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14. ABSTRACT

This final report is written to document briefly the essential discoveries and fundamental understanding we have accomplished over the three-year ARO program. Magnesium alloys are a very attractive type of lightweight materials that have been widely used for Army applications. However, their low strength and poor temperature stability have limited their applications as structural materials.
During this three-year ARO program, we have overcome those issues and successfully developed high strength and thermally stable nanostructured magnesium alloys by accomplished several important milestones: 1) manufacture

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Report Title

Development of High-Strength Nanostructured Magnesium Alloys for Light-Weight Weapon Systems and Vehicles

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Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Received		Paper
01/15/2014	9.00	M. Pozuelo, Y.W. Chang, J.-M. Yang. Enhanced compressive strength of an extruded nanostructured Mg–10Al alloy, Materials Science and Engineering: A, (01 2014): 0. doi: 10.1016/j.msea.2013.11.056
01/15/2014	10.00	M. Pozuelo, Y.W. Chang, J.-M. Yang. In-situ microcompression study of nanostructured Mg alloy micropillars, Materials Letters, (10 2013): 0. doi: 10.1016/j.matlet.2013.05.039
01/15/2014	11.00	M. Pozuelo, S.N. Mathaudhu, S. Kim, B. Li, W.H. Kao, J.-M. Yang. Nanotwins in nanocrystalline Mg–Al alloys: an insight from high-resolution TEM and molecular dynamics simulation, Philosophical Magazine Letters, (11 2013): 0. doi: 10.1080/09500839.2013.833353
01/15/2014	12.00	Marta Pozuelo, Wei H. Kao, Jenn-Ming Yang. High-resolution TEM characterization of SiC nanowires as reinforcements in a nanocrystalline Mg-matrix, Materials Characterization, (03 2013): 0. doi: 10.1016/j.matchar.2013.01.003
08/29/2011	3.00	Marta Pozuelo, Christopher Melnyk, Wei H. Kao, Jenn-Ming Yang. Cryomilling and spark plasma sintering of nanocrystalline magnesium-based alloy, Journal of Materials Research, (4 2011): 904. doi: 10.1557/jmr.2010.94

TOTAL: 5

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

Received	Paper

TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

1- Marta Pozuelo, Yuan-Wei Chang, Wei H. Kao, Jenn-Ming Yang
Talk: Nanotwins formation and their e?ect on the mechanical properties of nanocrystalline Magnesium-based alloys. MS&T 2012 - Materials Science & Technology. Pittsburgh, PA, October 2012.

2- Yuan-Wei Chang, Marta Pozuelo, Jenn-Ming Yang
Talk: Micro-Compression Test of Nanostructured Magnesium Alloy and Composites. MS&T 2012 - Materials Science & Technology. Pittsburgh, PA, October 2012.

3- Suveen Mathaudhu, Baolong Zheng, Khaled Youssef, Marta Pozuelo, Laszlo Kecskes, Yizhang Zhou, Wei Kao, Sungho Kim, Bin Li, Xiaolei Wu, Carl Koch, Jenn-Ming Yang, Enrique Lavernia, Yuntian Zhu: Phase Transformations and Deformation in Magnesium Alloys. TMS 2012 - Annual Meeting & Exhibition. Orlando, FA, March 11, 2012.

4- Marta Pozuelo, Wei H. Kao, Jenn-Ming Yang
Invited Talk: Development of High-Strength Nanostructured Magnesium Alloys for Light-Weight Weapon Systems and Vehicles. Army Research Laboratory (ARL), Aberdeen Proving Ground,MD, November 15, 2011.

5- Marta Pozuelo, Wei H. Kao, Jenn-Ming Yang
Invited Talk:Cryomilling-induced deformation twinning in nanocrystalline magnesium-based alloys. Thermec2011 - Processing & and Manufacturing of Advanced Materials. Quebec, Canada, August 2011.

6- Marta Pozuelo, Suveen N. Mathaudhu, Wei H. Kao, Jenn-Ming Yang
Talk: Deformation twins in a nanocrystalline Mg-based alloy. TMS 2011 - Annual Meeting & Exhibition. San Diego, California (USA), February 2011.

Number of Presentations: 6.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received	Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

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01/15/2014	8.00	Yuan-Wei Chang, Marta Pozuelo, Jenn-Ming Yang . HIGH THERMAL STABILITY OF NANOCRYSTALLINE Mg-ALLOY REINFORCED BY DIAMONDOIDS , Materials Science and Technology (MS&T) 2013. 27-OCT-13, . : ,

TOTAL: **1**

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received		Paper
01/15/2014	7.00	Y.W. Chang, M. Pozuelo, J.M. Yang . Size-induced strengthening in nanostructured Mg alloy micropillars , Scripta Materialia (01 2014)
01/15/2014	4.00	Marta Pozuelo, Yuan-Wei Chang, Jenn-Ming Yang. Enhanced compressive strength of an extruded nanostructured Mg–10Al alloy, Materials Science and Engineering: A (08 2013)
01/15/2014	5.00	Marta Pozuelo, Yuan-Wei Chang, Jenn-Ming Yang. In-situ microcompression study of nanostructuredMg alloy micropillars, Materials Letters (03 2013)
01/15/2014	6.00	M. Pozuelo, S.N. Mathaudhu, S. Kim, B. Li, W.H. Kao, J.-M. Yang. Nanotwins in nanocrystalline Mg–Alalloys: an insight from high-resolutionTEM and molecular dynamics simulation, Philosophical Magazine Letters (04 2013)

TOTAL: **4**

Number of Manuscripts:

Books

Received	Paper

TOTAL:

Patents Submitted

Patents Awarded

Awards

Graduate Students

NAME	PERCENT_SUPPORTED	Discipline
Yuan-Wei Chang	0.00	
FTE Equivalent:	**0.00**	
Total Number:	**1**	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
Marta Pozuelo	1.00
FTE Equivalent:	**1.00**
Total Number:	**1**

Names of Faculty Supported

NAME	PERCENT_SUPPORTED	National Academy Member
Jenn-Ming Yang	0.00	
Wei H. Kao	0.00	
FTE Equivalent:	**0.00**	
Total Number:	**2**	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:...... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:...... 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):...... 0.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:...... 0.00

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The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields: 0.00

