Severe Plastic Deformation of Mg-Fe Powders to Produce Bulk Hydrides

G F Lima¹, A M Jorge Jr², D R Leiva¹, C S Kiminami², C Bolfarini² and W J Botta²

¹ Programa de Pós-Graduação em Ciência e Engenharia de Materiais, Federal University of São Carlos – Via Washington Luiz, Km 235 – São Carlos – SP – Brazil
² Federal University of São Carlos – Department of Materials Engineering
E-mail: moreira@ufscar.br

Abstract. We describe in the present work the production of bulk Mg hydrides by hydrogenation treatment of samples processed by severe plastic deformation. The compact bulk samples of Mg-Fe have been obtained by high pressure torsion. The ternary complex Mg₂FeH₆ and the binary MgH₂ hydrides have been synthesized by hydrogenation treatment at 350°C, at 3 MPa during 24 h. The average grain refinement after HPT was modest as estimated by XRD. A comparison between the XRD patterns of the powders and of the HPT samples showed the formation, as expected, of a preferred orientation in the latter. The XRD of the hydride HPT samples (H-HPT) showed the presence of Mg, Fe, MgH₂ and Mg₂FeH₆. The first de-hydrating reaction of the alloys (after H-HPT) was studied by differential scanning calorimetry (DSC). These results showed a reduction in the hydrogen desorption temperature in comparison with commercial MgH₂, indicating thermodynamic destabilization of the hydrides as a result of the high density of dislocations in the H-HPT samples.

1. Introduction

Mg based alloys are relatively light, cheap and promising material for hydrogen storage mainly due to the high gravimetric and volumetric hydrogen capacities of their hydrides [1]. MgH₂ has the highest gravimetric storage capacity (7.6 wt.% of H), Mg₂FeH₆ presents the highest volumetric density of storage (150 g of H₂/l, that is 9.1x10¹⁵ atoms of H/cm³) twice as high as storage in liquid state. However, these alloys present high desorption temperatures and slow kinetics [2]. Non-conventional materials with nanocrystalline structures exhibit higher storage capacities and faster kinetics of absorption and desorption of hydrogen than crystalline materials; also nanocomposites may present even better hydrogen properties than each isolated component [2-11].

Currently, non-conventional routes of processing involving severe plastic deformation (SPD) have been shown as promising for the preparation of Mg alloy for hydrogen storage in bulk form. The improvements are: easier activation process or elimination of it, higher capacity, chemical stability, and kinetics. The use of the accumulative roll-bonding (ARB) method of SPD has been already reported by Ueda et al [12], in the production of Mg-Ni-Mg₅Ni, where they observed fast activation; by Huot and Dufour [13-14], in the production of Mg-2.5Pd (at.%) using high-energy ball milling, HEBM and ARB, where ARB-samples presented faster activation and faster kinetics than HEBM-samples to synthesize the intermetallic Mg₅Pd and by Takeichi et al [15] in the production of composites of Mg/Cu and Mg/Pd. Mg based alloys have also been produced by equal channel angular
pressing (ECAP), in which case it was observed better kinetics and in some cases absence of hysteresis of pressure giving an expectative of longer life time or cycling stability. Kusadome et al [16] used high pressure torsion (HPT) to process MgNi₂. This intermetallic does not form hydride like Mg₂Ni, but it was observed that the HPT-sample stored 0.1 wt.% of hydrogen.

Considering that there are no reports concerning synthesis of the ternary hydride Mg₂FeH₆ in bulk form, in this work we present an alternative route for production of bulk MgH₂ and Mg₂FeH₆ using the process of HPT and ARB.

