Magnesium Technology 2012
Edited by: Suveen N. Mathaudhu, Wim H. Sillekens, Neale R. Neelameggham, and Norbert Hort
TMS (The Minerals, Metals & Materials Society), 2012

HIGH PERFORMANCE MG-SYSTEM ALLOYS FOR WEIGHT SAVING APPLICATIONS: FIRST YEAR RESULTS FROM THE GREEN METALLURGY EU PROJECT

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Keywords: Magnesium alloys, ultrafine microstructure, sustainability, CO_2 reduction

Abstract

The GREEN METALLURGY Project, a LIFE+ project co-financed by the EU Commission, has just concluded its first year. The Project seeks to set manufacturing processes at a pre-industrial scale for nanostructured-based high-performance Mg-Zn(Y) magnesium alloys. The Project's goal is the reduction of specific energy consumed and the overall carbon-footprint produced in the cradle-to-exit gate phases. Preliminary results addressed potentialities of the upstream manufacturing process pathway. Two Mg-Zn(Y) system alloys with rapid solidifying powders have been produced and directly extruded for 100% densification. Examination of the mechanical properties showed that such materials exhibit strength and elongation comparable to several high performing aluminum alloys; 390 MPa and 440 MPa for the average UTS for two different system alloys, and 10% and 15% elongations for two system alloys. These results, together with the low-environmental impact targeted, make these novel Mg alloys competitive as lightweight high-performance materials for automotive components.

Introduction

The European Project "Green Metallurgy", a 2 ML€ project co-financed by the European Community, is one of the successful proposals submitted to the EU LIFE+ 2009 Programme. It was presented at the 2011 TMS Annual Exhibition, Magnesium Technology 2011 Symposium. The goal of the 3-year project, which officially started in September 2010, is to overcome the primary historic barriers that currently prevent magnesium from being widely applied as an ultra-lightweight material for the transport sector. The objective of the Green Metallurgy project is to demonstrate that it is possible to manufacture structural elements that are complex in shape using high performance magnesium alloys. Thanks to the Cenim team, nanostructured magnesium based alloys have been developed with drastically increased mechanical properties suitable for scaled-up processes. These lighter structural materials can substitute high performance aluminum alloys generally used in the transport sector and also substitute some low-carbon steel-made products, with greater weight saving possibilities. An additional objective is to set up and use a process route that targets a general reduction of energy intensity, and move the material from the laboratory directly to actual industrial use. A general reduction of total specific energy consumed and the overall carbon-footprint produced in cradle-to-exit gate phase is also targeted.

With the possibility to develop a fully integrated process lay-out, namely single or double process step prototype machinery, and demonstrate the possibility to industrialize an innovative single-step manufacturing process (or quasi double-step process for sheet parts) with a substantially reduced carbon footprint. With the additional capability to demonstrate a completely new nano-Powder Warm Compaction process (nano-PWC) route for Mg based products, based on a combination of warm extrusion and superplastic press-forging, the project could ultimately achieve:

- the avoidance of a secondary melting step,
- reduction of more than 25% of the process energetic input,
- elimination of any green-house gasses,
- facilitation of recycling operations,

which would lead to a compact and lean integrated product cycle that drastically reduces the number of process step and eliminates logistical displacement.

The key features of the new generation of magnesium alloys are the contemporary reduction of energy intensity per kg of finished part produced, the elimination of green-house gasses in the secondary production process steps (downstream steps after primary raw magnesium extraction and master alloy generation), dramatic increases in the specific strength (YS and UTS vs density) ratio while maintaining safe values in elongation and strength. The positive impact from the increased usage of such featured materials has already been evaluated. It is feasible to reduce the CO_2 emission approximately 15-20% over the total lifespan of such lighter weight vehicles as these multi-materials mature, especially in the design phase and could potentially reduce the weight of an average vehicle with an internal combustion engine by approximately 180 kg [1-4].

Perspective of Green Metallurgy process

Once past the primary cast step necessary for production during the magnesium extraction and master alloy generation, various process steps using different equipment often in different plants, are needed for conventional manufacturing routes to produce products needed.

For example, in Figure 1, to use process Route 1 to fabricate a magnesium cast-wheel it is necessary to start with ingots (raw materials), which are then melted at a temperature up to 600°C in a furnace using cover gases. Melted magnesium is then cast inside a die, leaving excess cast materials as recyclable scrap. Furthermore, depending on the final use of the component, further machine work and finishing operations may be required. Alternatively, to increase the mechanical properties that are too low for cast structure, a secondary forging step, perhaps using another machine or another plant, may be necessary. More complex is the route 2 shown in figure 1, but it is needed when higher mechanical property material is required. In fact a hot formed semi-finished product can achieve good mechanical properties up to 230 MPa Yield Strength and 11% elongation. Some semi-finished products currently available require long and complex machining operations.