Names of Personnel receiving masters degrees

NAME

Total Number:

Names of personnel receiving PHDs

NAME

Total Number:

Names of other research staff

NAME	PERCENT_SUPPORTED

FTE Equivalent:
Total Number:

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

- Contents pages

- Figures

- Statement of the problem studied

This final report is written to document briefly the essential discoveries and fundamental understanding we have accomplished over the last three-year ARO program. It is also our intend to point out and lay the ground for future work that can take advantage of these results in applied research areas for specific Army applications.
Magnesium alloys are a very attractive type of lightweight materials that have been widely used for Army applications as aircraft and vehicle transmission housing and structural platforms. In particular, this type of alloys is especially appropriate for ground and air vehicle structural applications as well as personnel protections and armor applications. However, their low strength and poor temperature stability have limited their applications as structural materials.
During this three-year ARO program, we have overcome those issues and successfully developed high strength, and thermally-stable nanostructured hexagonal-close-packed (hcp) magnesium alloys by accomplished several important milestones: 1) manufacture of high strength nanocrystalline Mg-alloys via cryomilling and spark plasma sintering (SPS) with shorter time and lower temperature than those required with the conventional methods, 2) development of a bimodal grain size distribution with fine-grains (30 nm) and coarse-grains (500 nm) after SPS, 3) demonstrate the unveil evidence of a special kind of atomic arrangements (the so-called "nanotwins") in nanocrystalline grains that will also contribute to enhance the strength, 4) improve

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These results point to a promising approach for the design of thermally stable nanocrystalline Mg-alloys with superior strength than the currently available commercial alloys such us AZ91, AM60, AS41 and AZ80. Our approach can also be directly applied to other lightweight materials system with the same hcp crystal structure such as Ti-based alloys and its composites. Our achievements will facilitate the transition from basic research to potential Army hardware component applications. As future work, we plan to uncover the specific role that nanodiamonds and nanotwins play on the strength and ductility of nanocrystalline alloys. Finally, our goal for the next phase of applied research will be to establish a comprehensive database on the processing and mechanical properties of nanocrystalline magnesium alloys and if possible, extend it to other materials such as titanium-based alloys, among others.

- Conclusions of current ARO work

During this three-year ARO program, we have successfully developed high strength and thermally-stable nanostructured magnesium alloys by achieving important engineering breakthroughs:

- We have successfully processed nanocrystalline magnesium alloys making use of a cutting-edge method via cryomilling and spark plasma sintering, which allow us to consolidate nanocrystalline magnesium powders without the disadvantages of traditional techniques.

- We have identified three potential strengthening/toughening mechanisms for developing high-strength and ductile nanocrystalline Mg-alloys: nanocrystalline/microcrystalline bimodal grain structure, deformation twins, and reinforcements of nanodiamonds.

- Extensive transmission electron microscopy work has been done illustrating firmly that both bimodal grain structure and deformation twins are contributing to the exceptional compressive mechanical properties.

- We have been able to increase up to three times the strength of the commercial cast Mg-alloys.

- An additional improvement of 40% in the compressive strength is obtained from our preliminary extrusion experiments. The measured compressive yield strength of 550 MPa and ultimate strength of 580 MPa are the highest compressive values reported for Mg-alloys (to the best of our knowledge).

- In-situ SEM compressive tests of Mg micro-pillars reveal that basal plane sliding and contraction twinning mechanisms are involved in the deformation under compression of high strength nanostructured Mg-micropillars.

- We have demonstrated the efficiency of the nanodiamonds as reinforcements in the Mg matrix giving an improvement up to 40% in compressive strength of the nanostructured Mg micro-pillars. In addition, we have demonstrated the effect of the nanodiamonds on the stability of the grain size at higher temperatures (up to 350° C), which leads to a stable nanocrystalline structure exposed to higher temperatures.

- The remarkable property improvement gives Mg-alloys new opportunities as potential vehicle and personnel armor protection applications.

- The approach presented here might be suitable for the design of other nanocrystalline hcp alloys, such as Ti alloys with superior strength.

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Technology Transfer

University of California Los Angeles,
Los Angeles, CA 90095

Development of High-Strength Nanostructured Magnesium Alloys for Light-Weight Weapon Systems and Vehicles

Final Report Prepared by

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ARO Supported Program
Program Manager: Dr. Larry Russell
U.S. Army Research Office

January 13, 2014

Contents

Figures

Abstract

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Magnesium alloys are a very attractive type of lightweight materials that have been widely used for Army applications as aircraft and vehicle transmission housing and structural platforms. In particular, this type of alloys is especially appropriate for ground and air vehicle structural applications as well as personnel protections and armor applications. However, their low strength and poor temperature stability have limited their applications as structural materials.

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1. Introduction

Magnesium alloys are a very attractive type of lightweight materials because of their low density (1.74 g/cm^3), which have been widely used for applications as aircraft and vehicle transmission housing and structural platforms. However, their low strength and poor temperature stability are the main scientific issues that limit their applications as structural materials. Therefore, many efforts have been devoted to develop stronger and ductile microstructures. Nanocrystalline materials have gained a lot of attention as a result of their unique microstructure, which leads to outstanding mechanical properties [1-3]. Among the number of methods that have been developed to achieve a material with nanometer-scale grains [4-8], cryomilling is one of the most effective methods, in terms of cost and productivity, to synthesize a large quantity of nanocrystalline material in powder form. Cryomilling is basically a mechanical milling process conducted in liquid nitrogen atmosphere, which results in much shorter milling times to reach the desired nanocrystalline structure. This method induces severe plastic deformation, which consists of repeated welding, fracturing, and re-welding of the powders.

To synthesize the cryomilled powders into a bulk material, a number of conventional consolidation methods, such as hot-isostatic-pressing (HIPing) [9] and cold-isostatic- pressing (CIP), [10] exist, which are generally accompanied by extrusion, [11] 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 nanocrystalline powders into a bulk material form with shorter time and lower temperature than those required in the conventional methods and without any secondary process [12,13]. 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 this work, we have done a remarkable progress on the processing of high-strength nanocrystalline magnesium alloys making use of these cutting-edge processing techniques: cryomilling followed by spark plasma sintering [14]. These techniques allow us to successfully consolidate nanocrystalline magnesium powders without the disadvantages of traditional techniques.

