are involved. From the results of our previous work on the samples without diamondoids [34,48], we attributed the size-induced strengthening to a less number of dislocation sources along with an enhanced activity of non-basal dislocation sliding and twinning. Finally the in-situ nanoindentation analysis also supports the microcompression results by showing a significant reinforcement effect of diamantane on the elastic modulus and hardness of the Mg-matrix. As shown in Fig. 5-8, reduced elastic modulus (E_r) values of the nanocomposite were always higher than those of the sample without diamantane for all penetration depths. In particular, at lower penetration depth h , a 2-fold increase of E_r (~ 120 GPa) was measured for the

nanocomposite compared to the sample without diamondoids (<75 GPa). Additionally, a maximum hardness value of the diamantane-reinforced nanocomposite (at lower contact depth) ~ 7 GPa was measured, which resulted 2-fold higher than that of the sample without diamondoids (4.3 GPa). It is well known that nanoindentation measurements are often prone to some errors from various sources. In particular, measurement of the contact area from indentation load-depth data might not be necessarily a straightforward process, as it depends on the amount pile-up or sink-in of material around the indenter-tip [49–52]. Pile-up/sink-in effect observed in various materials during nanoindentation might cause underestimation of the projected contact area resulting in an overestimation of the hardness values [51]. It is suggested that a material with a low ability of work harden such as these nanostructured materials and with a value greater than 0.7 for the ratio of the final indentation depth to maximum indentation depth (h_f/h_{max}) will exhibit pile-up [49]. However, the results obtained in this work for the sample without diamondoids that could serve as control experiment are in good agreement with those reported in the literature. The average E_r of ~ 75 GPa at lower h corresponds to the reported elastic modulus for the intermetallic $Al_{12}Mg_{17}$ compound. $E_r \sim 50$ GPa at higher h is also in good agreement with the elastic modulus of Mg-10Al alloy measured by different techniques as reported in our previous work [34]. Moreover, the highest and

lowest values of hardness measured in this work (Fig. 5-8c) are also in good agreement with the reported values of hardness for the intermetallic $\text{Al}_{12}\text{Mg}_{17}$ phase (4.3 GPa) and Mg-matrix (1.35 GPa), respectively [36]. Since our results are reasonable and in good agreement with the reported values in the literature, we believe that the effect of pile-up on the hardness and elastic modulus can be neglected in this study. Thus, the improved mechanical properties of the nanocomposite reinforced by diamondoids reported in this work are quite remarkable and can be explained by the microstructural changes discussed in the previous paragraphs.

5.4 Conclusions

Nanostructured Mg-10Al nanocomposites reinforced by 1 wt.% of diamantane were successfully processed via cryomilling and SPS. We report the effect of diamantane on the microstructure and mechanical behavior of the nanostructured Mg-10Al-1Dia nanocomposite compared with the diamantane-free Mg-10Al alloy. From HRTEM and STEM analyses, we identified diamantane located within the Mg-matrix, which induces a lattice distortion mainly along the c-direction. From the XRD analysis, no change of the nanocrystalline grain size was observed after adding diamantane to the Mg-10Al alloy. However, we found that the precipitation of $\gamma\text{-Al}_{12}\text{Mg}_{17}$ intermetallic phase in the

nanocomposite was quite different compared to that in the Mg-10Al alloy. It showed a dendritic morphology with no presence of large precipitates or discontinuous precipitation. We attribute these morphological changes in the precipitation of the γ -Al₁₂Mg₁₇ phase to the diamantane capacity for: i) constraining the GB motion by the Zener mechanism, ii) restricting diffusion processes along GBs and iii) accelerating the decomposition of the supersaturated Al solid-solution that promotes the precipitation of γ -Al₁₂Mg₁₇. Additionally, we demonstrate a remarkable effect of diamantane on the compressive strength, elastic modulus and hardness of the nanocomposite. From micro- and macro- compression tests, a compressive yield strength of ~ 470 MPa was measured for Mg-10Al-1Dia, which is a 30% improvement in strength of the Mg-10Al alloy. The reduced elastic modulus and hardness measured using in-situ SEM nanoindentation tests were always higher than those of the sample without diamantane. A 2-fold increase of E_r (~ 120 GPa) was measured for the nanocomposite compared to the sample without diamondoids (< 75 GPa). Additionally, a maximum hardness value of the diamantane-reinforced nanocomposite (at lower contact depth) ~ 7 GPa was reached, which resulted 2-fold higher than that of the sample without diamondoids (4.3 GPa). Since no changes in the grain size have been found after adding diamantane, we attribute the enhanced

mechanical behavior of the nanocomposite to the integration of precipitation hardening and the microscopic residual stress generated by diamantane-Mg matrix mismatch.

5.5 Reference

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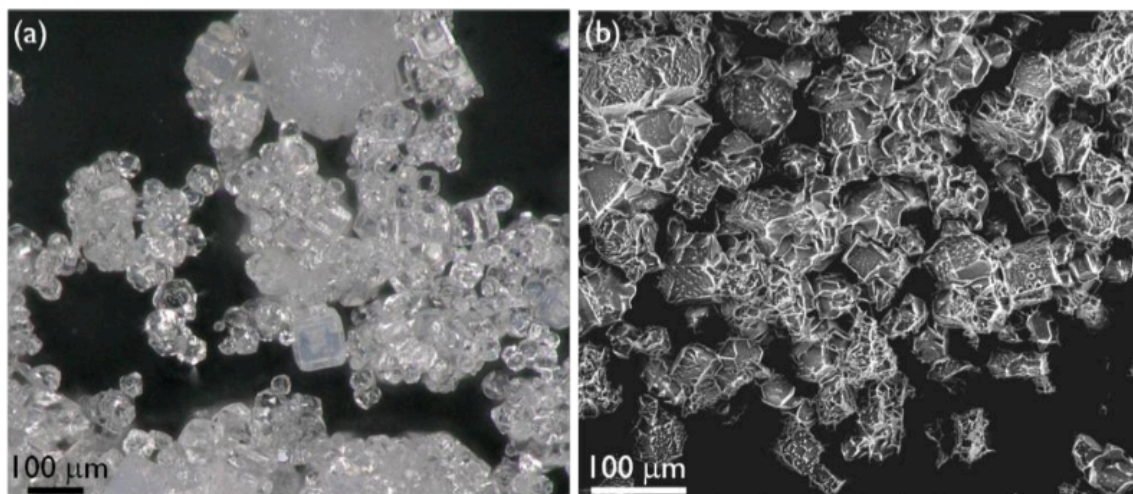


Fig. 5-1 Optical microscopy (a) and scanning electron microscopy (SEM) (b) images of diamantane powders.

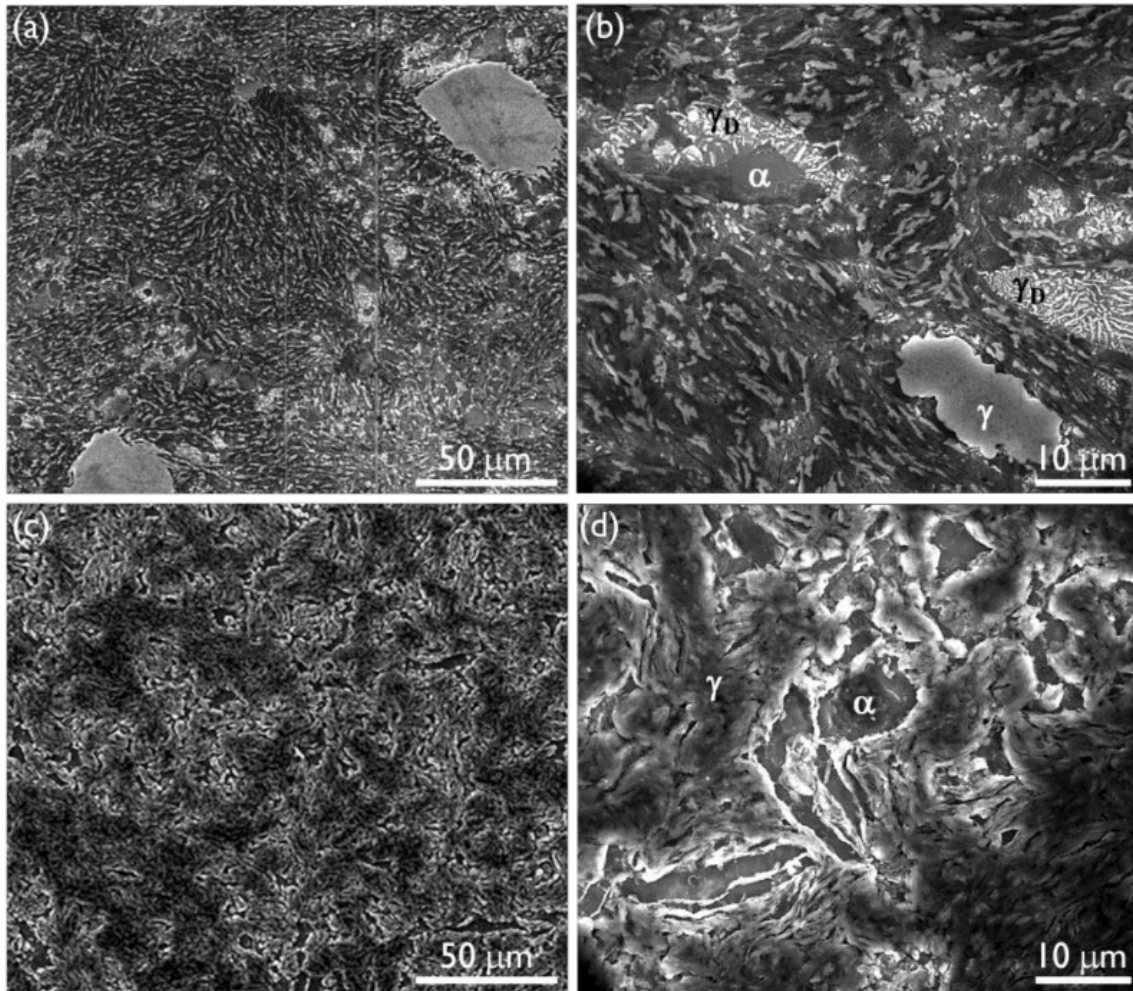


Fig. 5-2 SEM images of the bulk Mg-10Al alloy (a,b) and Mg-10Al -1 Dia nanocomposite (c,d).

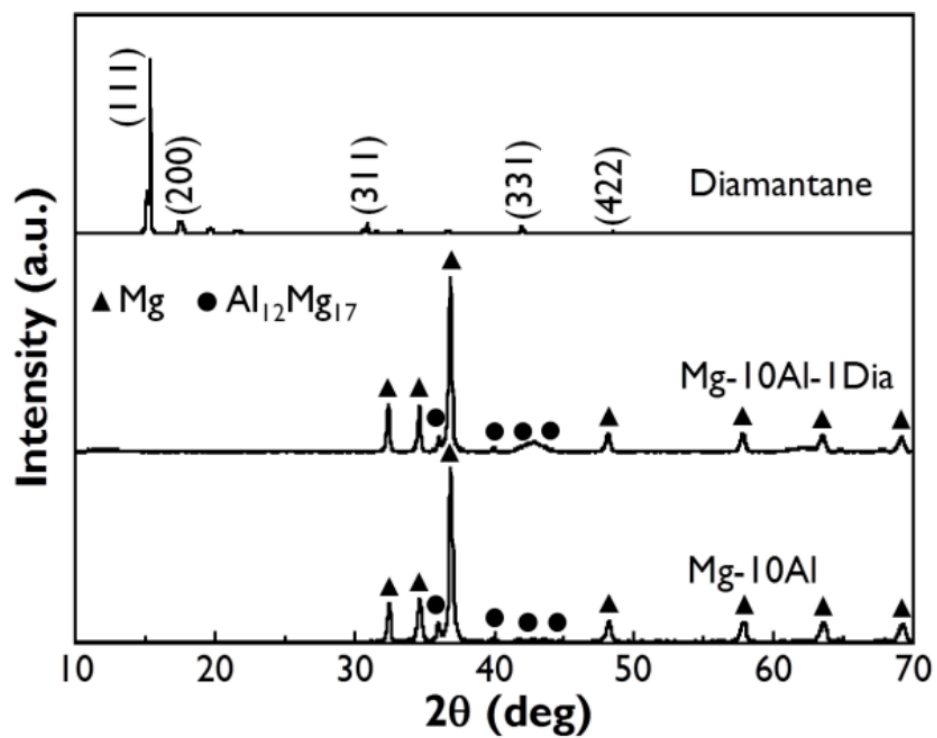


Fig. 5-3 X-ray diffraction (XRD) spectra for the bulk Mg-10Al and Mg-10Al-1Dia samples, and as-received diamantane powders.