Compared to the above mentioned routes, the goal of the Green Metallurgy process is to realize semi-finished products, bar and plate forms, starting with raw materials in the form of rapidly solidified powders[1] with very refined microstructure by employing a single-step[2] process. Furthermore, the already tested [5, 6] superplastic behavior of such semi finished products would allowed to net-shape complex component by deploying forging in superplastic regimes.

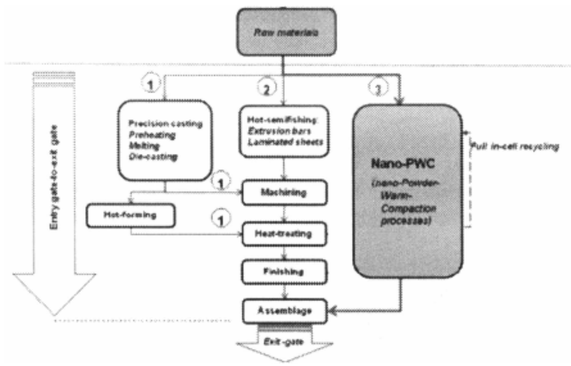


Figure 1. Schematic routes for common mass-part manufacturing: 1) casting into die and post-hot forging; 2) machining from semi-finished products; 3) GREEN METALLURGY process. The thick line identifies the Project manufacturing green-path for magnesium mass-part production.

With this premise, the basic Green Metallurgy process stages to be implemented into the final lay-out are described below :

1. raw material fabrication: a) atomized powders by rapid solidifications, namely the Basic Alloy System MgZn(Y) alloy based; b) machined chips of Eco-Magnesium® for the Alternative Alloy System to be tested.
2. Fabrication of Precursor Material (PMT);
3. Direct extrusion of PMT into semi-finished bars (SSB).
4. Secondary shaping operations (rolling for plates and forging for complex net-shape parts).

A fundamental innovation provided by the project is related to the environmental impact of Mg based alloys process manufacturing, compared to classic approaches. In the second year of the project, a Life Cycle Analysis is planned to measure the environmental impact of the best solution process lay-out resulting from the current preliminary actions.

Executive summary of project actions performed

Based on previous lab-scale experiences developed in the laboratory, the early process-layout is established using the following steps:

a) Preparation of precursor materials (PMT) made of cold compaction of atomized powders produced by conventional casting of master alloys, Basic Alloy System materials, BAS; BAS are produced basing on two chemical compositions (see table I) developed at CENIM laboratories. In figure 2 are details of the micro-structure of rapid solidified powders, while figure 3 shows the PMT result after the cold compaction of BAS powders.

Table I. Nominal chemical composition finely designed at Cenim laboratories.

Element	BAS1 (MgZn6Y1)	BAS2 (MgZn8Y1.5)
Zn	5,5-6,5 wt%	7,5-8,5 wt%
Y	0,8-1,2 wt%	1,3-1,7 wt%
Fe content	<50ppm	<50ppm
Si content	<0,1wt%	<0,1wt%
Cu content	<0,03Wt%	<0,03Wt%

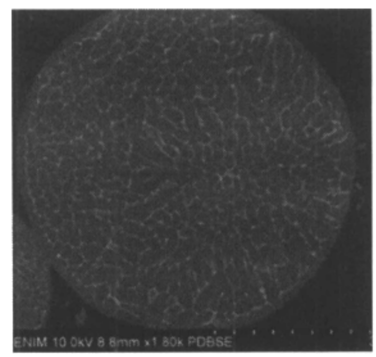


Figure 2 – Scanning Electron Microscope examination of BAS rapid solidified powder (>100micoms diameter) produced by rapid solidification in Argon atmosphere. In the picture two distinct finely distributed phases are clearly visible.

Figure 3 – Precursor material produced by cold compaction of rapid solidified powders made of BAS materials.

[1] Further test campaign on machined chips of Eco-Magnesium® alloys is already planned to be set in parallel with test campaign on Basic Alloy System made of atomized powders of MgY (Zn) alloys.