Nanocrystalline materials are well known for their high strength, but frequently suffer significant losses in ductility. However, it has been recently reported that the introduction of a special kind of atomic arrangements (the so-called "nanotwins") in nanocrystalline grains can result in extraordinarily high strength with concurrent ductility [15]. As a matter of fact, we have been one of the first groups to reveal the formation of nanotwins in nanocrystalline magnesium using high resolution transmission electron microscopy and atomistic molecular dynamics simulations [16]. Our striking results provide unique insights into the underlying mechanisms leading to the formation of nanocrystalline magnesium with extraordinarily high strength with concurrent ductility.

The use of nanocrystalline alloys at elevated temperatures has been severely limited by the inherent thermal instability of these materials. Here, we demonstrate a new approach to develop high strength and thermally stable nanostructured magnesium alloys using nanodiamonds (diamondoids) as the stabilizing (grain-boundary pinning) agent. Nanodiamonds are hydro- carbon nanoparticles with a diamond crystal structure. We use diamantane (two cages of diamond’s lattice structure) that is commercially available for pinning the grain boundaries and because of their high thermal stability and structural rigidity [17]. In short, we demonstrate that the nanodiamonds can inhibit the grain growth during processing and services at elevated temperatures, which leads to a stable nanocrystalline structure exposed to higher temperatures for long periods of time.

Finally, in order to evaluate the mechanical behavior of the sintered material, we performed compression tests at room temperature and *in-situ* SEM micro-compression tests on Mg-based micro-pillars. *In-situ* SEM micro-compression tests allow us to directly observe the stress-strain behavior of nanocrystalline Mg-based micro-pillars and demonstrate their outstanding mechanical properties.

Research findings in the fundamental investigation of the materials, critical manufacturing parameters and mechanics will facilitate the transition from basic understanding to scale-up production as lightweight, high strength and thermally stable nanostructured Mg-based structures for Army applications.

2. Experimental procedure

Commercially available gas-atomized Mg and Al powders are blended to formulate a final composition of Mg70Al30 and Mg90Al10 (wt.%). One kilogram of the blended powder for each composition was cryogenically-milled for 8 h in a Union Process, Szegvari mill, Model No. S1, (Akron, Ohio) extensively modified at California Nanotechnologies for light alloy processing. Hardened stainless steel balls (6 mm diameter) are used as milling media at a particular ball-to-charge ratio for a given material. A 30:1 ratio of ball diameter-to-charge size is common for milling metallic powders. Powder consolidation was conducted using a spark plasma sintering (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 in a controlled atmosphere glove box. The sintering process was performed in a vacuum and under a uniaxial pressure between 65 and 100 MPa and at 360 and 400 °C of temperature. 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 6 min) as a pulsed electric current is applied through graphite punches. The SPS-consolidated specimen resulted in 25.4 mm and 6 mm of diameter and thickness, respectively.

The morphology and composition of the as-received and cryomilled powders as well as the bulk nanocrystalline SPS samples were investigated with scanning electron microscopy (SEM). A FEI Nova 900 Variable Pressure SEM (VP-SEM) equipped with an Oxford Instruments EDS system at 15 kV accelerating voltage was used for this purpose. X-ray diffraction (XRD) was performed using a Panalytical X'Pert ProX-ray Powder Diffractometer using Cu Ka (l = 0.1542 nm) radiation in order to determine the crystalline size. High-resolution microestructural characterization was carried out using a FEI Titan 300 kV transmission electron microscope (TEM). A FEI Nova 600 Nanolab DualBeam focused ion beam (FIB) - SEM was used to prepare a thin film TEM sample from the bulk material and to prepare micro-pillars with 3-5 μm in diameter and aspect ratio of 1:3. *In-situ* micro-compression tests were performed using a PI 85PicoIndenter instrument (Fig.1) installed on the FEI NanoSEM 230 under a displacement rate control of 20 nm/s. A diamond flat-end tip of 8 μm in diameter was used as punch.

Figure 1. PI 85PicoIndenter

3. Program accomplishments

3.1. Nanocrystalline Mg grains

Figure 2 shows the SEM characterization of the as-received and cryomilled Mg70Al30 powders. The as-received powders with an average particle size of 26.8 ± 7.8 μm are shown in the Fig. 2a. The powders after 8 h of cryomilling (Fig. 2b) present a more faceted shape as a result from repeated fracturing involved in the cryomilling [5]. Note that the particle size of the cryomilled powders is smaller with an average value of 19.4 ± 6.7 μm. The composition of the cryomilled powders is confirmed by the EDX analysis shown in Fig. 2c resulting in 69 wt.% Mg and 31 wt.% Al.

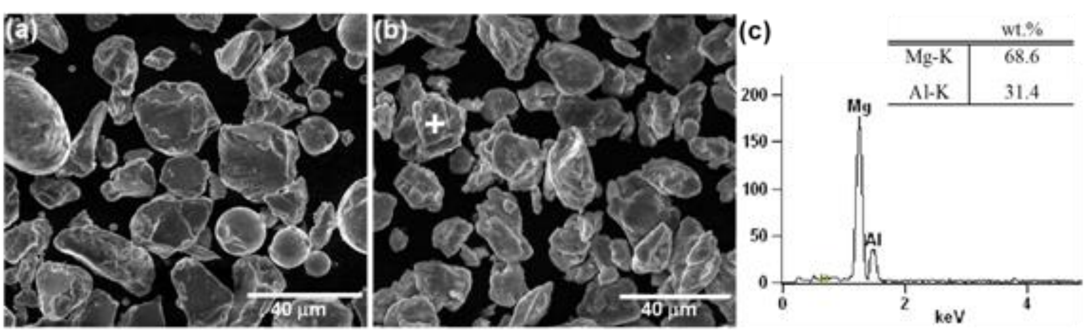


Figure 2. SEM images of the as-received (a) and cryomilled Mg70Al30 powders (b). (c) EDX analysis of the cryomilled powders.