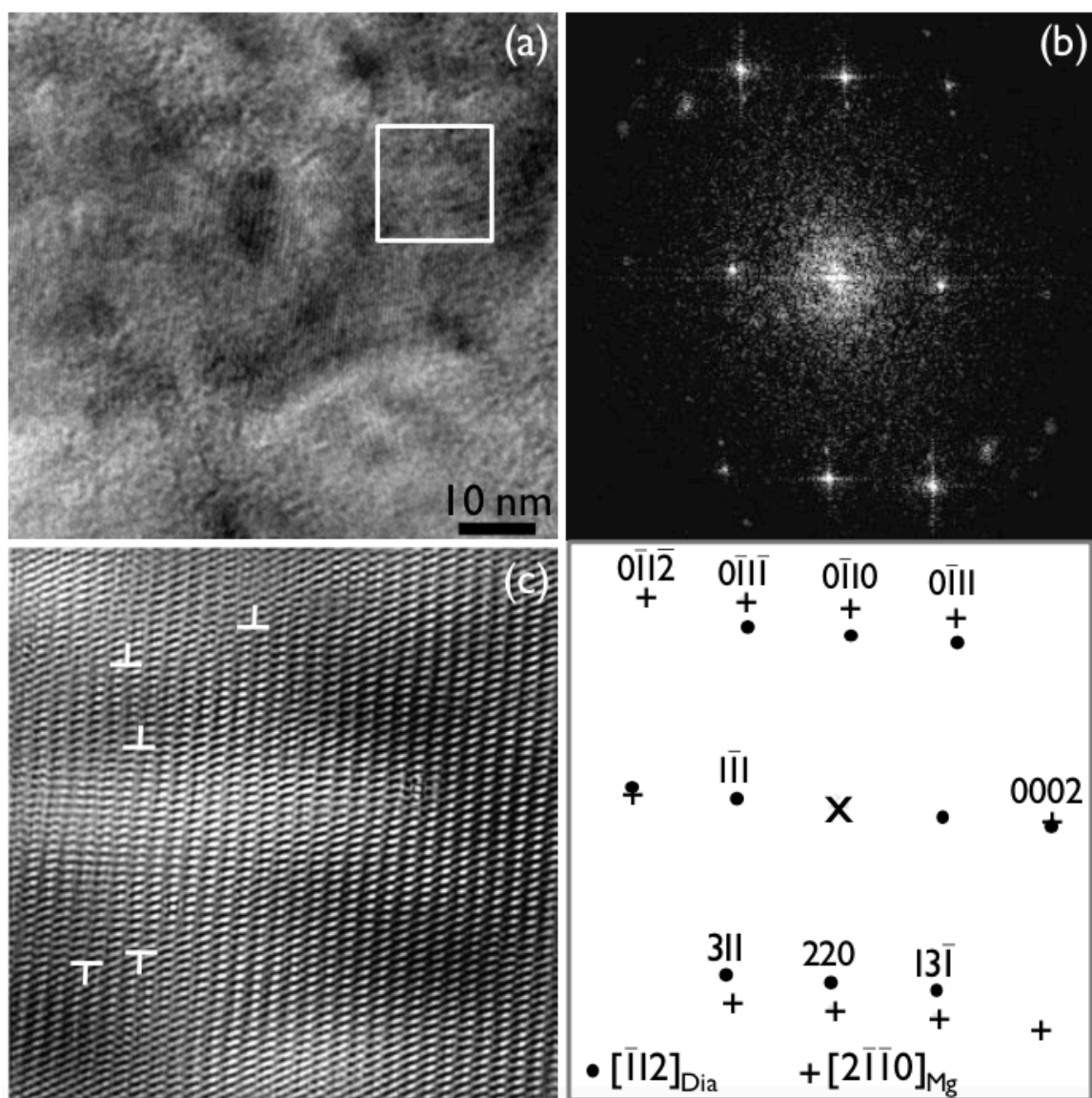


Fig. 5-4 Bright-field transmission electron microscopy (TEM) image of the Mg-10Al-1Dia nanocomposite. (b) Fast Fourier transform (FFT) from the region highlighted by the white rectangle in (a). Below is its indexed FFT for clarity. (c) Fourier filtered high-resolution TEM image of the region highlighted in (a).

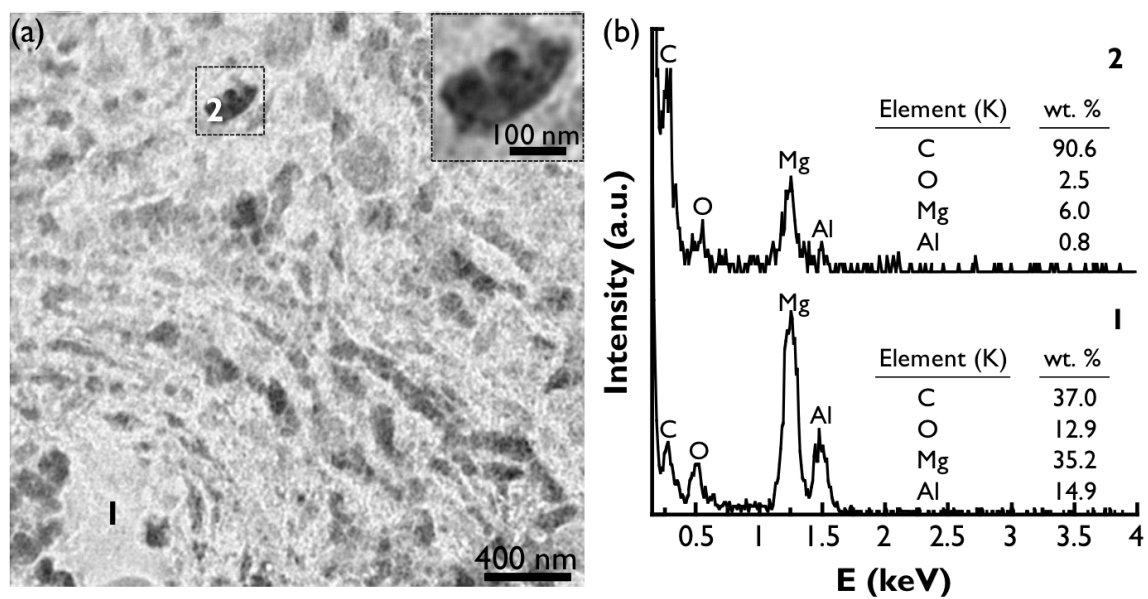


Fig. 5-5 (a) Scanning-TEM image of the Mg-10Al-1Di sample. Inset is an enlarge image of the region highlighted by the dashed square. (b) Energy dispersive X-ray spectroscopy (EDS) spectra and quantitative values (inset) from selected points of interest in (a).

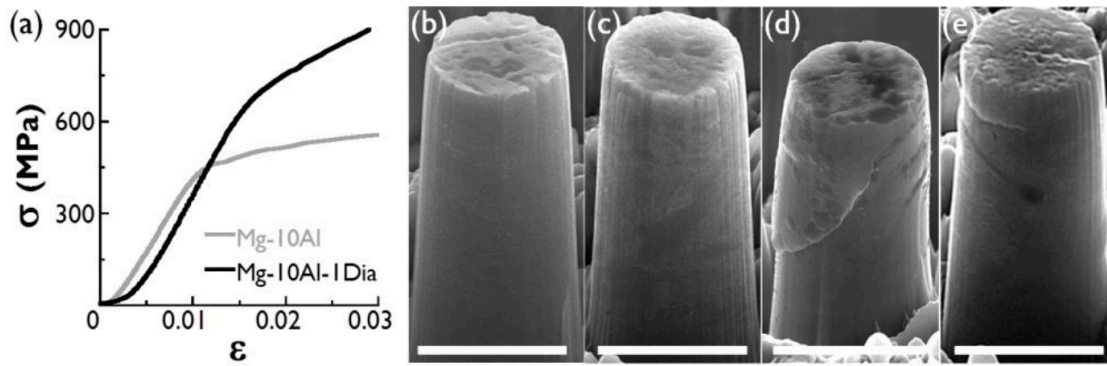


Fig. 5-6 (a) Compressive stress, σ , vs. strain, ϵ , curves of nanostructured Mg-10Al and Mg-10Al-1Dia micropillars. SEM images of nanostructured Mg-10Al (b,d), Mg-10Al-1Dia (c,e) micropillars before and after 2% of compressive strain. The scale bar is 4 μm in all the images.

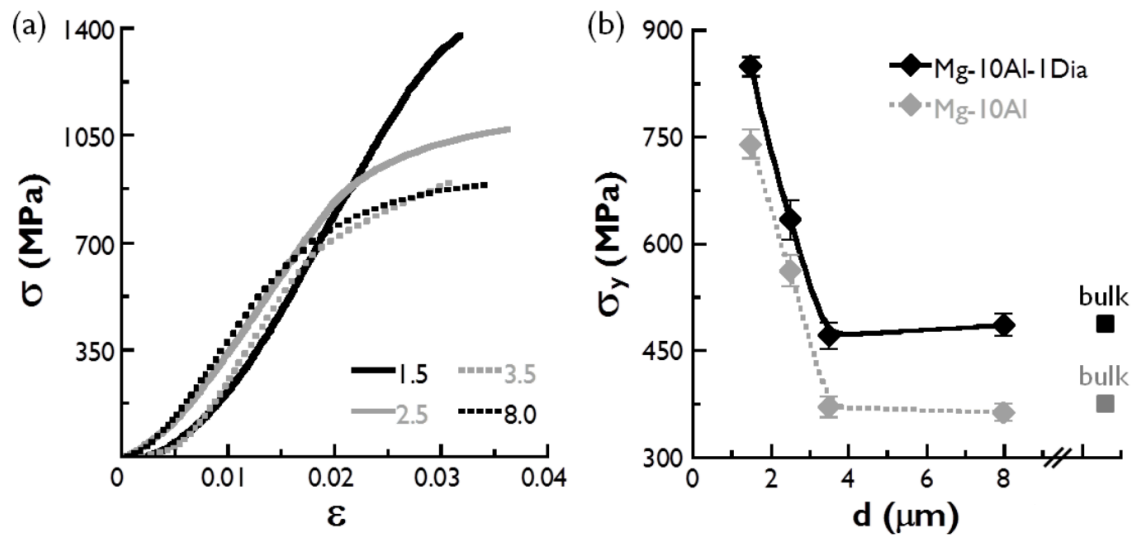


Fig. 5-7 (a) Compressive stress, σ , vs. strain, ϵ , curves of nanostructured Mg-10Al-1Dia micropillars with different diameters. Numbers correspond to the pillars diameter in μm . (b) Compressive yield strength, σ_y , of Mg-10Al and Mg-10Al-1Dia micropillars as a function of pillar diameter, d . σ_y of the bulk Mg-10Al and Mg-10Al-1Dia samples are also included.