[2] Single or two-step lay-out process will actually define when optimized lab-scale viable layouts shall be analyzed in order to be scale-up to pre-industrial process lay-out considering economical and technological constraints.

b) Once BAS precursor billets are ready, they are introduced into a lab-scale extrusion machinery available at Cenim laboratories. Results of 250°C extrusion of PMT are visible in figure 3 which shows some extruded bars (Semi-fished Sample Bars, or SSB) produced with different section shapes depending on the following validation mechanical and rolling tests to perform.

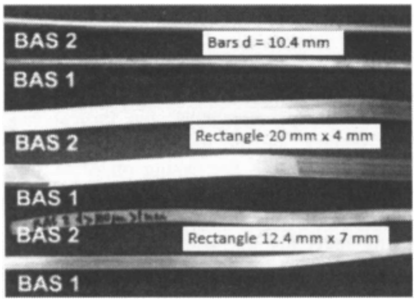


Figure 4 – Extruded bars with three different section shapes: round for tensile mechanical validation tests, square for fracture mechanics tests and flat section for secondary rolling tests.

c) Validation tests are conducted in order to check both microstructure and final mechanical properties obtained on SSB. Quality of the material processed is monitored by performance indicators listed in Table I compared to those targets defined by the project.

Table I. Performance indicators and project targets defined in the Green Metallurgy project.

Monitoring indicators	Target
SSB grain size	<1 micron
UTS	>150% of conventional Mg alloys (casting, wrought Mg alloys)
YS	>150% of conventional Mg alloys (casting, wrought Mg alloys)
E%	>15%
KIc	>15 MPa √m

Some metallographic samples cut from the semi-finished bars have been analyzed by Transmission Electron Microscope at Cenim to identify average grain size obtained after extrusion The average grain size obtained for SSBs, round and flat sections, respectively the lowest and the highest friction extrusion condition, that greatly affect further refining of grain size are shown in Table II.

Table II. Average grain size measured by TEM analyses on round and flat SSBs.

Material	Average grain size (nm) for round SSB	Average grain size (nm) for square (20x4) SSB
BAS 1	437 ± 24	525 ± 38
BAS 2	377 ± 39	502 ± 25

Validation of mechanical properties performed[3] of tensile tests on samples directly cut and machined from the semi-finished bars. Room temperature tensile tests were performed on samples in the as-received condition and after a heat treated condition that were defined during preliminary rolling tests conducted with laboratory rolling machinery. This particular heat treatment (1hour at 360°C) was initially set as optimal pre-heating and in-process heating treatment necessary to achieve best rolling conditions for flat samples cut directly from flat SSBs.
The data results from validation tensile tests are reported in Table III.

Table III. Static mechanical properties after validation test (Level I tests) conducted on round specimens (according to ASTM E8/E8M-09).

Material	Test condition	YS (MPa)	UTS (MPa)	E%
BAS1	Room temperature; as-extruded	376	394	12
BAS2	Room temperature: as-extruded	412	432	14
BAS1	Room temperature; Heat treated (1h@360°C)	238	315	20
BAS2	Room temperature; Heat treated (1h@360°C)	253	324	24

An extensive rolling test campaign was conducted using varying temperatures, reduction of ratio per rolling step (10%, 15% and 20% tested) and different rolling cylinder speed velocities (both testing asymmetric and symmetric conditions). As shown in figure 5, low temperature and/or high reduction ratio resulted in 45° angled fracture under rolling action; safer conditions were obtained by increasing pre-heating and rolling temperature (>300°C) at medium rolling speed and limiting reduction ratio per rolling step at 10%. As shown in figure 6, more satisfying results were obtained at 360°C (pre-heating), 300°C rolling temperature, medium rolling speed rate (symmetric rolling) and realizing a 30% of final reduction accumulating just 10% reduction ratio per each of three rolling steps that were intermediated by 360°C reheating treatment. Without considering border ruptures due to inhomogeneous friction caused by employing a not guided lab-scale rolling machinery, rolled sample in Figure 4 exhibited good surface finishing and no internal defects.
On the other hand, such satisfying results for a laboratory scale are not suitable for the next industrialization phase. It would not be economical or technologically viable to realize sheets starting from extruded SSB of BAS: at the least a 30% reduction is viable by an overly complex process lay-out of accumulated rolling single steps at high temperatures. While in industrialized lay-out the accumulative rolling step could be conducted under pre-heated roller cylinders, realistically limiting the total reduction ratio by 30%.

[3] When this manuscript is being written, non-standard mechanics fracture tests are in the designing phase. The fracture mechanics tests will not be conducted in standard condition because of limitations on sample geometry due to original dimensions of the SSB samples.