The nanostructure of the cryomilled powders is indicated by the TEM analysis shown in Fig. 3 and 4 for a cryomilled Mg70Al30 and Mg90Al10 powder, respectively. The nanocrystalline grains nearly equiaxed are clearly seen in the dark-field TEM images (Fig. 3b and Fig.4b). As shown by the histograms (Fig. 3d and Fig.4d) the average grain size is 27 and 30 for the cryomilled Mg70Al30 and Mg90Al10 powders, respectively.

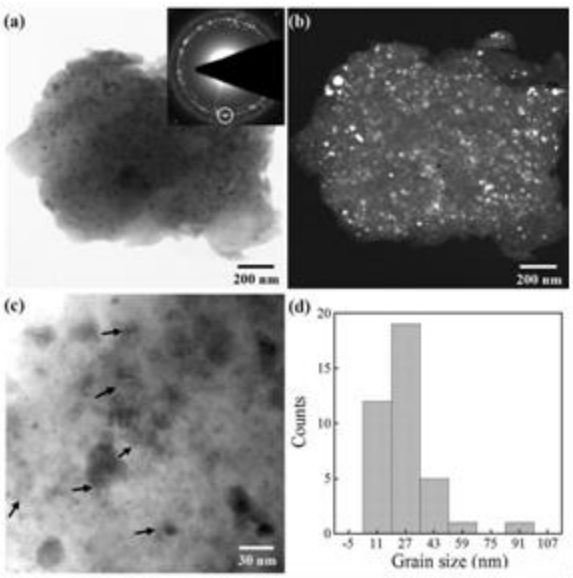


Figure 3. TEM study of the cryomilled Mg70Al30 powders [14].

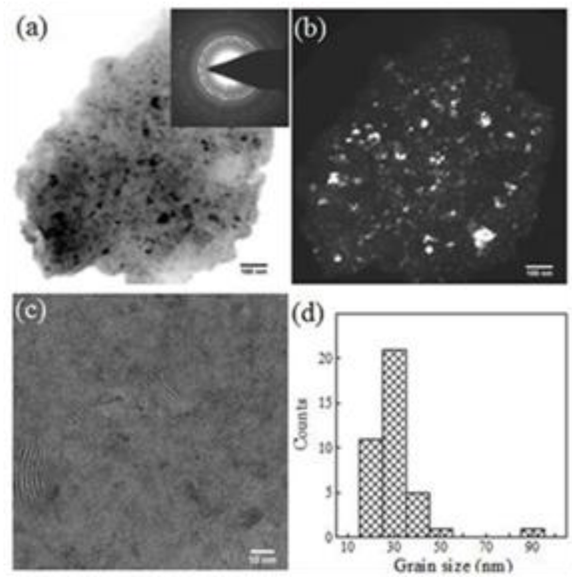


Figure 4. TEM study of the cryomilled Mg90Al10 powders [18].

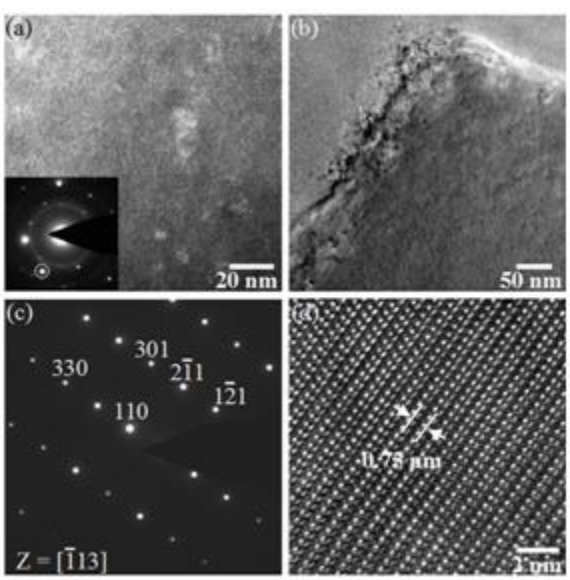
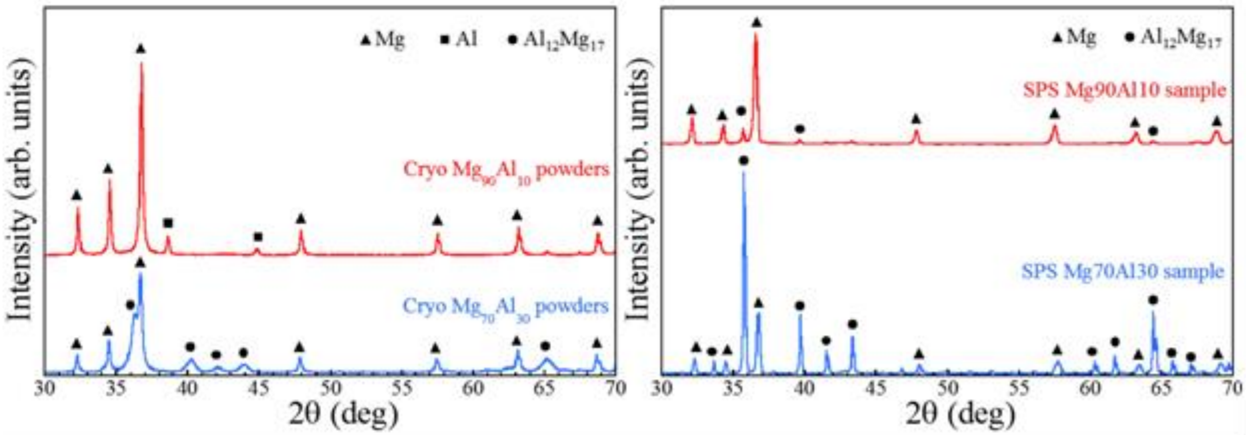


Figure 5. TEM analysis of the SPS Mg70Al30 sample [14].

TEM analysis of the nanostructured SPS sample (Fig. 5) suggests a bimodal grain size distribution as a consequence of the processing. There are basically fine-grain (25 nm) regions (Fig. 5a) along with some coarse-grains (around 500 nm) regions (Fig. 5b) as a result of locally heterogeneous grain growth during SPS. This bimodal grain size distribution is actually desirable in order to enhance the mechanical properties of the nanostructured bulk materials [19,20].



(a) (b)

Figure 6. X-ray diffraction spectra for the cryomilled Mg-based powders (a) and SPS Mg-based samples (b).