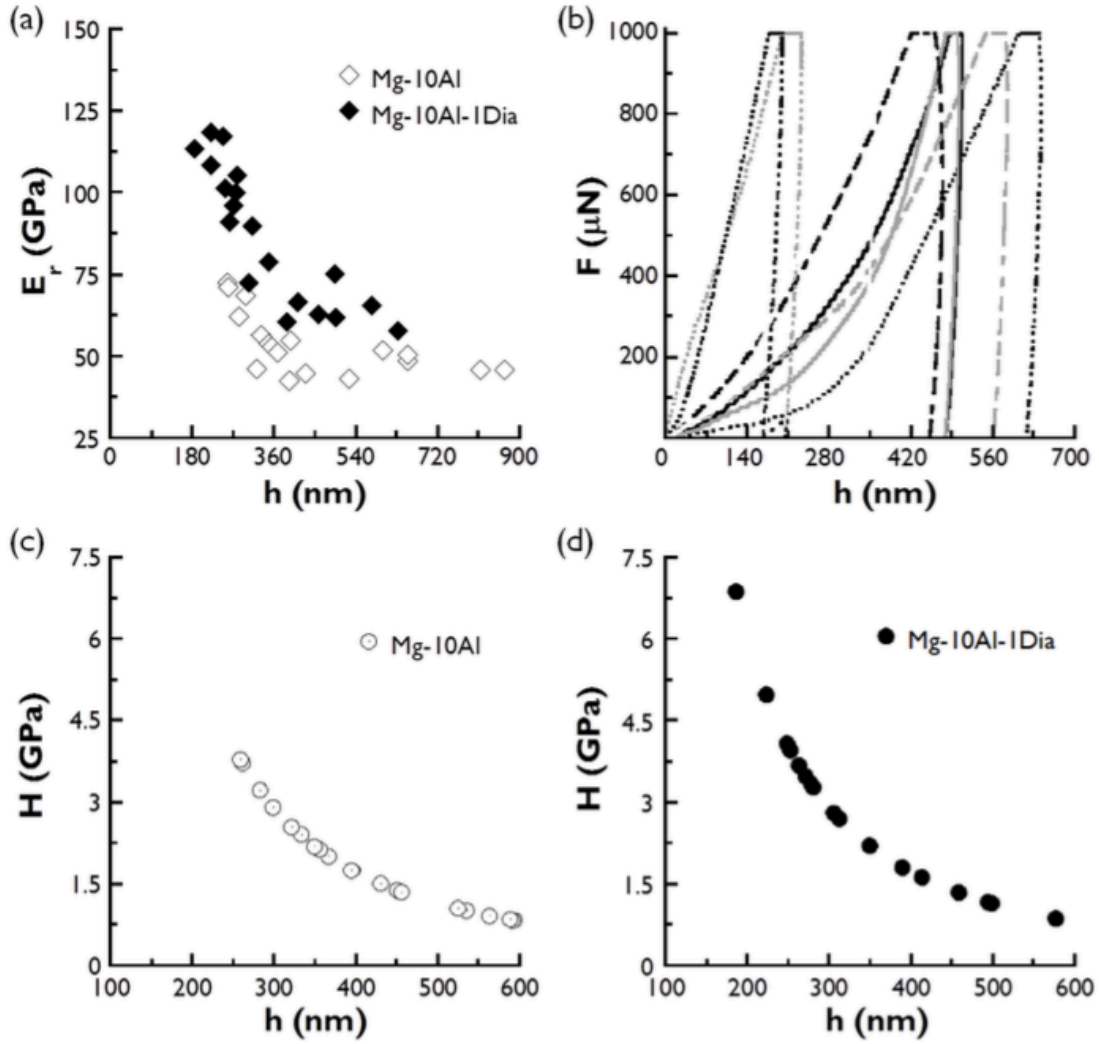


Fig. 5-8 (a) Reduced elastic modulus, E_r , of Mg-10Al and Mg-10Al-1Dia samples as a function of indentation contact depth, h . (b) Representative force, F , vs. h curves of indentations made at a peak force of 1000 μN on the Mg-10Al-1Dia samples. Hardness, H , vs. h of Mg-10Al (c) and Mg-10Al-1Dia (d) samples.

Thermally Stable Nanostructured Magnesium Nanocomposites Reinforced by Diamantane

Abstract

Diamantane-reinforced nanostructured Mg-10Al (wt. %) nanocomposites processed by cryomilling and spark plasma sintering were annealed at different temperatures between 100 to 400°C for several times up to 100 hours. The role of diamantane in the thermal stability of nanostructured Mg nanocomposites is investigated by X-ray diffraction, EDX and Micro-compression tests. We found that the grain size and the compressive yield strength of the sample with diamantane is thermally stable for all the annealing treatments while the yield strength of the alloy without diamantane decreases significantly. These results suggest that diamantane is pinning the grain boundaries and inhibit grain growth at elevated temperature.

6.1 Introduction

Magnesium based alloy is widely used for ultra-light weight structural applications. Advances in ultra-light weight structural materials can essentially improve efficiency of energy usage especially in aerospace and automobile industries while renewable energy is under developing. However, the relatively low strength and poor room temperature ductility limit the applications of magnesium in industry[1]. Although

solid solution and precipitation dispersion strengthening mechanisms can increase the bearing capability, refining crystallite size to nanoscale improves the strength of materials significantly[2–4]. However, excess free energy stored in the large volume fraction of grain boundaries in nanocrystalline bulk materials is detrimental for their thermodynamic stability. The high free energy in grain boundary areas [5,6] becomes driving force that makes nano-grains to grow even at room temperature [7]. Grain growth limits the applications at elevated temperature. Several strategies from kinetic and thermodynamics points of view have been reported to stabilize nanocrystalline structure[8–11]. For example, 3.6 at.% P is able to stabilize the onset temperature for grain growth of Ni[12]. 4 at.% Fe can stabilize Mg better compared to Y, V and Mn. However, Mg (-2.37V) will corrode if contacts to Fe that has higher potential (-0.44V)[13]. The thermal stability and strength of cast AM60 increase as a result of Ca additions[14]. Some studies focus on magnesium composites with adding different ceramic particles such as Al_2O_3 , SiC, and Y_2O_3 to increase the strength[15–19]. Orowan strengthening mechanism suggests composites are strengthened due to rigid and high Young's moduli of the reinforcements[20]. Besides ceramic nano-particle, carbon nanotubes (CNT) or multi-walled carbon nanotubes (MWCNT) can reinforce metals matrix as well[21]. CNT has high strength, flexibility and Young's modulus and was reported to enhance yield strength of AZ91D by 60MPa with 1 wt.% MWCNT[22]. Small dimensions of CNT reduce the possibility of thermal mismatch induced dislocation generation at matrix and CNT interface[23]. Diamondoids are carbon and hydrogen-based nanoparticles. The structure

of diamondoids resembles diamond and has one or more of the carbon cage molecules known as adamantane ($C_{10}H_{16}$). Diamondoids are believed having interesting and useful properties analogous to diamond, such as high thermal stability and structural rigidity[24]. Diamantane, a kind of diamondoids with two face-fused carbon cages, was reported that it can effectively stabilize grain boundary in nanocrystalline Al system by pinning grain boundaries at elevated temperature[25]. The yield strength of nanocrystalline Al with incorporating diamantane has been reported but the strengthening effect of diamantane is not significant on Al[26]. In retrospect, only a limited number of works to date, have investigated the effect of diamantane on strengthening Mg alloys. To the best of our knowledge, diamantane acts as thermal stabilizer of bulk nanocrystalline Mg alloy has not yet reported. In the present work, we evaluated thermal stability of nanocrystalline Mg alloy by combining various experimental techniques such as XRD, micro-compression and EDS analyses. To study the effect of diamantane on the thermal stability of the crystallite size at elevated temperature, annealing treatments were carried out ranging from 100 to 400°C for different periods of time up to 100 hours. The crystalline sizes were evaluated by X-ray diffraction and micro-compression tests at room temperature were performed to measure the mechanical properties after annealing at different temperatures.

6.2 Materials and Methods

Pure Mg and Al powders were blended to formulate the final composition Mg-10Al (wt. %) alloy. Cryomilling was performed for 8 hours in liquid nitrogen atmosphere. 1 wt.% of diamantane was incorporated during cryomilling to produce nanostructured Mg-10Al-1Diamantane (wt. %) powders (referred as Mg-10Al-1Dia sample). Spark-plasma-sintering (SPS) was used to consolidate the cryomilled powders. The SPS sintering process was carried out in vacuum for 5 min at 400 °C and under uniaxial pressure of 100 MPa. More details about the material processing can be found in ref.[27]. Different annealing treatments up to 100 hours at temperature of 100, 200, 300 and 400 °C were conducted in a vacuum quartz tube furnace. X-ray diffraction (XRD) was used to investigate the crystalline sizes and phases before and after annealing of both Mg-10Al and Mg-10Al-1Dia samples. XRD was conducted in a Bruker D8 Discover Powder X-ray Diffractometer using Cu K α ($\lambda=0.1542$ nm) radiation. Scherrer equation was applied to estimate the crystalline sizes. Electron dispersive spectroscopy (EDS) mapping analysis was conducted with A FEI Nova 230 Variable Pressure SEM (VP-SEM) equipped with a Thermo Fisher Scientific EDS system at 15-kV accelerating voltage. In order to perform microcompression tests, micropillars with diameters ~ 3.5 μm and aspect ratio of 1:3 were machined by focused-ion-beam (FIB) from both samples. A FEI Nova600 Nanolab DualBeam FIB-SEM was used for this purpose. In order to avoid any overestimation of the measured yield strength and strain hardening due to the tapering of the pillars, the diameter is considered at half-height of the pillar (~ 4 μm).

Micro-compression tests were carried out using MTS Nanoindenter XP at the strain rate of $3\text{-}5 \times 10^{-4} \text{ s}^{-1}$. A flat-ended diamond circular tip of 10 μm in diameter was used.

6.3 Results and Discussion

6.3.1 Grain Size Analysis After Annealing

The microstructural characterization of both Mg-10Al and Mg-10Al-1Dia samples processed by cryomilling and SPS can be found in our previous publication [28]. In order to study the effect of diamantane on the stability of the grain size, we measured the average crystallite size by the peak broadening from X-ray diffraction (XRD) spectra of the samples before and after annealing. As an example, Figs. 6-1 (a) and (b) show the most relevant peaks of Mg and $\text{Mg}_{17}\text{Al}_{12}$ phases present in both Mg-10Al and Mg-10Al-1Dia samples, respectively, before and after annealing for 100 h at 400 °C. It is interesting to note that while the peaks of the samples without diamantane show clearly some shrinking after annealing (Fig. 6-1a), the peaks width of the sample with diamantane remains unchanged (Fig. 6-1b). These results indicate that the grain size in the sample with diamantane is stable after 100 h of annealing at 400°C.

In addition, it is interesting to note that Mg peaks in both samples are slightly shifted to higher Bragg angle comparing with the spectrum reported for the α -Mg (JCPDS file #35-0821). According to the relation of Mg-Al lattice constant with variant Al concentration, the amount of Al dissolved in Mg matrix can be calculated based on

Lubarda's theory[29]. About 6.5 wt. % and 6.3 wt.% of aluminum dissolved in Mg matrix for Mg-10Al and Mg-10Al-1Dia, respectively. The equilibrium concentration of Al at room temperature is less than 1 wt. %.

The crystalline sizes of Mg-10Al and Mg-10Al-1Dia samples before annealing was reported in our previous work [28] ~35 nm and 36 nm, respectively. Grain size measurements based on the XRD analyses after different annealing treatments are included in Fig. 6-1 (c) and (d). These plots display the average grain size as a function of the annealing time at different temperatures for Mg-10Al and Mg-10Al-1Dia samples, respectively. Five scans of XRD were conducted per composition and annealing condition. It is evident to observe the grain growth with time for all the annealing temperatures for the sample without diamantane (Fig. 6-1c). In fact, the grain growth as a function of the annealing time is more pronounced increasing with the annealing temperature. For instance, the grain size increases from 35 nm to 110 nm after 100 h of annealing at 400 °C. In contrast, the grain size measurements for the sample with diamantane (Fig. 6-1d) are significantly more stable with the annealing time at all temperature conditions. In particular, after annealing at 400°C for 100 hours the average grain size of the Mg-10Al-1Dia sample remains below 70 nm, while the average grain size of the Mg-10Al sample is higher than 100 nm. These results suggest that diamantane effectively pin the grain boundaries and inhibit the grain growth at high temperatures. In nanocrystalline materials, volume fractions of grain boundary, triple line junctions (TJs) and quadruple point junctions (QPs), that are zero-dimensional objects where four or

more TJs meet, are significantly higher compare to their coarse-grain counterpart. TJs and QPs are structural elements and have their own mobilities. As a consequence, the coupled motion of grain boundaries and TJs/QPs needs to be taken into consideration. TJs and QPs are capable of exerting dragging force on grain boundaries (GBs) during grain boundary migration [7,30]. Typical TJ/QP-controlled grain growth has the following phenomena: 1) TJs and QPs -controlled growth exhibit concave upwards curvature while all the curvatures in the present study are concave downwards 2) TJ and QP -controlled growth usually dominate when grain size is below 10nm while the grain sizes discussed here are all above 35nm [7]. By analyzing the curvature of an isothermal grain growth curve in the present study, TJ/QP-controlled grain growth-controlled can be neglected. Grain growth can be described by the kinetic equation: $d^n - d_0^n = Kt \exp-(Q / RT)$. Where d is the grain size at the time t, while d₀ is the original grain size. K is a constant and Q is the activation energy for grain growth. R and T are gas constant and temperature respectively. By fitting the data from XRD measurements, Q can be obtained and it is 51.2kJ/mol and 63.5kJ/mol for Mg-10Al and Mg-10Al-1Dia respectively. The activation energy for grain growth of Mg-10Al-1Dia is higher than that of Mg-10Al. Higher activation energy of grain growth means slower kinetics of recrystallization for a given temperature. In other word, diamantane particles can hinder grain growth in Mg-Al alloy. Since the grain sizes of Mg-10Al and Mg-10Al-1Dia are similar (~35nm) and the amounts of Al dissolved in Mg-10Al and Mg-10Al-1Dia are comparable (~6.5 wt.%) before annealing, it is worth to analyze the effect of diamantane

on $\text{Al}_{12}\text{Mg}_{17}$ precipitation. Precipitation enhances the strength and enhancement depends on the size, distribution and volume fraction of the precipitation as suggested by Orowan strengthening model [31,32]. $\text{Al}_{12}\text{Mg}_{17}$ can strengthen Mg alloy by acting as obstacles hindering dislocation movement. It was reported that for AZ80 with similar synthesis process, the strengthening contribution of nano-sized secondary phase dispersions is about 132 MPa [33]. Although the volume fractions of $\text{Al}_{12}\text{Mg}_{17}$ forming in Mg-10Al and Mg-10Al-1Dia are similar based on the relative intensity of characteristic peaks in the XRD spectra, the distributions are different as shown in Fig. 6-2. Fig. 6-2 (a) and (c) show the EDS mapping of Al atoms in the Mg-10Al and Mg-10Al-1Dia samples before annealing, respectively. As expected the $\text{Al}_{12}\text{Mg}_{17}$ phase (Al-rich areas) are distinguished by the bright contrast while Mg matrix is clearly identified in the dark zones. It is interesting to observe that the size of $\text{Al}_{12}\text{Mg}_{17}$ precipitates in the Mg-10Al sample (Fig. 6-2a) is bigger ($\sim 7 \mu\text{m}$) than that observed in Mg-10Al-1Dia sample ($\sim 1.4 \mu\text{m}$) (Fig. 6-2c). In addition, Al atoms can also be found distributed in the Mg matrix. However, after annealing at 400°C for 100 hours (Fig. 6-2b), Al atoms in the Mg-10Al sample are mainly observed in the $\text{Al}_{12}\text{Mg}_{17}$ precipitates as a result of Al diffusion processes following the kinetics of precipitation coarsening [34]. However, the distribution of Al atoms in the Mg-10Al-1Dia sample after annealing (Fig. 6-2d) remains similar to that before annealing (Fig. 6-2c). These observations suggest that diamantane is restricting Al diffusion processes in the Mg-10Al-1Dia nanocomposite. This is in good agreement with our previous work [28].

