Improvement of hydrogen storage properties of magnesium alloys by cold rolling and forging

Jacques Huot\textsuperscript{a}, Sofiene Amira\textsuperscript{a}, Julien Lang\textsuperscript{a}, Nataliya Skryabina\textsuperscript{b}, Daniel Fruchart\textsuperscript{c}

\textsuperscript{a}Hydrogen Research Institute, Université du Québec à Trois-Rivières, 3351 des Forges, Trois-Rivières, Québec Canada
\textsuperscript{b}Perm State University, Department of Physics and Chemistry, 15 Bukireva st. 614990 Perm, Russia
\textsuperscript{c}Institut Néel & CRETA - CNRS, BP 166, 38042 Grenoble Cedex9, France

E-mail: jacques.huot@uqtr.ca

Abstract. In this talk we show that cold rolling (CR) could be used to enhance hydrogen sorption properties of magnesium and magnesium alloys. In particular, cold rolling could reduce the first hydrogenation time, the so-called activation. Pure magnesium, commercial AZ91D alloy, and an experimental creep resistant magnesium alloy MRI153 in the as-cast and die-cast states were investigated. We found that both MRI and AZ91 alloys present faster activation kinetic than pure magnesium. This could be explained by the texture, higher number of defects, and nanostructure in CR materials but also precipitates at the grain boundaries. The effect of filing was also investigated.

1. Introduction

Hydrogen storage is a key element in the development of hydrogen economy. Much effort is presently made in discovering new materials and technique to store hydrogen in a safe and economical way. Metal hydrides are especially suitable for many applications because they have high volumetric capacities. Magnesium is particularly attractive because of its relatively large gravimetric hydrogen storage capacity (7.6 wt%), low cost and high abundance in the earth’s crust. Unfortunately, magnesium hydride is thermodynamically very stable which means high temperatures of operation (300°C). The absorption/desorption kinetics are also relatively slow and the first hydrogenation (the so called activation step) is particularly slow.

Recently, it has been reported that severe plastic deformation such as cold rolling (CR), Equal-Chanel Angular Pressing (ECAP), High Pressure Torsion (HPT) and forging could be used to process hydrogen storage alloys\cite{1-6}. In this paper, we report the investigation of the effect of forging repeated cold rolling on the structure and hydrogen storage properties of magnesium and magnesium alloys. We mainly investigated the first hydrogenation (activation) of these alloys. The activation of metal hydrides is usually time consuming and involves high temperatures and pressures. This is...
especially the case for magnesium. For commercial product, such expenditure in terms of time and energy translates to higher production cost. Therefore, to reduce cost of magnesium hydride the problem of activation has to be solved. It has been shown that severe plastic deformations and particularly cold rolling could drastically reduce activation time [1, 4, 7, 8].

2. Experimental details

Pure magnesium was obtained from Norsk-Hydro. Table 1 shows the chemical compositions of the cast AZ91D and MRI153 alloys. A small plate was cut from each ingot and cold rolled between two Stainless Steel (316) plates using a Durston DRM 100 rolling mill. The plates were rolled 50 times in air. After each roll, the plates were folded in two and rolled again thus obtaining a 50% thickness reduction at each rolling pass. Final thickness was about 0.3 mm. After the final roll, the material was mixed with 5%wt of MgH₂ and ball milled in a SPEX8000 mill for 30 minutes. This ball milling step is essential for activation purpose because it adds nucleation points for the hydride phase [9].

Table 1. Chemical composition of magnesium alloys.

| Alloy   | Al  | Zn  | Mn  | Ca  | Sr  | RE  | Mg   |
|---------|-----|-----|-----|-----|-----|-----|------|
| AZ91D   | 9.0 | 0.7 | 0.25| --  | --  | --  | bal. |
| MRI153  | 8.3 | 1.0 | 0.16| 0.84| 0.1 | 0.11| bal. |

A Sieverts’ type apparatus was used to measure the hydrogen activation and sorption kinetics. Specimens were first heated under vacuum at 623 K to insure that the magnesium hydride introduce at the ball milling step was dehydrogenated. Thereafter, the samples underwent an activation treatment at 623 K under hydrogen pressure of 2 MPa for the hydrogenation and 0.01 MPa for the dehydrogenation. A second cycle of hydrogenation/dehydrogenation was then carried out at the same conditions of temperature and hydrogen pressure.

The microstructures of the specimens before rolling were studied by scanning electron microscope (JEOL 840-A). The composition of phases was determined by CAMECA SX-100 electron probe microanalyser (EPMA). The microstructures of the cold rolled specimens before and after the hydrogenation/dehydrogenation cycles were analyzed by X-rays diffraction on a Bruker D8 Focus apparatus with Cu-Kα radiation.