The XRD data for both composition alloys are shown in Fig. 6 as a comparison. After cryomilling (Fig. 6a) only the characteristic peaks of Mg and Al can be observed with no presence of the brittle and not desirable intermetallic Al12Mg17 compound in the Mg90Al10 powders as expected from the phase diagram. After SPS (Fig. 6b) the Mg90Al10 sample presents some amount of intermetallic compound but in much lower volume fraction than for the Mg70Al30 alloy.

- *The above results indicate that Cryomilling with SPS is a successful processing route, which provides unique opportunities for developing bulk nanostructured Mg-based alloys.*

3.2. Nanotwins

Contrary to what is observed in nanocrystalline face-centered cubic metals, nanocrystalline hexagonal close-packed (hcp) metals are rarely observed to deform by twinning, although twinning is a major deformation mechanism in their coarse-grained counterparts. Twinning in hcp metals is reported to be unfavorable when the grain size is reduced below a couple of microns and suppressed at the nanoscale. This is mainly attributed to the high stress required to nucleate, that increases drastically with decreasing grain size to the nanometer scale [21]. Fig. 7 shows a detailed TEM analysis of twin boundaries (TB) (left panel) that are confirmed by MD simulations (right panel) performed in collaboration with Dr. Sungho Kim and

Dr. Bin Li from the Center of Advance Vehicular system (CAVS), at Mississippi State University. It is theorized that the specific thermomechanical conditions offered by cryomilling (in particular, the combination of high-intensity, high-strain-rate, and low temperature plastic deformation) facilitate the generation of deformation twins that are not observed with conventional deformation processing methods [16].

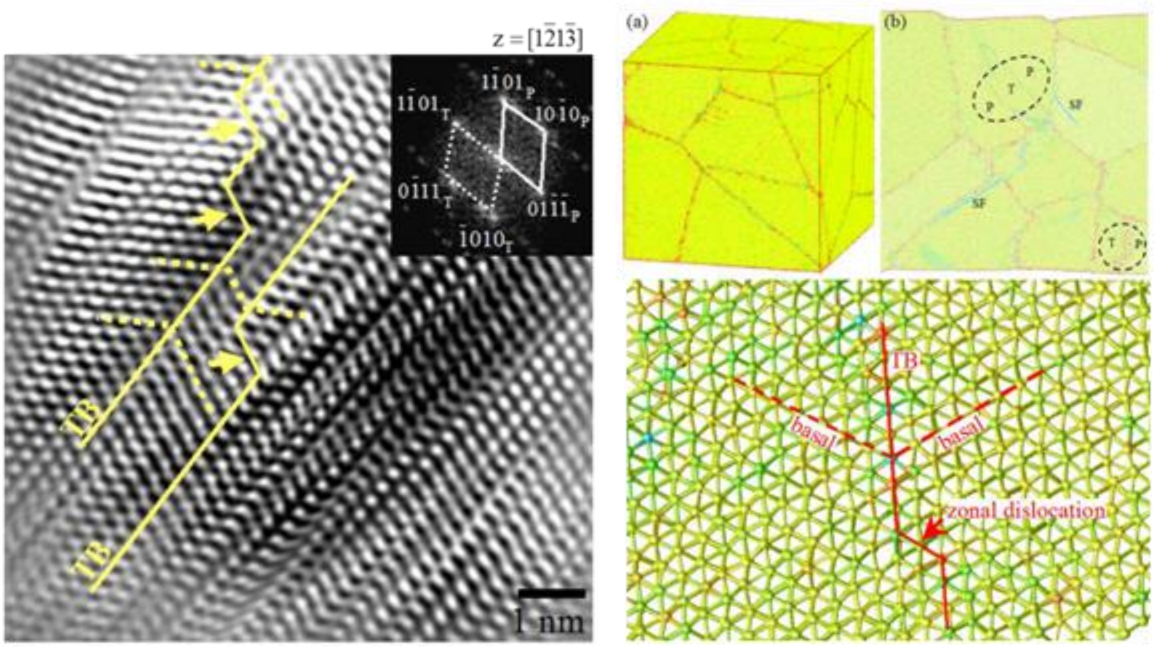


Figure 7. High-resolution TEM image showing twin boundaries (TBs) within nanocrystalline grains (left panel) and the confirmation by MD simulation (right panel).

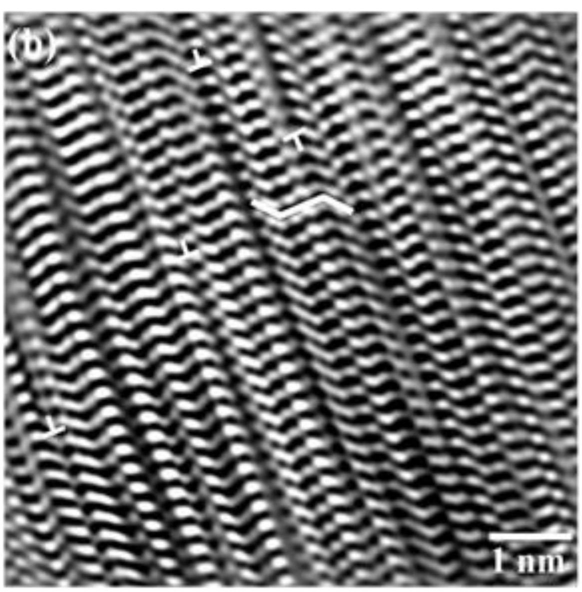


Figure 8. High-resolution TEM (HRTEM) image showing nanotwins of only 0.5 nm width.

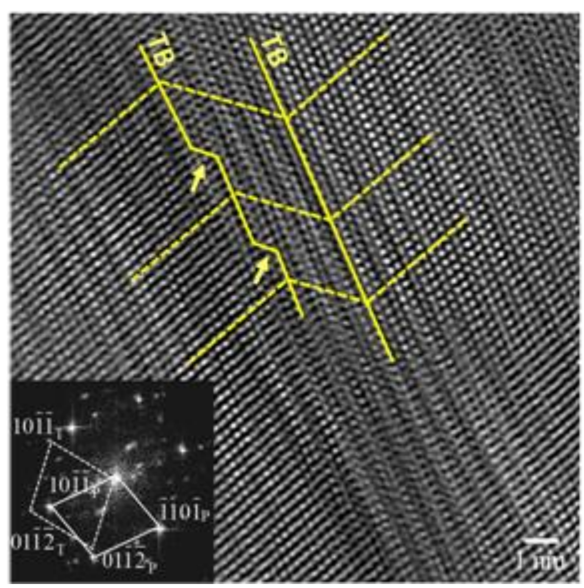


Figure 9. HRTEM image showing twin boundaries (TB) in the sample after SPS.