6.3.2 Micro-Compression Analysis After Annealing

Micro-pillar compression tests was adopted to study the mechanical properties of Mg-10Al and Mg-10Al-1Dia. Representative engineering compressive stress, σ , vs. strain, ϵ , curves of Mg-10Al and Mg-10Al-1Dia micropillars before and after annealing (at 400 °C for 6 hours and 100 hours) are shown in Fig. 6-3(a) and (b), respectively. At least 5 pillars were tested per composition and annealing condition, although only one for each sample is shown here as a comparison. Yielding points are highlighted by arrows. It is clearly observed that the yield strength of Mg-10Al micropillars decreases with increasing annealing time (Fig. 6-3a). For instance, we measured a σ_y of 375 MPa before annealing, which decreases to 154 MPa after annealing at 400 °C for 100 h. On the contrary, it is interesting to observe that the yield strength of Mg-10Al-1Dia micropillars remains relatively stable after annealing. The yield strength value before annealing is 470 MPa that only decreases to 328 MPa after annealing at 400 °C for 100 h. The yield strength, σ_y , of Mg-10Al and Mg-10Al-1Dia micropillars as a function of annealing time at different temperatures is summarized in Fig. 6-3 (c) and (d), respectively. Before annealing, the average yield strength value for the Mg-10Al micropillars was ~370 MPa, while a remarkable yield strength of ~470 MPa was obtained for Mg-10Al-1Dia micropillars. Thus, a 30% improvement in strength of the Mg-10Al alloy can be attained by adding diamantane [28]. The σ_y of Mg-10Al and Mg-10Al-1Dia decreases gradually for longer annealing time. This trend is more pronounced increasing the annealing temperature to 200 °C, 300 °C and specially at 400 °C. The σ_y of Mg-10Al dropped to

~280 MPa, ~220 MPa and ~150 MPa after annealing for 100 hours at 200 °C, 300 °C and 400 °C, respectively. However, the σ_y of Mg-10Al-1Dia micropillars remains stable for all the annealing times ~440 MPa, and ~400 MPa for 100 hours at 200 °C and 300 °C, respectively. Only in the worst case scenario, after 100 h at 400 °C, the yield strength reduces to ~330 MPa. The result shows that diamantane hinders grain growth and precipitation coarsening. Therefore, the a higher yield strength of Mg-10Al-1Dia after annealing can be attributed to a finer grain size and more uniformed dispersion of smaller precipitates.

Another phenomenon worth to be pointed out is the yield strengths of Mg-10Al and Mg-10Al-1Dia increase after annealing at 100°C for 3 hours. The so-called “grain boundary relaxation” is a kinetic process. During the process, defects are allowed to annihilate upon heating and grain boundary transforms to a more stable configuration. This phenomenon not only has been observed in coarse-grained but also nano-grained materials. [35,36] Grain boundary relaxation is related to strengthening materials and has been reported in Cu, Pd and Al-1.5%Mg [37,38] and also supported by theoretical studies [30,39,40]. By annealing with mild temperature and short period of time, the hardness can be improved. Thus, it can explain the yield strengths of Mg-10Al and Mg-10Al-1Dia increase with annealing at 100°C for 3 hours. With low temperature annealing, grain boundary can be relaxed without appreciably altering grain size and grain boundary relaxation can be considered as an additional factor that contributes strengthening impact on the mechanical properties. If the annealing temperature is too high or the period of

annealing time is too long, grain growth will be dominant and suppress the contribution from grain boundary relaxation thus resulting yield strength degradation. Changes in the yield strength of Mg-10Al and Mg-10Al-1Dia therefore likely reflect changes in the state of the grain boundaries.

Fig. 6-4 (a) and (d) show 52° tilted-view SEM images of Mg-10Al and Mg-10Al-1Dia micropillars, respectively. Before compression, all the pillars were slightly tapered as a consequence of the annular milling method by FIB. Micropillar dimensions and the tapering angles are indicated in Fig. 6-4 (a) and (d). Fig. 6-4 (b) and e show the SEM images of the Mg-10Al and Mg-10Al-1Dia pillars after compression, respectively. Both Mg-10Al and Mg-10Al-1Dia pillars fractured along their shear bands during compression. Fig. 6-4 (c) and (f) show the SEM images of the annealed Mg-10Al and Mg-10Al-1Dia micropillars (at 400°C for 100 hours) after compression. Explain the differences between the pillars after compression at room temperature and the ones after annealing.

6.4 Conclusions

In summary, thermal stabilities of nanostructured Mg-10Al and Mg-10Al-1Dia were evaluated by XRD, EDS and micro-compression. Mg-10Al-1Dia reinforced by 1 wt.% of diamantane shows excellent thermal stability. The grain size of Mg-10Al-1Dia retain below 70nm while the grain size of Mg-10Al grows to over 100nm after

annealing with 400°C for 100 hours. Diamantane nano-particles can essentially pin GBs and constrain grains from growth. In addition, diamantane particles prevent Al atom diffuse through grain boundary to aggregate so the strengthening effect of $\text{Mg}_{17}\text{Al}_{12}$ is more evident in Mg-10Al-1Dia after annealing. As the results, strength of Mg-10Al-1Dia can be retained after annealing.

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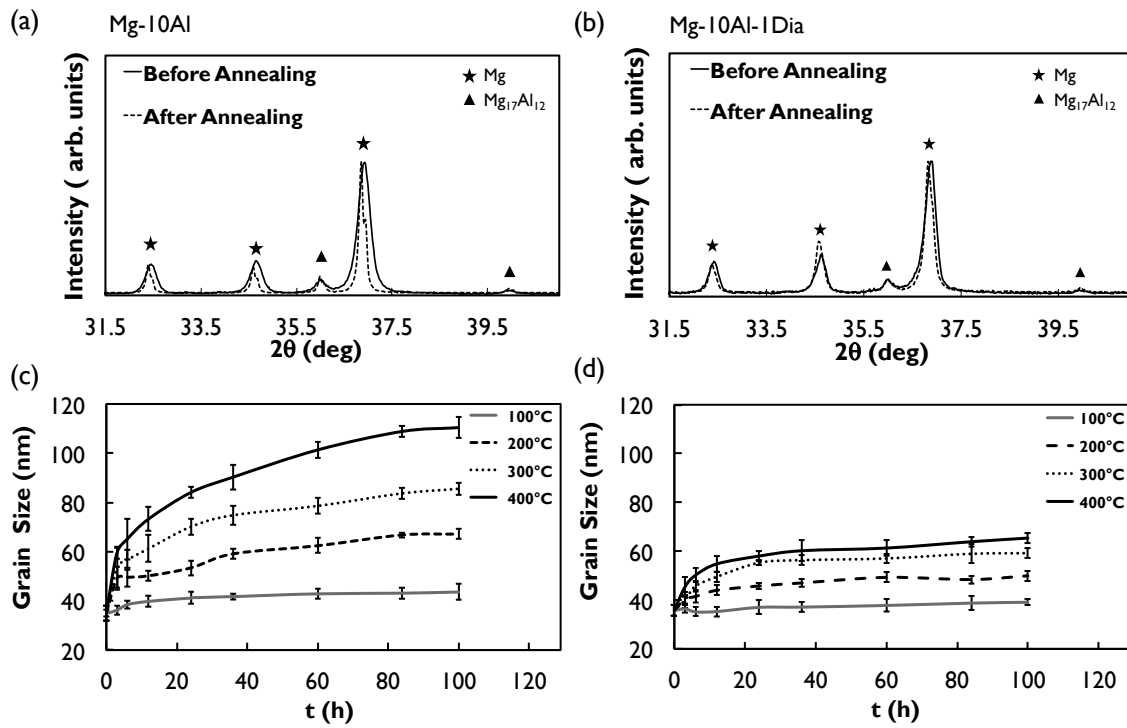


Fig. 6-1 XRD spectra before and after 100 hours of annealing at 400°C for (a) Mg-10Al and (b) Mg-10Al-1Dla alloy. Average grain size as a function of the annealing times at different temperature for (c) Mg-10Al and (d) Mg-10Al-1Dla alloy.

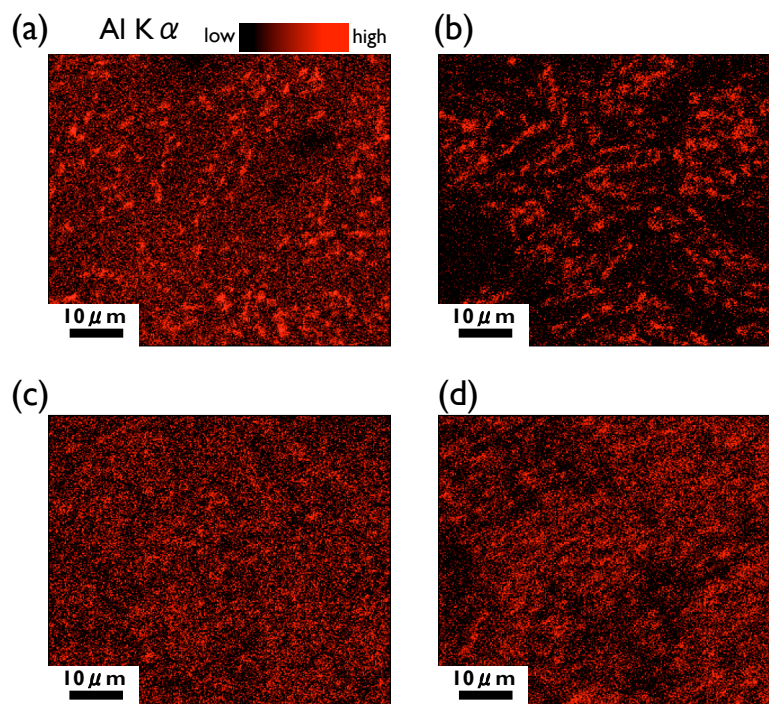


Fig. 6-2 EDS maps of Al atoms for (a) Mg-10Al and (c) Mg-10Al-1Dia before annealing and (b) Mg-10Al and (d) Mg-10Al-1Dia after annealing at 400°C for 100 hours.