2. Experimental Procedure
Powders of Mg (98% pure, micro size) and Fe (99.998% pure, nano size) were mixed in atomic stoichiometries 2Mg-Fe. Each sample (mixture of powders) with approximately 0.0250 g was severe plastic deformed by high pressure torsion equipment, where was applied 5GPa at room temperature and ten turns. The deformed disk was hydrogenated under a hydrogen pressure of 3 MPa at 350°C for 24 h in a Sieverts apparatus. The structural and phase characterization was performed by X-ray diffraction (XRD) using monochromatic Cu Kα radiation, angular pass of 0.032°, in Rigaku D-max equipment. The hydrogenated disk was heated in a Netzsch DSC 404, differential scanning calorimeter (DSC). Hydrogen desorption temperatures were measured during continuous heating of the hydrides with constant heating rate of 10°C/min, using purified and dried argon gas under overflow regime. The apparent activation energy was extracted from the DSC data using an adapted Kissinger equation [17].

3. Results and Discussions
The close-up view in Fig. 1 shows the XRD pattern after HPT and H-HPT compared with the precursor powder. The peaks were identified as hcp-Mg and bcc-Fe solid solutions, in all samples, and MgH₂ and Mg₂FeH₆ phases in the H-HPT disk. It is also relevant to note the acquired preferential orientation (002) by the Mg phase after HPT. This effect is more pronounceable in H-HPT sample. The preferential orientation is expected due to the high level of the applied stress in the HPT process leading to an unrecovered high deformed structure. After H-HPT, as shown by Goltsov et al [18], hydrogen acts stimulating the evolution of the recrystallization and recovery at lower temperatures taking place at classical recrystallization annealing. Thus, it is expected that the recrystallized microstructure follows the previous texture imposed by the mechanical processing as can be seem in the H-HPT pattern.

![Figure 1 – XRD patterns of the powder, the as-HPT and the as-H-HPT samples.](image-url)
Fig. 2a shows DSC analyzes comparison between H-HPT sample and commercial MgH₂. The endothermic peak corresponding to H₂ desorption in the H-HPT started at about 376°C as compared with 416 °C for MgH₂ samples. From this picture it can depicted the apparent activation energy for de desorption process. The apparent activation energies for dehydrogenation of pure and Fe doped magnesium hydride were $E_A \approx 354$ and 334 kJ/mol, respectively. The relatively high activation energies are due to magnesium oxide surface layers, retarding the diffusion of hydrogen out of MgH₂/Mg. The observed difference in $E_A$ of 20 kJ/mol is likely due to the catalytic effect of Fe on the recombination of H atoms to hydrogen molecules. These energy results show that the addition of Fe is expected to lower the dissociation barriers for H₂ dissociation significantly and lowering the starting temperature to dehydrogenation. Also, from this Figure, the volume of hydrogen liberated by the H-HPT sample was about 7.5% larger than that by the MgH₂ sample, this value was deduced comparing the area under the DSC curves.

The reaction, metals with hydrogen, consists of several steps: (i) nucleation and growth of Mg (ii) diffusion of hydrogen in bulk Mg/MgH₂, (iii) surface penetration, i.e. through MgO for oxidised samples, (iv) 2D surface diffusion of H, (v) recombination of 2H to H₂ a catalysed process. Furthermore, (vi) for alloys cation migration can also be of importance during phase formation/phase separation induced by hydrogenation or dehydrogenation. The rate-determining step (the slowest) has the largest contribution to the apparent activation energy. This might indicate that the dissociation of H₂ and recombination of H to H₂ mainly occur on in association with iron due to its lower barrier compared to pure magnesium even with as little as % Fe present. This may suggest that Fe mainly catalyzes the dissociation/recombination reaction barrier for H₂ and has minor influence on other processes as will be mentioned later. Iron, like magnesium, is oxidized in air to the oxide, FeO. In contrast to MgO, FeO is readily reduced by hydrogen gas.