Fig. 8 shows nanotwins of only 0.5 nm width (highlighted by white solid lines) as a result of the remarkably high density of stacking faults. Fig. 9 reveals that the nanotwins are also stable during consolidation after SPS process.

- *We have unveiled evidence of the formation of nanotwins in a nanocrystalline Mg-based alloy processed by cryomilling and SPS. We demonstrate (see next section) that the introduction of nanotwins in nanocrystalline hcp Mg can result in extraordinarily high strength.*

3.3. Compressive behavior

a) Compression tests of the bulk samples

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 [18]. Their representative engineering stress–strain curves are shown in Fig. 10 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) [18].

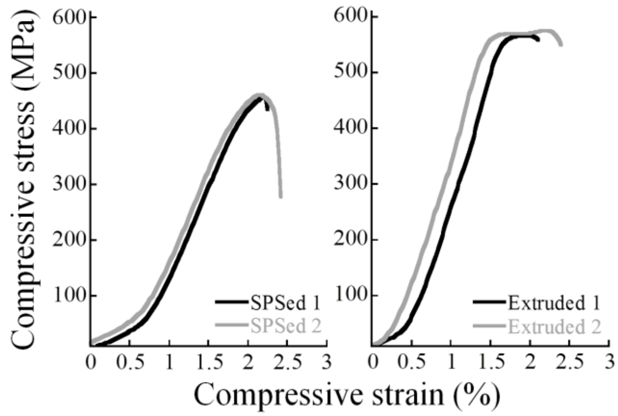


Figure 10. Compressive stress-strain curves of SPS'ed $Mg_{90}Al_{10}$ before (left plot) and after extrusion (right plot) [18].

Table I. Compressive properties of SPS'ed and Extruded $Mg_{90}Al_{10}$ samples.

Samples	No.	Yield strength (MPa)	Ultimate strength (MPa)	Strain at failure (%)
SPS'ed	**1**	**369.6**	**464.2**	**2.2**
	2	**365.9**	**467.5**	**2.4**
Extruded	**1**	**541.0**	**572.0**	**2.1**
	2	**539.2**	**579.7**	**2.4**

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) [22]. 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) [23] and AZ31 (160 MPa) [24], respectively. In the case of a nanostructured AZ80 alloy processed by cryomilling and SPS a compressive YS of 442 MPa is reported [25].

➢ *Our preliminary results after extrusion (compressive yield strength of 550 MPa, ultimate strength of 580 MPa) are the highest compressive values for Mg-Al alloys reported in the literature (to the best of our knowledge).*

b) *In-situ* SEM micro-compression tests of nanocrystalline Mg micro-pillars.

In-situ SEM micro-compression tests allow direct observation of stress-strain behavior in material with micro-scale dimensions. In order to perform these tests, we machined by FIB micro-pillars of the Mg90Al10 composition alloy with different diameters (0.438 < x < 5.15 μm) and aspect ratio of 1:3. Figure 11a displays the compressive stress-strain curve of a micro-pillar with 4.4 μm in diameter. Remarkable mechanical properties are obtained with yield strength of 460 MPa and an ultimate strength higher than 1000 MPa [26].

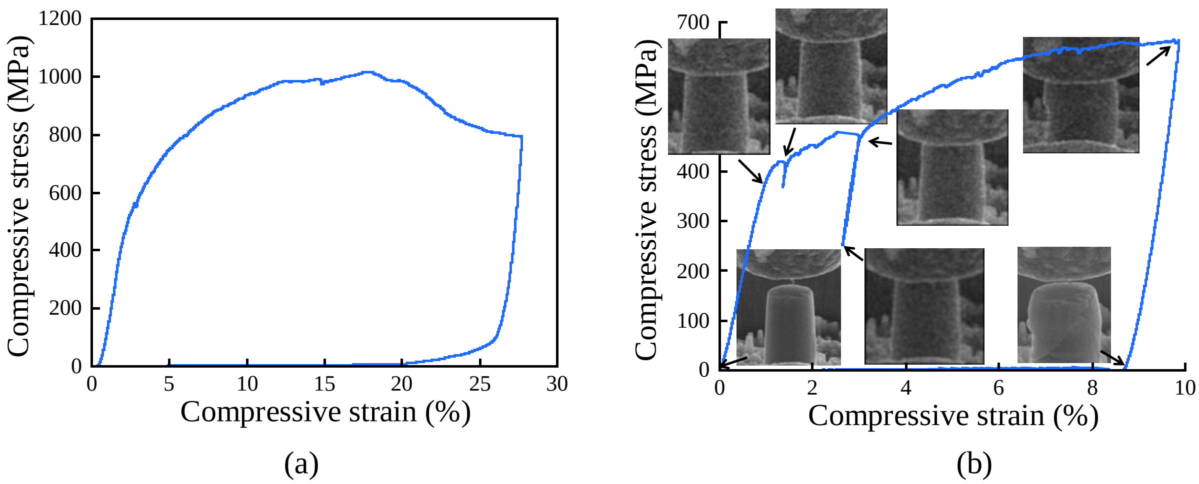


Figure 11. (a) *In-situ* SEM compressive stress-strain curves of the Mg90Al10 micro-pillars after SPS at 360 °C. (b) SEM images acquired simultaneously along with the compressive stress-strain curves. The test was stopped at 10 % of strain.