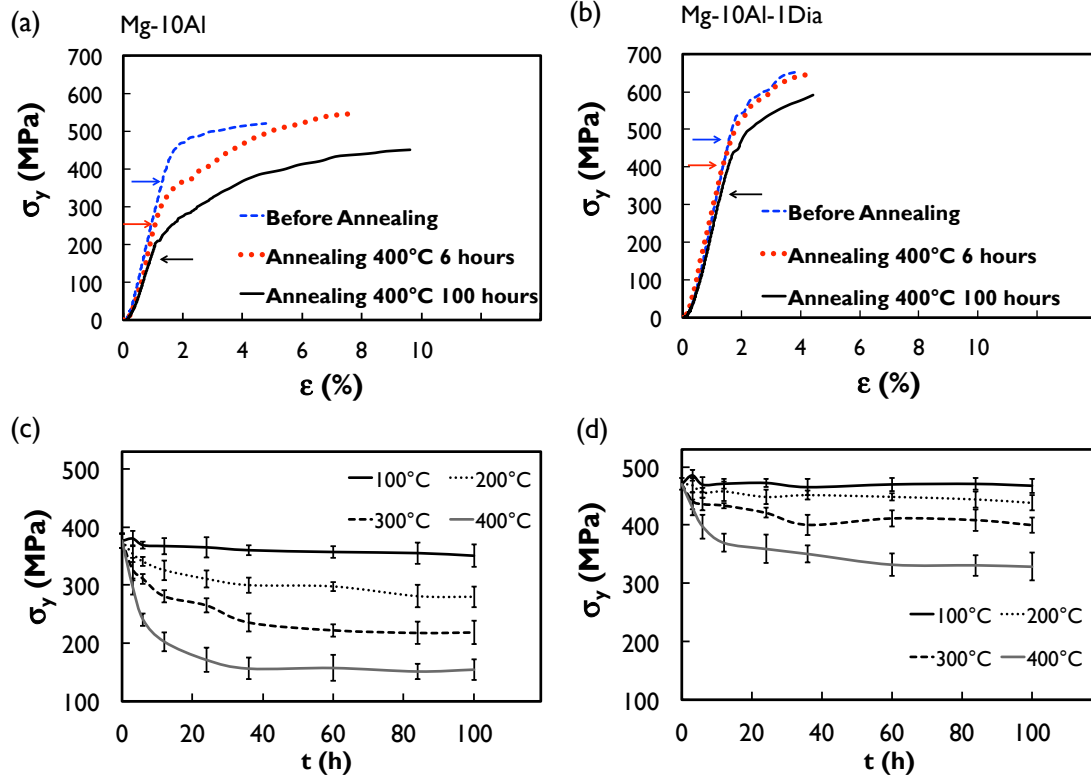


Fig. 6-3 Engineering stress-strain curves of (a) Mg-10Al and (b) Mg-10Al-1Dla alloys before and after annealing at 400°C for 6 and 100 hours. Yield strength of (c) Mg-10Al and (d) Mg-10Al-1Dla alloys as a function of the annealing time at the temperature ranging from 100°C to 400°C.

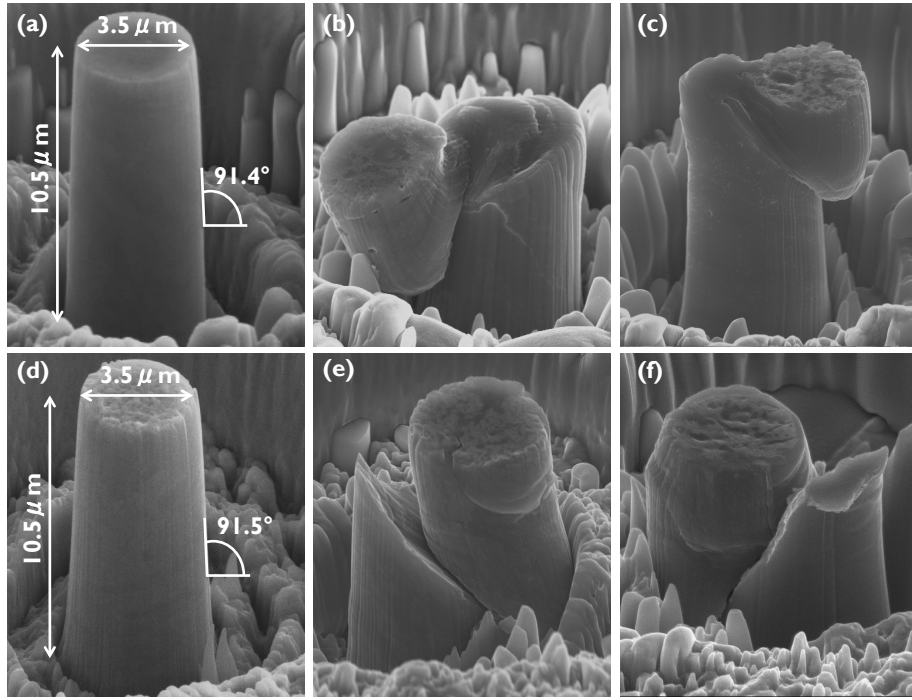


Fig. 6-4 (a) Mg-10Al and (d) Mg-10Al-1Dia micro-pillars before compression. Before annealing, (b) Mg-10Al and (e) Mg-10Al-1Dia micro-pillars after compression. After annealing at 400°C for 100 hours, (c) Mg-10Al and (f) Mg-10Al-1Dia micro-pillars after compression.

Chapter 7

Simulations of Mechanical Behavior in Magnesium and Micropillars

Abstract

In this chapter, molecular dynamics simulations (LAMMPS) are used to study the mechanical properties of magnesium under tensile loading. An inverse Hall-Petch relation is found when the grain size of magnesium is below the critical grain size. The dominant deformation mechanism below and above the critical grain size will be discussed. In addition, finite element analysis (Abaqus) is used to correct the tapering issue in the micro-compression experiment, allowing for a more accurate measure of the yield strength.

7.1 Introduction

The plastic deformation mechanism of metals with nanostructures has gained much interest in the past decade. The mechanical properties of nanocrystalline materials are not well understood due to difficulties of synthesizing impurity free samples with uniform grain size. Therefore, molecular dynamics (MD) has started to be used as a tool to explore the mechanical behavior of nanocrystalline materials. Currently, most literatures simulate face-centered cubic (FCC) materials such as copper because the slip system of FCC is symmetric and simple compared to that of hexagonal close-packed structured (HCP) metals such as magnesium [1]. Schiøtz et al. used MD simulations to simulate the tensile strength of copper with grain sizes

ranging from 5 to 50 nm. The results show that when the grain size is below 10 nm, grain boundary sliding dominates instead of dislocation movement. This produces a softening effect which is reported as the inverse Hall-Petch relation [2,3]. The general prediction of the critical grain size of copper is about 13nm, but the critical grain size of magnesium is not yet reported. In this chapter, we will use Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) to simulate the tensile strength of magnesium with different grain sizes to identify the critical grain size.

Regarding finite element simulations, we will use Abaqus to correct for the tapering effect in micro-compression tests. The tapering effect originates from micropillar preparation. To prepare micropillars with FIB, there are generally two major approaches: lathe milling and annular milling. The advantage of lathe milling is the ability to produce taper-free micro-pillars. However, a drawback of this method is the larger ion dose the tested volume is exposed to. High ion dose significantly affects compressive strength [4]. In addition, smaller pillars cannot be machined through lathe milling because fiducial mark is needed. After weighing the pros and cons between the two approaches, we adopted the annular milling process because we can machine smaller pillars while maintaining reasonable yield strengths. In the annular milling process, tapering of the pillars is typically a result of fabrication inaccuracies and it produces artificial strain hardening [5]. By using finite element analysis, this tapering effect can be alleviated.

7.2 Materials and Methods

7.2.1 Molecular Dynamic Simulations (LAMMPS)

In the present study, LAMMPS is used to simulate mechanical behavior of magnesium with grain sizes ranging from 5 to 50 nm. The interatomic potential of magnesium reported by Sun, et al. [6] is considered in the present study. The simulation temperature and pressure are set to be 300K and 0 bar, respectively. Tensile testing is conducted along the x axis with a strain rate of 10^{10} (1/s). To create polycrystalline magnesium, we use the concept of the Voronoi diagram. In mathematics, a Voronoi diagram is the partitioning of a plane into regions based on the distance to points in a specific subset of the plane. That set of points (called seeds, sites, or generators) is specified beforehand, and for each seed there is a corresponding region consisting of all points closer to that seed than to any other. These regions are called Voronoi cells as illustrated in Fig. 7-1. Put simply, it's a diagram created by taking pairs of points that are close together and drawing a line that is equidistant between them and perpendicular to the line connecting them. That is, all points on the lines in the diagram are equidistant to the nearest two (or more) source points [7]. The concept of Voronoi diagrams could also be applied to robotics to prearrange the routes beforehand to help the robots figure out the best route to the goal without encountering any obstacles. These properties are also good for modeling applications. In mathematics, Voronoi diagrams are a way to separate the space into several parts. By scattering a set of seeds in the space that we are interested in and each seed could correspond to the region. Each region is called Voronoi cells. In materials science, we can take advantage of the concept of Voronoi diagrams to model microscopic structures, especially for defects and grain boundaries.

Therefore, it is easier to calculate the properties of polycrystalline materials since grain boundaries are always the starting point for crack intimation and propagation. The procedure for grain boundary generation in a perfect crystal is listed as follows:

1. Randomly positioned the seeds in the lattice sites
2. Connect these sites with their nearest neighbors with lines
3. Bisect each of these lines with perpendicular lines then connect them to a surface.

7.2.2 Finite Element Simulation (Abaqus)

A parameter-based finite element analysis (FEA) was used to simulate the micro-compression of pillars. In the model, von Mises yield criterion was used to determine the yield strength of elements in the model. The commercial software ABAQUS version 6.8 was used to perform the computational modeling.

7.3 Results and Discussion

7.3.1 Single Crystal Magnesium Tensile Simulation

Before simulating polycrystalline magnesium, the simulation of tensile testing in single crystal magnesium is conducted to compare it with the experimental results from the literature. Yu et al. conducted in-situ tensile test of single crystal magnesium in a transmission electron microscope as illustrated in Fig. 7-2 (a). After testing, the stress-strain curves are shown in Fig. 7-2 (b) and a yield strength of 700-750 MPa was measured. Twinning forms after the tensile test as shown in Fig. 7-2 (c) [8]. After generating a single crystal magnesium system, the LAMMPS

data is input into a tensile test script. The stress and strain values are generated separately, and can be imported in graphing applications for plotting stress-strain curve as shown in Fig. 7-3. The slope of the stress-strain curve in the elastic part is ~ 45 GPa, which is the Young's modulus of pure magnesium. The yield strength is obtained as ~ 750 MPa. The results are in good agreement with that reported from literature [8]. In addition, during the single crystal Mg simulation, the twin formation could be observed when the system applies a tensile stress along the [0001] direction as shown in Fig. 7-4. This outcome also agrees with the experimental results of single crystal measurement done by Minor's group as shown in Fig. 7-2 (c). Once we confirmed the results of tensile testing for single crystal magnesium were consistent with experimental results, polycrystalline Mg with different grain sizes were prepared based on the Voronoi approach. Fig. 7-5 shows systems of nanocrystalline magnesium with average grain sizes of 6.4nm and 16 nm. Nanocrystalline magnesium systems with grain size ranging from 5 nm to 50 nm are prepared to run the MD simulation. The stress-strain curves of different grain sizes Mg are plotted in Fig. 7-6 (a) and the relation of yield strengths with respect to grain sizes is shown in Fig. 7-6 (b). Below the critical grain size (inversed point), the yield strengths drop due to grain sliding deformation. Above the critical grain size, the yield strengths retain around the same values; this behavior is different from that of Cu [1]. The critical grain size predicted here is about 19nm. The simulation result shows that Mg can achieve high yield strength when the grain size is between 30-45nm. The reason for different behaviors between Cu and Mg above critical grain size is due to different deformation mechanisms. Although FCC and HCP are closed-pack structures, HCP materials have deformation twins while FCC materials do not. A

twin boundary is a coherent grain boundary which can not only enhance the strength of a material but also increase ductility at the same time. However, nanocrystalline hexagonal close-packed (HCP) metals are rarely observed to deform by twinning because twin boundary energy, γ_{TB} , is higher than in FCC metals. For example, twin boundary energy of pure Mg is around 85 mJ/m² for the (10 $\bar{1}$ 1) twin boundary, while that of an FCC structure, such as Cu, is about 20 (mJ/m²) [9, 10]. Magnesium twins are less thermodynamically stable in smaller nano-size grain. Therefore, the larger the grain size, the more easily a twin can form. Grain boundary strengthening mechanisms need to be taken into consideration as well; with larger grain sizes there are fewer grain boundaries to hinder the movement of dislocations. By combining the two effects, we can explain how yield strength remains the same even when the grain size is above the critical size. We expect there is an inversed point at which Mg can achieve maximum strength and high ductility because twins can improve ductility.