3. Results: cold rolling of Mg alloys

3.1. Structure

Figure 1 shows the microstructure of as-cast AZ91D and MRI153. In the case of AZ91D (1a) the dark gray areas are primary α-Mg grains and the light gray is Mg₁₇Al₁₂ eutectic. The white particles are Al₈Mn₅ compound (γ-brass phase). The microstructure of as-cast MRI530 as shown in figure 1B is composed of large primary α-Mg grains surrounded by lamellar and divorced eutectic which is a mixture of (Mg,Al)₂Ca and (Mg,Al)₂(Sr,Ca) phases.
Figure 1. Microstructures of as cast (A) AZ91D, (B) MRI153.

Figure 2 shows the X-ray diffraction patterns of samples cold rolled 50 times and thereafter milled with 5 wt.% of MgH₂ for 30 minutes. After cold rolling magnesium and magnesium alloys usually present a strong texture along (002). In the present case, short milling had an effect of reducing this texture but the reduction was not the same for all alloys. Magnesium and AZ91D retained some texture while MRI153 had almost no texture.

Figure 2. X-ray diffraction patterns after cold rolling and ball milling of pure magnesium, MRI153, and AZ91D alloys.

The lattice parameters, crystallite size and strain were evaluated from Rietveld refinement. Results are shown in Table 2. We see that the lattice parameters of both alloys are slightly smaller than those of pure magnesium. This could be explained by the smaller metallic radii of aluminium, zinc, and manganese compared to magnesium. Crystallite size and microstrain of AZ91D and MRI153 are comparable. Pure magnesium has bigger crystallite size and smaller microstrain that the alloys, probably due to the different mechanical properties.
Table 2. Lattice parameters, crystallite size, and microstrain of magnesium and magnesium alloys after cold rolling and milling.

| Sample   | Lattice parameter $a$ (nm) | Lattice parameter $c$ (nm) | Crystallite size (nm) | Microstrain (%) |
|----------|-----------------------------|-----------------------------|-----------------------|-----------------|
| Mg       | 0.32093(1)                  | 0.52112(2)                  | 72(1)                 | 0.091(6)        |
| MRI153   | 0.31931(3)                  | 0.51877(5)                  | 45(2)                 | 0.205(3)        |
| AZ91D    | 0.31941(4)                  | 0.51881(7)                  | 40(2)                 | 0.199(5)        |

3.2. Hydrogen sorption

It is well known that the first hydrogenation, the so-called activation step, is difficult for magnesium [10]. We have shown in a recent paper that ball milling a small amount of MgH$_2$ with magnesium leads to a drastic decrease of activation time [9]. The same procedure was used for magnesium and magnesium-alloys studied here. Figure 3 shows the first hydrogenation (activation) of Mg, AZ91D, and MRI153 at 623 K under hydrogen pressure of 2 MPa. Both alloys absorb faster than pure magnesium, the main difference being the small incubation time of about 30 minutes shown by the magnesium sample. For all samples the hydrogenation continues at a slow rate. The ultimate hydrogen capacity reached by magnesium and AZ91D is 6 wt.% while the MRI153 sample reach a higher value of 7.0 wt.%. Therefore, even pure magnesium did not reach its theoretical capacity (7.6 wt.%) because of the very slow activation kinetic and the fact that the hydride phase form a barrier for the hydrogenation of magnesium core. In the case of alloys, the amount of foreign elements (mainly Al) is relatively low and do not significantly reduce the theoretical capacity. Also, most of Al atoms are in fact in solid solution in magnesium and will not drastically change the hydride capacity.

![Figure 3](image-url)

Figure 3. First hydrogenation at 623 K under 2 MPa of hydrogen of pure magnesium, MRI153, and AZ91D alloys.

First dehydrogenation kinetic is shown in Figure 4. We see that desorption of AZ91D hydride is faster than magnesium hydride but MRI153 hydride has a relatively slow desorption kinetic.
Figure 4. First dehydrogenation at 623 K under 0.01 MPa of hydrogen of pure magnesium, MRI153, and AZ91D alloys.

Figure 5 presents the second cycle hydrogenation kinetic. For all samples the absorption kinetic is much faster than the activation step. All curves could be broken down in two steps: first a very rapid kinetic followed by a much slower absorption. This slow step may be due to the formation of a magnesium hydride shell around the particles. As hydrogen usually diffuses much slower in magnesium hydride than in magnesium, this hydride shell effectively slow down diffusion and makes the full hydrogenation much slower than the initial hydrogenation.