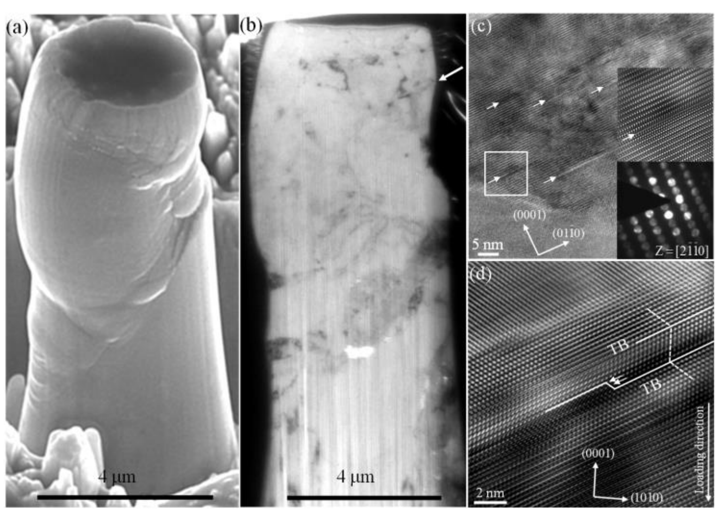


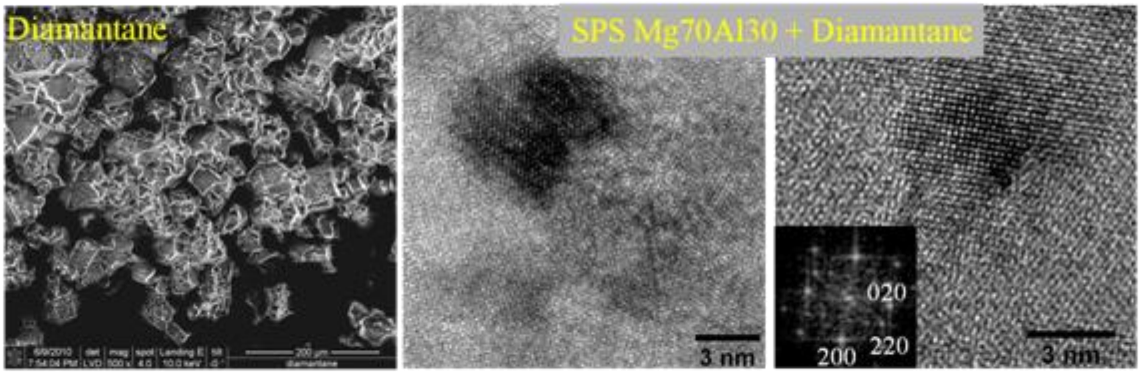
Figure 12. (a) 52° tilted-view SEM image of a compressed micropillar at 10 % of strain. (b) Bright-field TEM image of the compressed micropillar. (c) TEM analysis showing basal stacking faults. (d) HRTEM image showing contraction nanotwins [26].

Fig. 11b shows the SEM images acquired simultaneously along with the compressive stress-strain curve of a Mg micro-pillar. In this case, the test was stopped at 10% of strain once a deformation band was visible at 45° respect to the compressive direction. Figure 12 shows the SEM and TEM characterization of the pillar deformed up to 10% of strain (Fig. 11b). We found shear bands formed ~60° with respect to the loading direction at 10% of deformation (Fig. 12a). From the stress-strain curves, it was also interesting to note a few stress drops just after the transition from elastic to plastic flow, which might be associated with the nucleation and propagation of twins. In addition, we demonstrated the important role that the grain orientation plays during deformation. A nc grain with <c> direction oriented ~30° with respect to the loading direction mainly deforms by basal plane sliding (Fig. 12c). In contrast, another grain where <c> direction is almost parallel to the loading direction deforms by contraction twinning (Fig. 12d).

- ✓ *In-situ SEM compressive tests of Mg micro-pillars reveal that basal plane sliding and contraction twinning mechanisms are involved in the deformation under compression of high strength nanostructured Mg-micropillars.*

3.4 High-thermal stability

We successfully incorporated nanodiamonds (1 wt. %) as reinforcement materials into the Mg-matrix in order to thermally stabilize the grain growth at higher temperatures. Nanodiamonds or diamondoids are hydro-carbon nanoparticles with a diamond crystal structure. We use diamantane (two cages of diamond's lattice structure) for pinning the grain boundaries and because of their high thermal stability and structural rigidity. Fig.13a shows the SEM images of diamantane that were incorporated into the Mg70Al30 powders during cryomilling. TEM images of the SPS sample with diamantane (Fig. 13b and 13c) display the nanodiamonds perfectly bonded with the Mg matrix.



(a) (b) (c)

Figure 13. (a) SEM image of diamantane. (b) and (c) TEM analysis of diamantane embedded into the Mg-matrix.

In order to study the effect of the nanodiamonds on the stability of the grain size at higher temperatures, we performed several annealing treatments at different temperatures and times. Fig. 14 displays the average grain size as a function of the annealing conditions for the samples with/out diamantane in red and blue color, respectively. It is interesting to note the stability of the grain size for all the annealing conditions in the sample with diamantane while the grain size grows with time and temperature for the sample without diamantane.

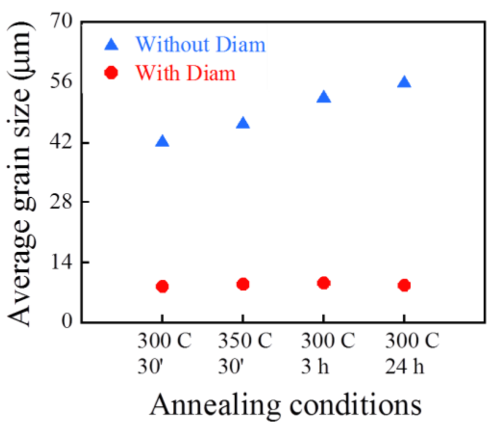
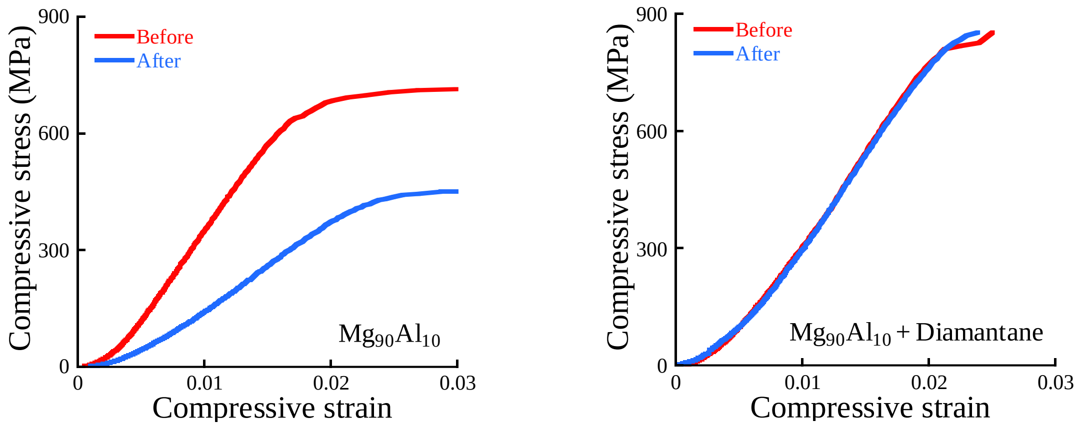


Figure 14. Plot showing the average grain size as a function of annealing conditions for the Mg70Al30 samples with/out diamantane.