7.3.2 Finite Element Analysis of Micro-compression Test

A finite element model was developed to correct the tapering effect on micro-compression tests. The software ABAQUS standard v6.8 is used to perform the computational modeling of pillars under compression. Fig. 7-7 displays the schematic figure of the model of pillars with and without tapering. Both pillars have an aspect ratio of 1:3. Fig. 7-7 (a) shows a pillar with tapering where the tapering angle is defined as the angle between the pillar side-wall and the vertical line. In the present case, the tapering angle is $\sim 1.5^\circ$. Fig. 7-7 (b) is the pillar without tapering, which is the ideal case in micro-compression. Those two types of pillar will be

subjected to uniaxial compressive loading along the pillars' vertical axis. Fig. 7-8 displays the evolution of the simulation during compression for the pillar with tapering. It is notable that the load is not uniformly applied on the pillar, which will cause the inaccuracy of stress measurements. The stress-strain curves of both the experimental and simulation studies under compression are presented in Fig. 7-9. The simulated curve corresponding to a taper-free pillar is also included. The experimental and simulation curves of tapered pillars match well, indicating that the simulation can accurately describe the present study. These results are in good agreement with the ones for the non-tapered pillars. Similar yield strength values are shown, i.e. 370 ± 14 MPa (experiment), 365 MPa (simulation-tapered pillar) and 360 MPa (simulation-non tapered pillar). Therefore, it is proven that by taking the cross-section area at the middle height, the experimental result will be very close to those of taper-free pillars.

7.4 Conclusions

The mechanical behaviors of single crystal magnesium and magnesium with nano-sized grains are discussed. The tensile test simulation for single crystal Mg is in good agreement with in-situ TEM tensile tests regarding the morphology and yield strength. The critical grain size for polycrystalline Mg is 19nm but we expect there is an inversed point. In addition, using finite element simulation to simulate micro-compression tests, we have demonstrated that the tapering of micro-pillars does not affect their compressive yield strength if the cross-section area at middle height is considered. For a tapered pillar, yield strengths of 370 ± 14 and 365 MPa were

obtained from the experimental and simulation studies, respectively, while a yield strength of 360 MPa was the computational result for a taper-free pillar.

7.5 Reference

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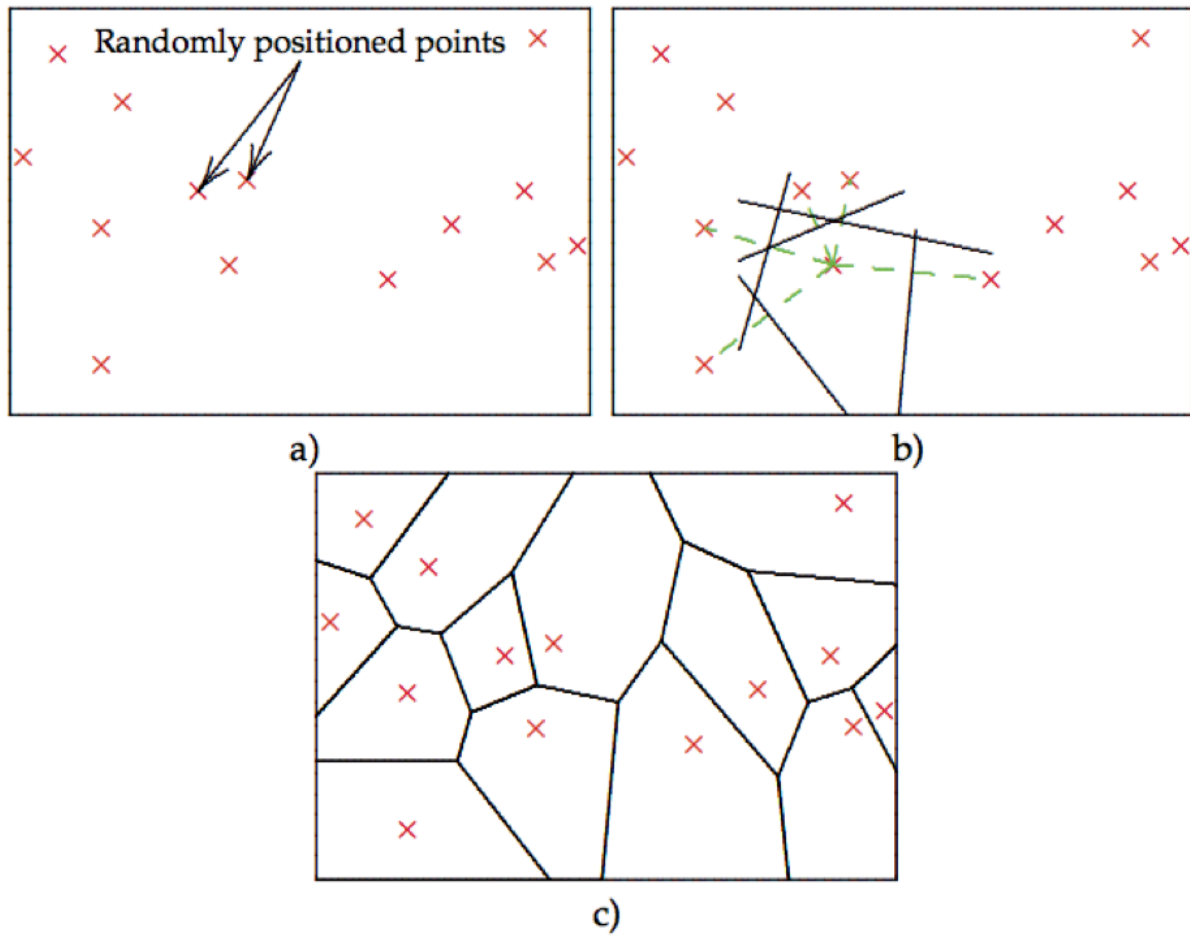


Fig. 7-1 Construction of a Voronoi tessellation in 2D: a) Poisson points, b) perpendicular lines are introduced to lines connecting neighboring Poisson points and c) final Voronoi tessellation [7].

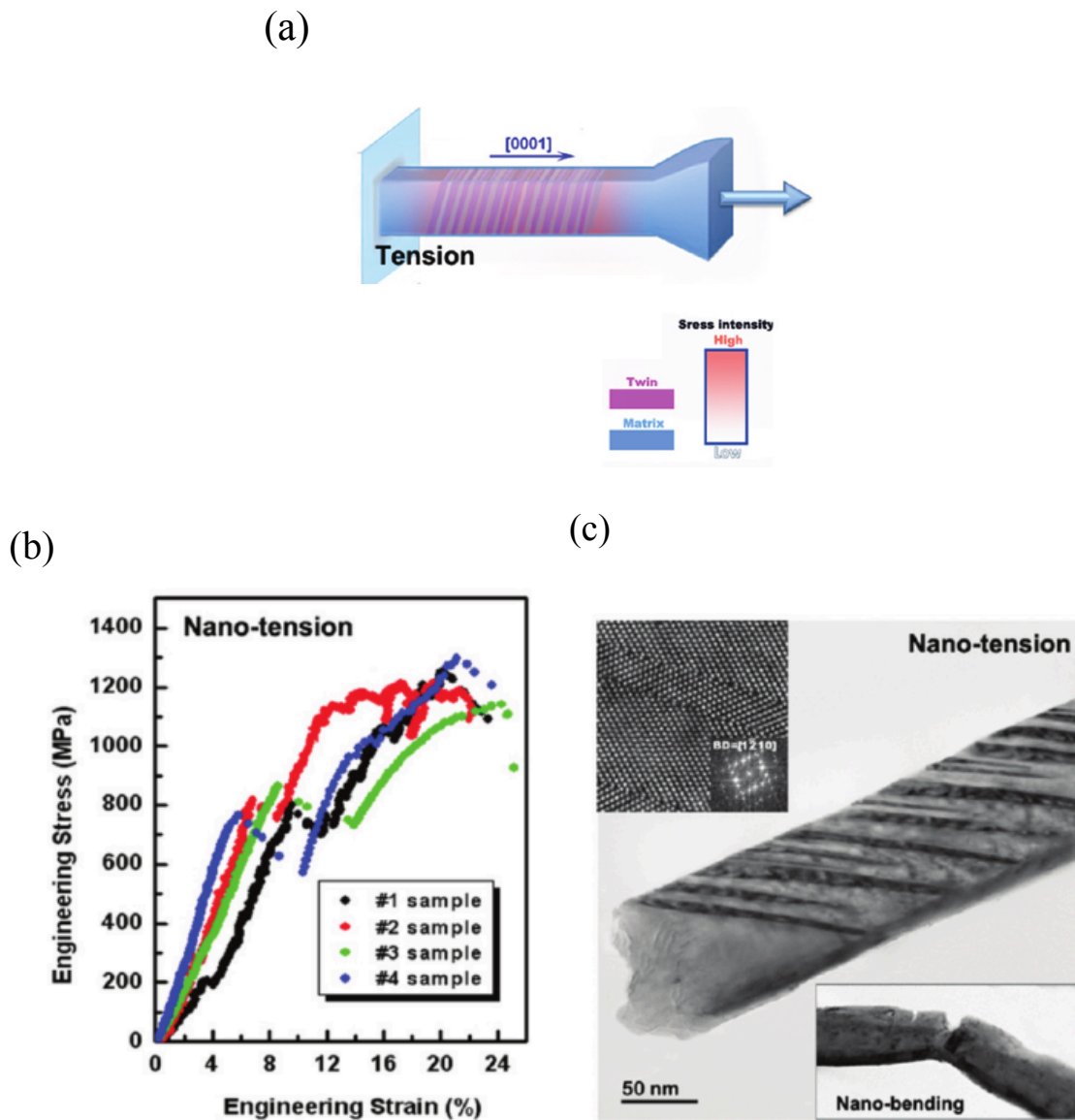


Fig. 7-2 (a) Schematic figure of the in-situ TEM tensile test. (b) The stress-strain curve of the tensile test. (c) TEM image of the single crystal magnesium sample after tensile test [8].

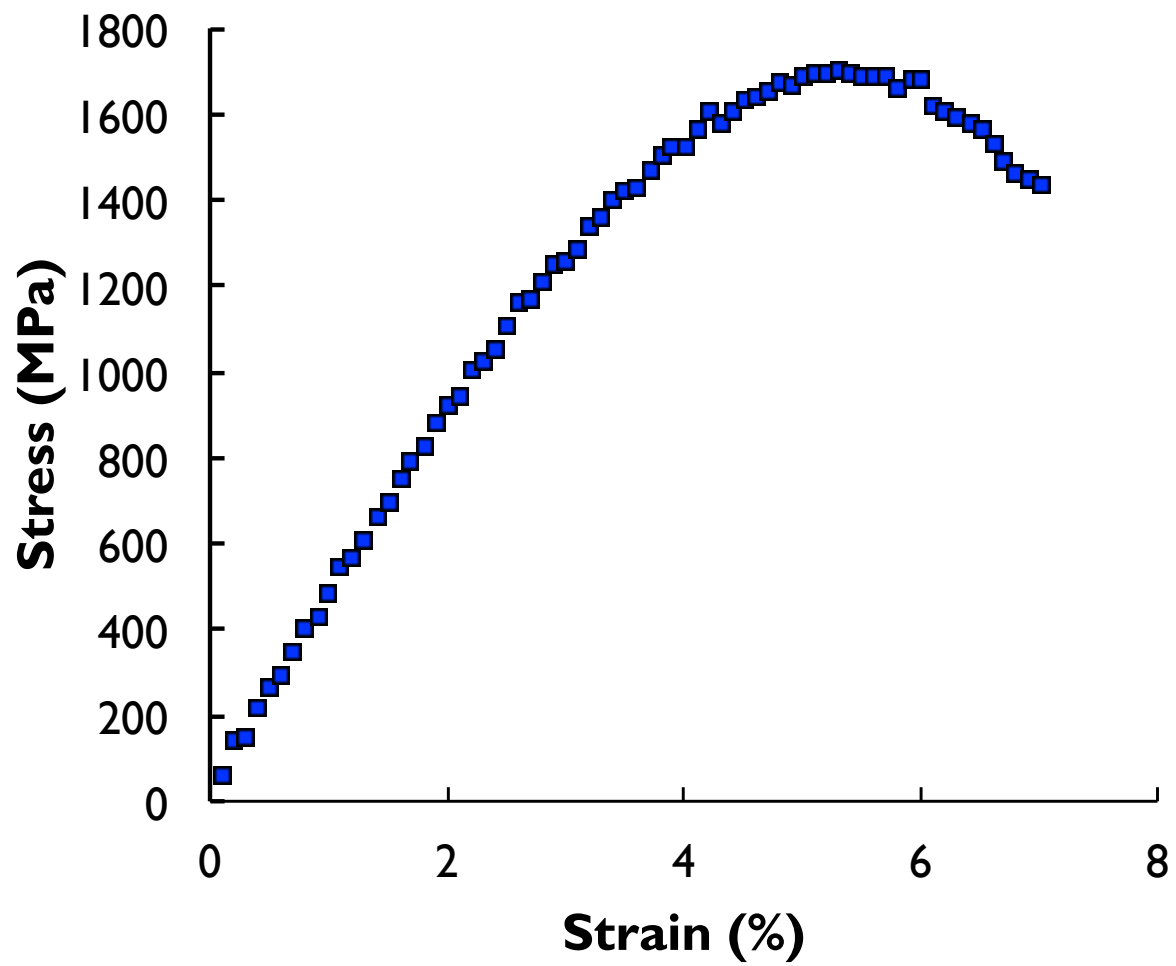


Fig. 7-3 The stress-strain curve of single crystal Mg in tensile test simulation along [0001] direction.