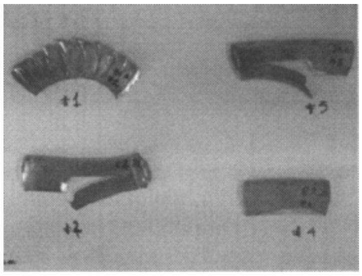
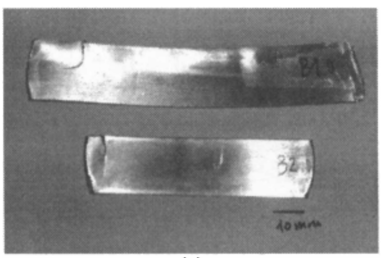
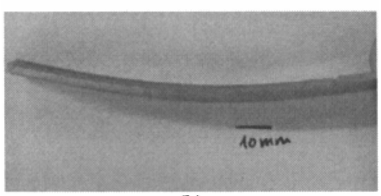


Figure 5 - Different cases from rolling tests: sample#1 ruptured 45° angle, because of low rolling temperature and high reduction ratio; sample#2 and sample#3) longitudinal crack caused by good temperature with too much high reduction ratio; sample#4)n safe rolling condition at higher rolling temperature and 10% of reduction ratio.



(a)



(b)

Figure 6 - Particular of safe rolling test: a) front view for 30% (accumulative rolling, 10% each step) reduction ratio of rolling test conducted at 300°C (360°C preheating temperature).

Eco-magnesium® selected a unique Alternative Alloy System for full-recycling plate fabrication route

Below is a brief description of the advancements in magnesium technology.

- Korean Institute of Technology (KITECH), one of the co-authors of this work, recently developed an environmentally friend magnesium alloy system called Eco-Magnesium®; these unique magnesium alloys are based on commercial chemical compositions (i.e. AZ91D, AZ31, AM60, etc.) but with the addition of CaO. KITECH discovered that CaO modified magnesium alloy systems can achieve a dramatic increase in oxidation resistance in the melt phase and avoid protective greenhouse gases, as SF_6 usually used in casting operations, which can lead to refinement of grain structure and diffusion strength and inhibiting oxidation in solid state [11-17]. Such magnesium CaO modified alloys are called Eco-Magnesium™ (Eco-Mg) since it is a less expensive "cleaner" to cast, with no oxidation or cover gas required, and potentially easy to recycle as it is more resistant to oxidation.

- Consolidated results of magnesium recyclability [18-20] obtained in the past by Japanese researchers shows that machined magnesium alloy chips can be extruded in a solid-state directly from recycled chips.

Basing on the above developments, the Project Management Board recently entered into an agreement of cooperation with KITECH for support during the testing phase of various Eco-AZ31 systems. This will allow them to check the capability of material to be processed by the Green Metallurgy full-recycling route, thus fully recycling machined chips that could be used successfully as raw material for the Green Metallurgy process route.

Conclusions

The first completed mechanical test campaign (level 1, static mechanical properties) through to test toughness behavior (level 2, fracture mechanics test campaign) on Basic Alloy System - two MgZn(Y) systems - produced by CENIM, very impressive mechanical properties were achieved by room temperature tensile tests conducted on the as-extruded materials.
BAS materials exhibited up to 420 MPa UTS and 380 MPa YS with minimum 9% of elongation, so that UTS and YS resulted 200% higher than conventional magnesium alloys, thus exceeding the planned target objectives.

Furthermore, when YS and UTS are heat-treated by a very short heating cycle, reduction is reduced by 30% compared to as-extruded conditions, but elongation increased dramatically, up to 22%. A closer investigation of the optimized microstructure modification by heat treatment is planned. BAS materials offer a more extensive combination of mechanical properties that can lead to optimization opportunities of engineering structural applications. These range from high performance applications that prefer the highest specific resistance with limited ductility or safer lightweight components favoring elongation at the UTS rupture.
Furthermore, previous experience [5] show that secondary heat treatments could ultimately be substituted by increasing the extrusion temperature: this would lead to further simplification of the optimized lay-out for single-step production of semi-finished bars
On the other hand, BAS showed not to be suitable for secondary rolling operations intended for flat parte generation. This does not mean that BAS cannot be rolled, but it is an overly complex and inefficient secondary operation that is not particularly suitable to be moved up to an industrial application.
For these reason, the Green Metallurgy project recently entered into a collaborative agreement to test Eco-AZ31 as a potential candidate as a low-impact and inexpensive material to apply in a fully-recycling route for flat components.