In order to study the effect of the nanodiamonds on the mechanical behavior at elevated temperature, we performed compressive tests before and after annealing at 300 °C for 24 h. We measured the compressive properties before and after annealing of at least three Mg90Al10 alloy micro-pillars. However, just one is shown here in Fig. 15 as a comparison. Fig. 15a indicates the compressive stress-strain curves for the micro-pillars without diamantane. As expected, the yield strength decreases (from 550 to 320 MPa) as a consequence of the grain growth after annealing. On the contrary, Fig. 15b shows the yield strength of the sample with diamantane thermally stable after annealing with a value much higher around 700 MPa. These results indicate once again that the nanodiamonds are pinning the grain boundaries and then inhibit the grain growth. In addition, it is shown a strong reinforcement effect (up to 40% in compressive strength) of the nanodiamonds on the Mg-matrix.



(a) (b)

Figure 15. Compressive stress-strain curves before and after annealing at 300 ℃ for 24 h for the SPS (at 400 ℃) Mg90Al10 micro-pillars (a) and Mg90Al10 with diamantane micropillars (b).

- *These striking results confirm the effect of the nanodiamonds as reinforcement materials in the Mg matrix giving an improvement up to 40% in compressive strength. In addition, we demonstrate the effect of the nanodiamonds on the stability of the grain size at higher temperatures (up to 350°C), which leads to a stable nanocrystalline structure exposed to higher temperatures.*

4. Conclusions of current ARO work

During this three-year ARO program, we have successfully developed high strength and thermally-stable nanostructured magnesium alloys by achieving important engineering breakthroughs:

- ✓ We have successfully processed nanocrystalline magnesium alloys making use of a cutting-edge method via cryomilling and spark plasma sintering, which allow us to consolidate nanocrystalline magnesium powders without the disadvantages of traditional techniques.

- ✓ We have identified three potential strengthening/toughening mechanisms for developing high-strength and ductile nanocrystalline Mg-alloys: nanocrystalline/microcrystalline bimodal grain structure, deformation twins, and reinforcements of nanodiamonds.

- ✓ Extensive transmission electron microscopy work has been done illustrating firmly that both bimodal grain structure and deformation twins are contributing to the exceptional compressive mechanical properties.

- ✓ We have been able to increase up to three times the strength of the commercial cast Mg-alloys.

- ✓ An additional improvement of 40% in the compressive strength is obtained from our preliminary extrusion experiments. The measured compressive yield strength of 550 MPa and ultimate strength of 580 MPa are the highest compressive values reported for Mg-alloys (to the best of our knowledge).

- ✓ *In-situ* SEM compressive tests of Mg micro-pillars reveal that basal plane sliding and contraction twinning mechanisms are involved in the deformation under compression of high strength nanostructured Mg-micropillars.

- ✓ We have demonstrated the efficiency of the nanodiamonds as reinforcements in the Mg matrix giving an improvement up to 40% in compressive strength of the nanostructured Mg micro-pillars. In addition, we have demonstrated the effect of the nanodiamonds on the stability of the grain size at higher temperatures (up to 350° C), which leads to a stable nanocrystalline structure exposed to higher temperatures.

- ✓ The remarkable property improvement gives Mg-alloys new opportunities as potential vehicle and personnel armor protection applications.

- ✓ The approach presented here might be suitable for the design of other nanocrystalline hcp alloys, such as Ti alloys with superior strength.

5. Future work proposed

Based on our previous ARO work, we believe that the scientific understanding developed can be transitioned and advanced to applied research area. To this end, the knowledge acquired on Mg-based alloys might be extended to other materials systems with similar crystal structures, such as Ti-based alloys with an important value in terms of lightweight and high-strength materials for ARO needs, as well. The specific tasks that will extend our accomplished efforts to applied research areas are proposed below:

Task 1: Design and fabrication of high-strength composite materials for light-weight systems and vehicles.

1.1. Optimize the compositions of the selected Magnesium and Titanium alloys, and the amount of strengthener materials to achieve cost-effective and scale-up requirements.

1.2. Determine the processing parameters of the cutting-edge technique via cryomilling and spark plasma sintering, for further application to other materials systems with similar crystal structure.

1.3. Determine and design feasible secondary processing techniques.

Task 2: Validate the ideal nanostructures via extensive transmission electron microscopy (TEM) work in order to guarantee the enhanced mechanical behavior.

2.1. Planning an extensive TEM work in the FEI Titan 300 kV STEM to deeply characterize the grain structure and the deformation mechanisms.

2.2. Determine the effect of the processing conditions on the final structure and their further influence on the mechanical properties.

2.3. Design and planning of *in-situ* TEM heating experiments to direct observation of the effect of the nanodiamonds (as reinforcements for grain boundary pinning) on the stability of the grain growth.

Task 3: Establish an extensive database on the mechanical properties of nanocrystalline Mg and Ti alloys for fabrication and scale-up.

3.1 Design and planning of *in-situ* SEM/TEM micro- and nano-compression tests to direct acquisition of stress-strain behavior in material with micro- and nano-scale dimensions.

3.2 Control the size-dependent effect on the mechanical properties and the role of the different deformation mechanisms during *in-situ* SEM micro-compression tests and in-situ TEM nano-compression tests.

3.3. Multiscale modeling and prediction of the overall mechanical properties.

Acknowledgments

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