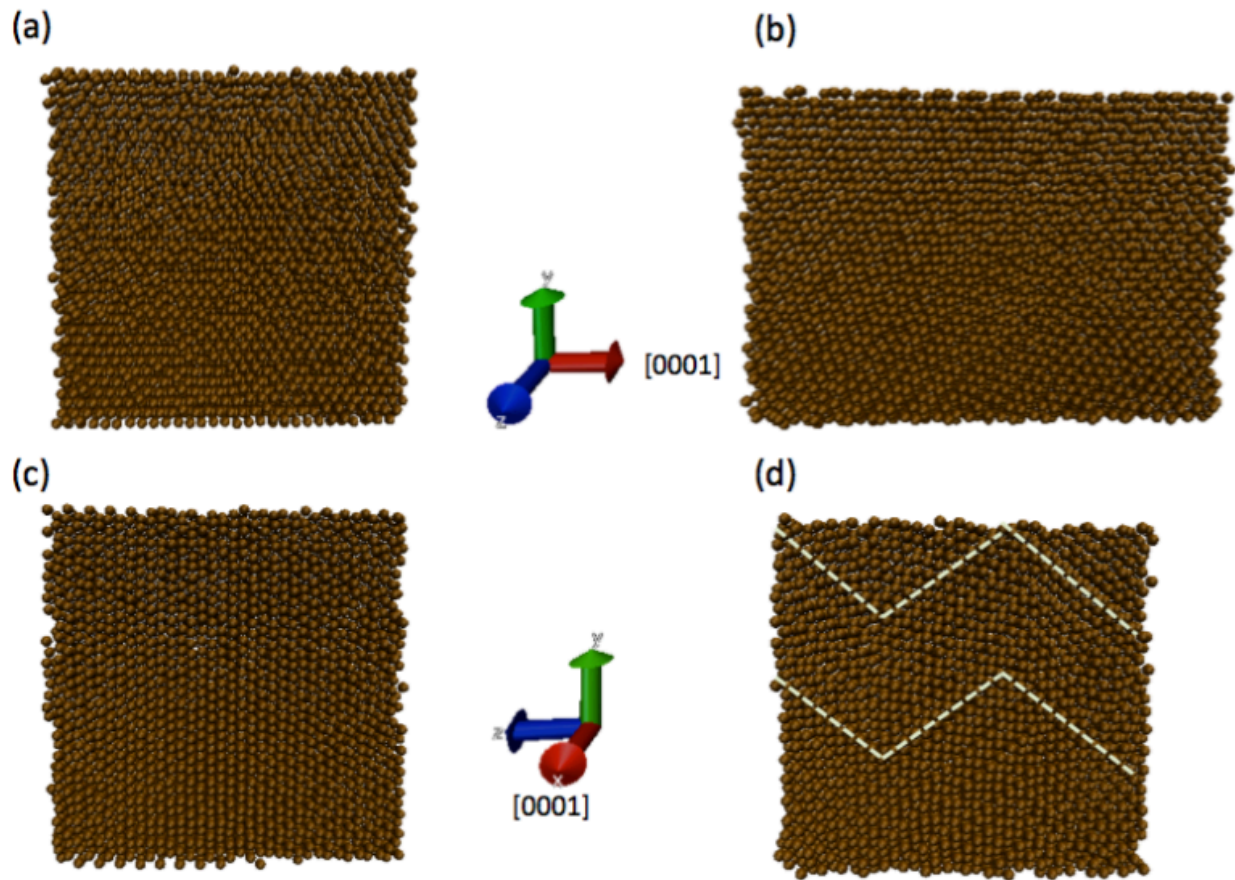


Fig. 7-4 (a) Lateral view of the tensile test of single crystal Mg before tension (b) Lateral view after tension (c) The view faced [0001] before tensile test (d) The view faced [0001] after tensile test with twin formation as labeled by dot lines.

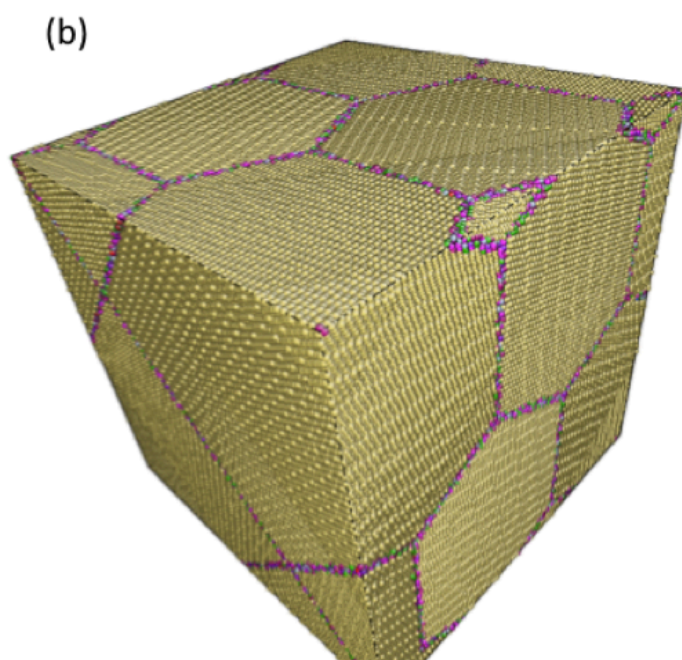
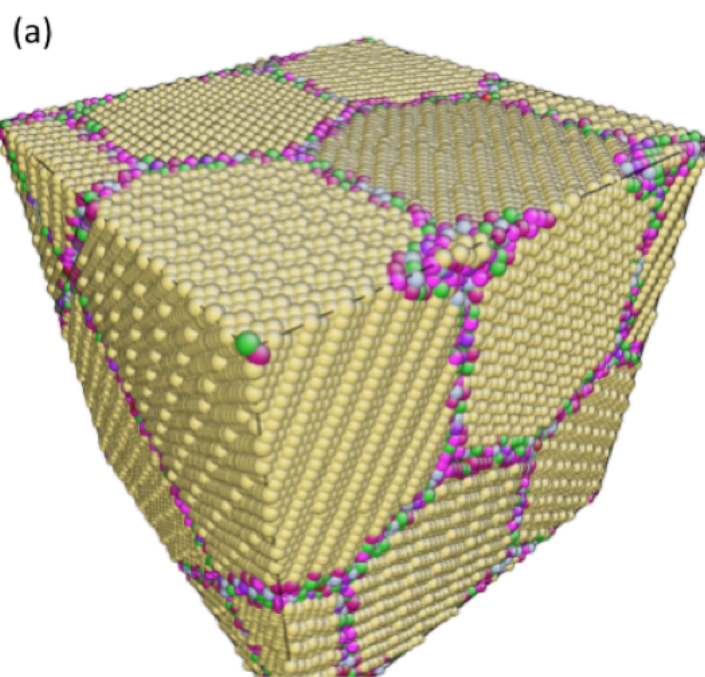


Fig. 7-5 simulation system of polycrystalline magnesium with grain size (a) 6.4nm (b) 16nm.

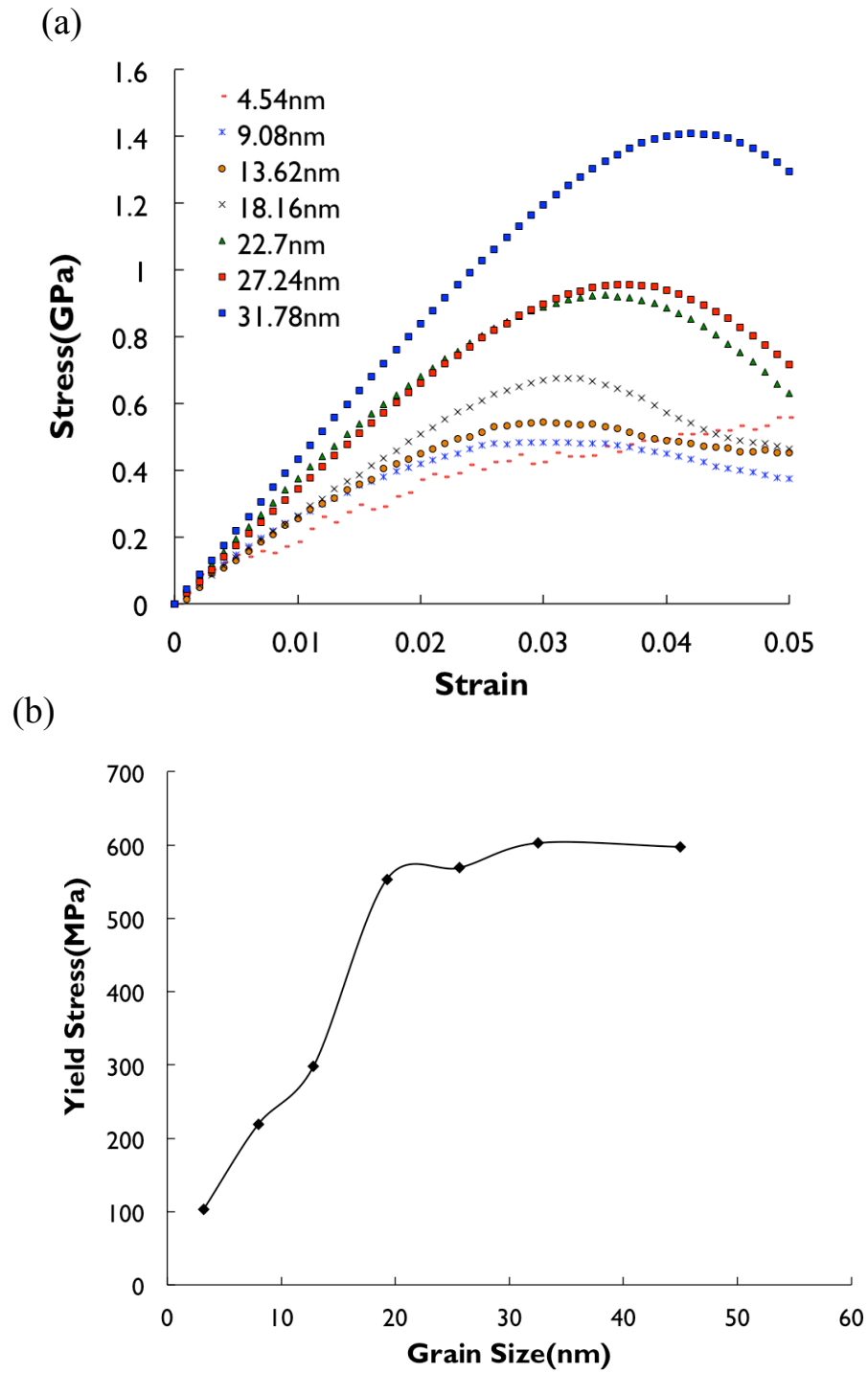
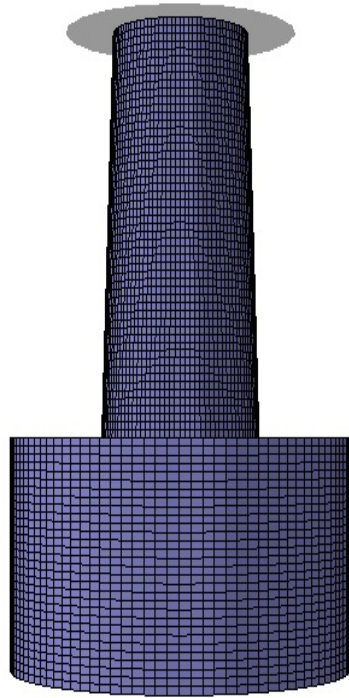


Fig. 7-6 (a) Stress-strain curved of polycrystalline Mg with different grain sizes (b) The relation of yield strengths with respect to different grain sizes.