Acknowledgements

This work makes use of results produced by the Green Metallurgy project (http://www.green-metallurgy.eu), co-funded by the European Commission within the 2009 LIFE+ Programme.

Authors thank support provided by European Commission for supporting project dissemination activities. This work reflects only the authors' views. The Community is not liable for any use that may be made of the information contained therein.

References

1. L. Ridge, EUCAR - Automotive LCA Guidelines - Phase 2, In: Total Life Cycle Conference and Exposition; Graz, SAE paper 982185, 193-204 (1998).

2. A.Tharumarajah, and P.Koltun, "Is There an Environmental Advantage of Using Magnesium Components for Light-Weighting Cars?" *Journal of Cleaner Production*, 15 (2007), 1007–1013.

3. H.Friedrich, S. Schumann, "The second age of magnesium" (Paper presented at the Second Israeli International Conference, Sdom, Israel, February 2000).

4. H. Friedrich, S. Schumann, "Research for a new age of magnesium in the automotive industry", Journal of Material Process Technology, 117 (2001), 276–281.

5. G.Garces, M. Maeso, P. Pérez and P. Adeva, "Effect of Extrusion Temperature on Superplasticity of PM-WE54", Materials Science and Engineering A, 462(1-2), (2007), 127-131.

6. P.Pérez, S.Gonzales, G.Garces, G. Caruana, and P.Adeva, "High-strength Extruded Mg96Ni2Y1RE1 Alloy Exhibiting Superplastic Behaviour", Materials Science and Engineering A, 485(1-2), (2008) 194-199.

7. E.Mora, G.Garces, E.Onðrbe, P.Perez and P.Adeva, "High-strength Mg–Zn–Y Alloys Produced by Powder Metallurgy", *Scripta Materialia*, Volume 60, 2009, 776–779.

8. G. Garcés, A. Müller, E. Oñorbe, P. Pérez and P. Adeva, "Effect of Hot Forging on the Microstructure and Mechanical Properties of Mg-Zn-Y alloy", Journal of Materials Processing Technology, 206 (1-3), (2008), 99-105.

9. E.Mora, G. Garcés, E. Oñorbe, P.Pérez, and P.Adeva, "High-strength Mg-Zn-Y alloys Produced by Powder Metallurgy", Scripta Materialia, 60 (9), (2009), 776-779.

10. P. Pérez, G. Garcés, and P.Adeva, "Influence of Texture on the Mechanical Properties of Commercially Pure Magnesium Prepared by Powder Metallurgy", Journal of Materials Science, 42(11), (2007), 3969-3976.

11. S. K. Kim et al., "The behavior of CaO in Mg alloys," Proc. Magnesium Technology 2005, (2005), 285-289.

12. J. K. Lee et al., "Development of CaO added wrought Mg alloy for cleaner production," Proc. Magnesium Technology 2006, (2006), 185-189.

13. J. K. Lee et al., "Effect of CaO addition on ignition behavior in molten AZ31 and AZ91D Magnesium alloys." Rare Metals, 25 (2006) 155-159.

14. S. H. Ha et al., "The behavior of CaO and Ca in pure Mg", Rare Matals, 25 (2006) 150-154.

15. S. H. Ha et al., "Effect of CaO on oxidation resistance and microstructure of pure Mg", Materials Transactions, JIM, 49 (2008), 1081-1083.

16. D. I. Jang et al., "Effect of CaO on AZ31 Mg Strip Castings", Materials Transactions, JIM, 49 (2008), 976-979.

17. J. K. Lee et al., "Development of Novel Environment-friendly magnesium alloys", Advanced Materials Research, 47-50 (2008), 940-943.

18. M.Mabuchi,K.Kubota and K.Higashi, "New Recycling Process by Extrusion for Machined Chips of AZ91 Magnesium and Mechanical Properties of extruded Bars", Mater. Trans, JIM,36(1995), 1249-1254.

19. Y.Chono and M.Mabuchi,"Recycling of Magnesium Alloys Using Plastic Forming Process", Journal of the Japan Society for Technology of Plasticity, 44 (2003), 15-19.

20. K. Matsuzaki, Y. Murakoshi and T. Shimizu, "Microstructure and Mechanical Properties of Solid State Recycled Magnesium Alloy Chips", Magnesium Technology 2011, Proceedings of TMS (The Minerals, Metals & Materials Society), April 2011, 485-489.