Fig. 2b shows sigmoidal curves for each sample. The observed data seem to indicate a nucleation time prior to the onset of dehydrogenation. As it can be observed in this Fig., the incubation time for the MgH₂ sample is larger than for the Fe doped sample. However, faster dehydrogenation kinetics from MgH₂ samples is visible (0.55%/s for MgH₂ and 0.47%/s for 2Mg-Fe) along with the sigmoidal curves, which can be explained by the higher dehydrogenation temperatures occurring in the MgH₂ sample.

![DSC curves](image)

Figure 2 – (a) DSC curves of: comparing the hydrogenated disk of 2Mg-Fe and the commercial MgH₂ alloys. (b) Sigmoidal curves obtained from Fig. 2a, showing the incubation time and the kinetics behavior from the two samples.
4. Conclusions

It was possible to produce hydrides in bulk samples processed by high pressure torsion method of severe plastic deformation.

Hydrogen absorption and desorption kinetics are improved by the addition of iron in magnesium that produces a catalytic effect that lowers the desorption temperature.

The incubation time to start the $H_2$ desorption process in the MgH$_2$ sample is larger than for the Fe doped, but the desorption kinetics is faster in the former probably due to the highest desorption temperature in this case.

The values of activation energy for the desorption process are relatively high possibly because oxide layers on the samples surfaces. The lower activation energy for the Fe-doped sample suggests that Fe catalyzes the recombination of H to $H_2$.

Acknowledgements: The authors are acknowledged for financial support from FAPESP, CAPES and CNPq.

References

[1] Züttel A, Wenger P, Sudan P, Mauron P and Orimo S-I 2004 Mater. Sci. and Eng. B. 108 9-18.
[2] Didisheim J J, Zolliker P, Yvon K, Fischer P, Schefer J, Gubelmann M and Williams A F 1984 Inorg. Chem. 23 1953-57.
[3] Sakintuna B, Lamari-Darkrim F and Hirscher M 2007 Int. J Hydrogen Energy. 32 1121 –40.
[4] Reiser A, Bogdanovic B and Schlichte K 2000 Int. J Hydrogen Energy. 25 425–30.
[5] Gennari F C, Castro F J and Andrade Gamboa J J 2002 J. Alloys and Compd. 339 261–67.
[6] Songlin L, Varin R A, Morozova O and Khomenko T 2004 J. Alloys and Compd. 384 231–48.
[7] Sai Raman S S, Davidson D J, Bobet J-L and Srivastava O N 2002 J. Alloys and Compd. 333 282-90.
[8] Herrich M, Ismail N, Lyubina J, Handstein A, Pratt A and Gutfleisch O 2004 Mater. Sci. and Eng. B. 108 28–32.
[9] Yavari A R, Lemoulec A, De Castro F R, Deledda S, Friedrichs O, Botta W J, Vaughan G, Klassen T, Fernadez A and Kvick Å 2005 Scripta Mater. 52 719-24.
[10] de Castro J F R, Yavari A R, LeMoulec A, Ishikawa T T and Botta W J 2005 J. Alloys and Compd. 389 270-74.
[11] Deledda S, Borissova A, Poinsignon C, Botta W J, Dornheim M and Klassen T 2005 J Alloy Compd, 404 409-12.
[12] Ueda T T, Tsukahara M, Kamiya Y and Kikuchi S. 2005 J. Alloys and Compd. 386 253-57.
[13] Dufour J and Huot J 2007 J. Alloys and Compd. 439 L5–L7.
[14] Dufour J and Huot J 2006 J. Alloys and Compd. in press.
[15] Takeichi N, Tanaka K, Tanaka H, Ueda T T, Kamiya Y, Tsukahara M, Miyamura H and Kikuchi S 2006 J. Alloys and Compd. in press.
[16] Kusadome Y, Ikeda K, Nakamori Y, Orimo S and Horita Z 2007 Scripta Materialia. 57 751-53.
[17] Kissinger H E 1957 Anal. Chem. 29 1702-06.
[18] Goltsov V A, Glyakov D A and Zhirov G I 2006 Intern. J. Hydrogen Energy. 31 (2) 211-16