(a)



(b)

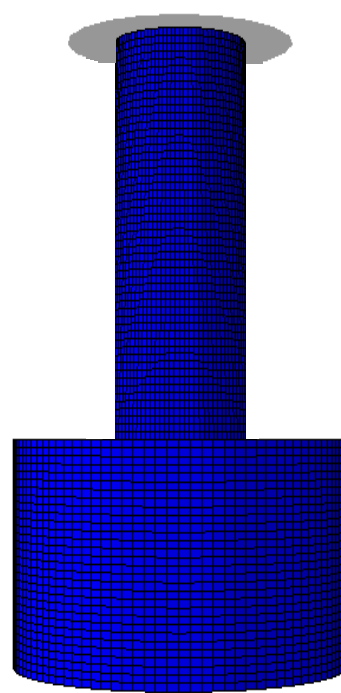


Fig. 7-7 Schematic figure of the model of pillars (a) with and (b) without tapering

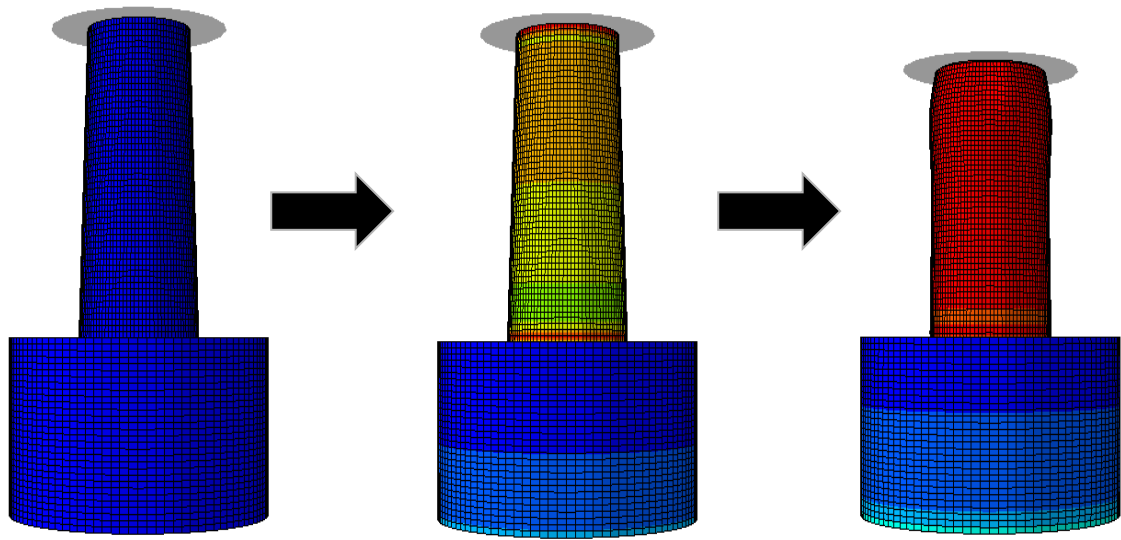


Fig. 7-8 The evolution of compression for the pillar with tapering.

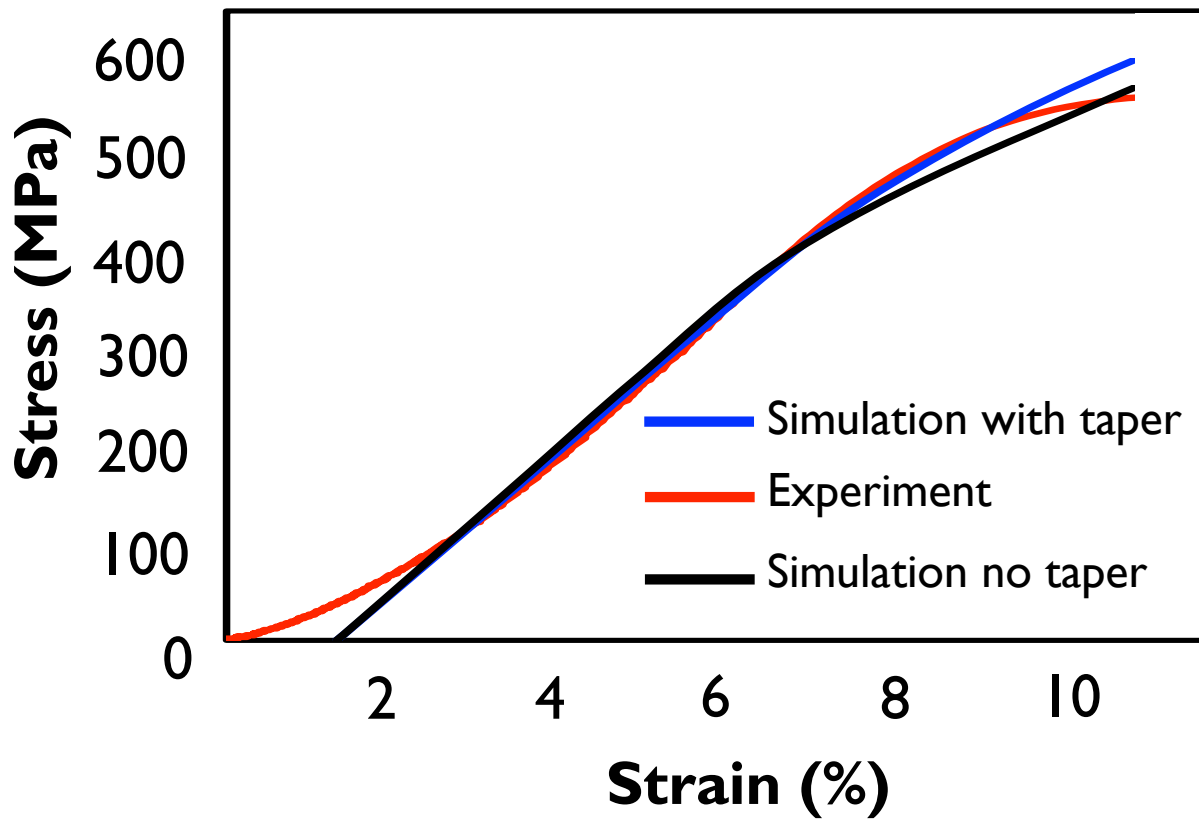


Fig. 7-9 Stress-strain curves of the simulation and experimental pillar compression

Chapter 8

Conclusions

8.1 The Current Research Accomplishments

The newly developed nanostructured magnesium alloy and composite have been shown to be promising candidate materials for structural application in terms of high strength and high thermal stability. High strength nanostructured Mg–10Al alloys are successfully processed via cryomilling and SPS followed by hot extrusion. Remarkable compressive strength (YS of 550 MPa, UCS of 580 MPa) are measured at room temperature for nanostructured Mg–Al alloys. The high strength achieved is attributed to a combination of grain size strengthening, precipitation hardening and texture strengthening mechanisms. We found that the preexisting γ -Al₁₂Mg₁₇ phase can be deformed and fractured during the extrusion process, which leads to the formation of γ -Al₁₂Mg₁₇ nanoprecipitates. We believe that these nanoprecipitates play an important role in the enhancement of strength as obstacles for dislocation movement. In addition, by using in-situ SEM microcompression tests we have demonstrated high strength with concurrent ductility for Mg-micropillars. The orientation effect of two neighboring grains on the deformation mechanism at 10% of strain has been studied by HRTEM. One grain oriented to the $[2\bar{1}\bar{1}0]$ zone axis with the basal planes at $\sim 60^\circ$ with respect to the loading direction mainly deforms by basal plane sliding. Basal SFs defects have also been observed. And another grain oriented to the $[1\bar{2}1\bar{3}]$ zone axis with the basal planes

almost parallel to the loading direction deforms by twinning. In fact, contraction nanotwins of ~ 2 nm width have been identified. These results indicate that basal plane sliding and contraction twinning mechanisms are involved in the deformation under compression of high strength and ductile nanostructured Mg-micropillars. A strong specimen size effect on the compressive strength of nanostructured Mg–10Al alloy micropillars is also observed. We find that the yield strength increases significantly when the pillar diameter is $< 3.5 \mu\text{m}$. An increase of around 50% and 100% is obtained when the pillar diameter decreases to 2.5 and 1.5 μm , respectively. In contrast, no size effect is observed for pillar diameter $\geq 3.5 \mu\text{m}$. We attribute the size-induced strengthening to a less number of dislocation sources along with a higher activity of non-basal dislocation sliding and twinning.

In order to strengthen and improve the thermal stability of nanostructured magnesium alloys, 1 wt% of diamantane is successfully incorporated via cryomilling and SPS. We report the effect of diamantane on the microstructure and mechanical behavior of the nanostructured Mg–10Al–1Dia nanocomposite compared with the diamantane-free Mg–10Al alloy. From HRTEM and STEM analyses, we identified diamantane located within the Mg-matrix, which induces a lattice distortion mainly along the *c*-direction generating a microscopic residual stress. Moreover, we found that the precipitation of γ - $\text{Al}_{12}\text{Mg}_{17}$ intermetallic phase in the nanocomposite was quite different compared to that in the Mg–10Al alloy. It showed a dendritic morphology with no presence of large precipitates or discontinuous precipitation. We attribute these changes in the precipitation

of the $\gamma\text{-Al}_{12}\text{Mg}_{17}$ phase to the diamantane for: (i) constraining the GB motion by the Zener mechanism, (ii) restricting diffusion processes along GBs and (iii) accelerating the decomposition of the supersaturated Al solid-solution that promotes the precipitation of $\gamma\text{-Al}_{12}\text{Mg}_{17}$. Additionally, we demonstrate a remarkable effect of diamantane on the compressive strength, elastic modulus and hardness of the nanocomposite. From micro- and macro-compression tests, compressive yield strength of ~ 470 MPa was measured for the Mg–10Al–1Dia nanocomposite, which resulted to be 30% higher than that for the Mg–10Al alloy. The reduced elastic modulus and hardness measured using in-situ SEM nanoindentation tests were always higher than those of the sample without diamantane. A 2-fold increase of E_r (~ 120 GPa) was measured for the nanocomposite compared to the sample without diamantanes (< 75 GPa). Additionally, a maximum hardness value of the diamantane-reinforced nanocomposite of ~ 6 GPa was reached, which was 50% higher than that of the sample without diamondoids (3.7 GPa). The enhanced mechanical behavior of the nanocomposite is attributed to the integration of precipitation hardening and the microscopic residual stress generated by diamantane–Mg matrix mismatch. Thermal stabilities of nanostructured Mg-10Al and Mg-10Al-1Dia are evaluated by XRD, EDS and micro-compression. Mg-10Al-1Dia reinforced by 1 wt.% of diamantane shows excellent thermal stability. The grain size of Mg-10Al-1Dia retain below 70nm while the grain size of Mg-10Al grows to over 100nm after annealing with 400°C for 100 hours. Diamantane nano-particles can essentially pin grain boundaries and constrain grains from growth. Diamantane particles prevent Al atom diffuse through grain

boundary to aggregate so the strengthening effect of $\text{Mg}_{17}\text{Al}_{12}$ is more evident in Mg-10Al-1Dia after annealing. As the results, strength of Mg-10Al-1Dia can be retained after annealing.

Finally, the mechanical behaviors of single crystal magnesium and magnesium with nano-grained size are discussed. The tensile test simulation for single crystal Mg is in good agreement with in-situ TEM tensile test in terms of the deformation mechanism and yield strength. The critical grain size for polycrystalline Mg is 19nm. In addition, using finite element simulation to simulate micro-compression tests, we have demonstrated that the tapering of micro-pillars does not affect their compressive yield strength measurement if the cross-section area at middle height is considered. For a tapered pillar, yield strength of 370 ± 14 and 365 MPa were obtained from the experimental and simulation studies, respectively, while 360 MPa was the computational result for a taper-free pillar.

8.2 Recommendations for future work

In the present research, Mg-Al alloys and composites with grain sizes ranging from 35 nm to 100 nm are studied. However, the mechanical properties and behaviours are still unknown for smaller grain size Mg-alloys due to a lack of experimental results. The mechanisms based reason for the observed grain size effect on twinning in

nanostructured Mg is not well developed. Therefore, it is recommended to study the mechanical deformation processes of nanostructured Mg with grain sizes on the scale of ~10 nm. This will give a deeper understanding of the deformation behaviours of nanostructured Mg. In-situ TEM compression tests are suggested to study the deformation mechanisms during compression. In addition, recently an usage for magnesium alloys in powertrain applications such as transmission cases and engine blocks increases. These applications require good elevated temperature performance at service conditions of around 200 °C and strength in the range of 50-70 MPa. Therefore, the behavior of grain boundary diffusional creep of nanostructured Mg is worth studying due to a high volume fraction of grain boundaries. Another factor that limits the structural application of Mg alloys is poor corrosion resistance. Corrosion resistance is especially poor when Mg alloys contain specific metallic impurities or when the alloys are exposed to electrolyte species such as Cl^- ions. There is not yet a comprehensive understanding of the magnesium corrosion mechanism; a study of the corrosion behavior of nanocrystalline Mg alloys and alloys with diamantine could prove beneficial to bringing them into the industry.