Figure 5. Second hydrogenation at 623 K under 2 MPa of hydrogen of pure magnesium, MRI153, and AZ91D alloys.
The explanation of the faster activation and sorption kinetics of AZ91D and MRI153 compared to pure magnesium is not obvious. As both alloys contain about 9 wt.% of aluminum, the hydrogen sorption improvement may be attributed to the addition of this alloying element to magnesium. However, these two alloys have different microstructures. The matrix of both alloys consists of primary $\alpha$-Mg phase but in the case of AZ91D alloy a compound of $\alpha$-Mg + $\beta$ ($\text{Mg}_{17}\text{Al}_{12}$) eutectic is formed at grain boundaries while in MRI153 the eutectic consists of supersaturated $\alpha$-Mg phase and a ($\text{Mg,Al})_2\text{Ca}$ compound, with the presence of ($\text{Mg,Al})_2(\text{Sr,Ca})$ and small amount of $\text{Mg}_{17}\text{Al}_{12}$.

The effect of texture should also not be ruled out. In a recent paper Botta et al showed that the samples with refined microstructure and strong component of (002) Bragg diffraction peak presented enhanced H-sorption properties [4].

3.3. Effect of filing

Cold rolled magnesium samples are coming out in the form of a thin plate. This means that the specific surface area is very small and thus makes sorption kinetics slow. The standard procedure is that after cold rolling or ECAP (Equal Chanel Angular Pressing) the material is filed with a rasp and the powder collected is used for hydrogen storage characterization. Therefore, it is vital to know the intrinsic effect of filing in order to see the impact of severe plastic deformation on hydrogen storage properties. In order to do so, we used a bastard file to process magnesium ingot and magnesium cold rolled 25 times. Figure 7 shows the morphology of the obtained material. One side of the filings presents a smooth surface where the file’s passed while the other side presents buckling due to the high level of stress during filing. Filing of cold rolled samples gives identical structures.
Figure 7. SEM micrographs of magnesium block filed with a bastard file.

Figure 8 presents the effect of filing on magnesium and cold rolled magnesium on the first hydrogenation at 350°C under 20 bar of hydrogen. As expected, the magnesium plates do not activate at all but filing made the absorption much faster, mainly due to the higher specific surface area. Cold rolling improves the hydrogenation kinetics even without filing. However, the final capacity is relatively small. This is probably due to the fact that rolling is a surface effect. After rolling the surface is more active than before but the reaction could not proceed very deep into the sample. Beneficial effect of rolling is kept after filing as shown in Figure 8. Reaction is faster and capacity is higher than the untreated magnesium. Therefore, we could conclude that cold rolling has a true beneficial effect on the hydrogen sorption properties of magnesium.

Figure 8. First hydrogen absorption of magnesium and cold rolled magnesium in their as synthesized and filed states.
4. Conclusion

The effect of cold rolling on MR1153 and AZ91D magnesium alloys has been investigated. For these alloys, the first hydrogenation (activation) is faster than pure magnesium. The reason for this improvement may be associated to the presence of Mg17Al12 and (Mg,Al)2Ca which may act as nucleation point for the hydride phase and also could play a role in the deformation process during cold rolling. For industrial synthesis a fast activation means cost reduction. Therefore, using alloys instead of pure magnesium may decrease production cost of magnesium hydride and open new markets for the use of this hydride.

Industrial process also means that the material will have to be reduced in powder at some step in order to increase the specific surface area and consequently the reaction kinetics. We showed that the beneficial effect of rolling is kept after reduction of the cold rolled material by filing with a bastard file.

Cold rolling and other severe plastic deformation techniques have been used to enhance hydrogen storage properties of materials only recently. However, it has been already showed that these techniques are good candidates for improvement of sorption kinetics and cost reduction for the industry. More work is still needed to have a better fundamental and practical understanding of the effect of these techniques on metal hydrides.

Acknowledgements

This investigation was supported in part by the Ministry of Education of Perm Region (Russia), funding project C-26/211 and by NSERC Canada.

References

[1] J. Huot, et al.: 2012 Metals 2(3) 329-343.
[2] J. Huot: 2012 Metals 2(1) 22-40.
[3] D. R. Leiva, et al.: 2009 International Journal of Materials Research 100(12) 1739-1746.
[4] W. J. Botta, et al.: 2013 Journal of Alloys and Compounds 580(1) S187-S191.
[5] S. Amira, et al.: 2010 Intermetallics 18(1) 140-144.
[6] S. Couillaud, et al.: 2009 Journal of Alloys and Compounds 484(1-2) 154-158.
[7] S. Amira and J. Huot: 2012 Journal of Alloys and Compounds 520(0) 287-294.
[8] D. R. Leiva, et al.: 2011 Materials Science Forum 667-669 1047-1051.
[9] P. Jain, et al.: 2013 Journal of Alloys and Compounds 575(0) 364-369.
[10] B. Vigeholm, et al.: 1983 Journal of the Less-Common Metals 89 135-144.