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An investigation of hydrogen storage in a magnesium-based alloy processed by equal-channel angular pressing

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ABSTRACT

Equal-Channel Angular Pressing (ECAP) can be successfully used to process Mg and Mg-based hydrides to produce bulk samples with enhanced hydrogen sorption properties. The primary advantages associated with ECAP processing are the shorter processing time, lower cost and the production of safer and more air-resistant bulk material by comparison with powders produced by high-energy ball milling. ECAP can produce special features for hydrogen absorption such as preferential textures, an increased density of defects and submicrometer grain sizes. In this research, ECAP was used to process a commercial AZ31 extruded alloy in order to evaluate its use as a hydrogen storage material. The ECAP was conducted under conditions of temperature and number of passes in order to avoid grain growth. Additional experiments were conducted on commercial coarse-grained magnesium to evaluate the effect of sample thickness on the sorption properties. The ECAP sample was evaluated in two different orientations and it is shown that better hydrogen properties are related to a refined microstructure allied to the (0001) texture.

1. Introduction

Hydrogen storage is currently attracting considerable attention with special emphasis on the fabrication of appropriate storage materials [1,2]. Magnesium alloys are especially attractive for hydrogen storage in the solid state because these alloys are light-weight and they can absorb up to ~7.6 wt.% of hydrogen in the form of reversible magnesium hydride (MgH_2) [1,3]. In addition, together with the abundance and low cost of magnesium, these alloys represent an outstanding potential

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for commercial applications and they are more effective and safe as hydrogen storage media in the solid state than in the pressurized or liquefied conditions. Nevertheless, the kinetics of the reaction is very slow even at elevated temperatures and this effectively places a limit on their practical utility. The kinetics is reduced primarily because of two factors. First, the diffusion rate of hydrogen is very low within the magnesium hydride [4,5]. Second, there are oxide layers on the surfaces which prevent or delay the penetration of hydrogen [6,7]. There is also evidence that the presence of porosity may create easy paths for hydrogen penetration in bulk samples [8,9].

Many studies have been conducted in attempts to solve these problems and in recent years there has been a remarkable improvement in the desorption kinetics associated with the use of oxides and catalysts especially in nanocrystalline magnesium [10–13]. High-energy ball milling (HEBM) techniques have been applied successfully for the preparation of Mg-based nanocomposites which provide fast H-sorption kinetics at 300 °C or even at lower temperatures [1,14–18]. However, there are several disadvantages in processing by powder metallurgy including the occurrence of surface contamination, the expended time, the potential fire risk and health concerns.

These various shortcomings may be overcome by using severe plastic deformation (SPD) processing techniques which provide the capability of converting conventional coarse-grained metals into ultrafine-grained or nanocrystalline materials under a high hydrostatic pressure and at relatively low deformation temperatures [19–21]. Processing by SPD produces multiple defects in the crystalline lattice such as vacancies and dislocations and this has a positive effect on the diffusion kinetics. Nevertheless, the presence of porosity, which is an important factor in improving the diffusion kinetics, is essentially non-existent after processing by SPD techniques. In practice, investigations suggest there is improved diffusion and H_2 storage capacity in Mg alloys after processing by SPD due to the presence of excess vacancies which dramatically accelerate the diffusion process and allow the entrapment of up to six hydrogen atoms per vacancy [22–26].

Processing by an SPD technique such as equal-channel angular pressing (ECAP) [20] has been widely used for introducing ultrafine grain sizes into light metal alloys, especially magnesium-based alloys where it is possible to attain remarkable superplastic ductilities [27–34]. In practice, as already observed for ZK60 alloy processed by ECAP, defect structure [35] and refinement of the microstructure [35,36] are also important in improving the H-kinetics sorption properties and structural stability during cycles of absorption/desorption and ECAP may produce textures which improve the H-sorption properties [37,38]. There is also evidence that hydrogen absorption is improved in magnesium processed by the alternative SPD technique of high-pressure torsion (HPT) [39].

In an investigation of the structural and hydrogen storage properties in nanostructured thin films of Mg deposited on Si (001) substrates, X-ray diffraction showed that the conversion of Mg to MgH_2 follows a martensitic-like orientation relationship with Mg (002) // MgH_2 (110) and Mg $[1\bar{2}0]$ // MgH_2 [111] [40]. Experiments combining ECAP, cold rolling (CR) and HEBM to process commercial extruded AZ31 alloy showed the deformability of the alloy during ECAP processing was suitable for temperatures above 150 °C. However, a [002] texture favorable for the absorption of hydrogen was obtained only with a combination of ECAP and subsequent cold rolling [41]. These results suggest that the presence of excess vacancies and the reduced grain size produced by ECAP are not sufficient to produce an improvement in the absorption properties and instead other aspects, such as the density of nucleation sites for the hydride formation, must also be considered. An early study of the ECAP processing of Mg showed that the basal planes become aligned with the theoretical shearing plane and it follows that different directions within the processed samples may have different properties relating to the texture [42]. Based on these results, the objective of this investigation was to use ECAP processing on a commercial magnesium alloy to determine the processing route that produces the best texture for hydrogen absorption and to analyze the differences in the hydrogenation behavior for samples cut in different orientations.

2. Experimental materials and procedures

The experiments were conducted using a commercial AZ31 magnesium alloy, supplied by Timminco Co. (Aurora, CO) in the form of extruded rod having diameter of 10 mm. The chemical composition of this alloy (in wt.%) was 2.50 Al, 0.37 Mn and 0.92 Zn with the balance as Mg. Inspection showed the initial grain size in the as-received extruded condition was ~14.5 μm.

Billets were cut from the rod with lengths of ~60 mm for processing by ECAP and these billets were processed using a hydraulic press of 150-tons capacity operating at a pressing speed of ~7 mm s^{-1}. All processing by ECAP was performed using a solid die having an internal channel angle of $\Phi = 110^\circ$ and an angle at the outer arc of curvature of the two parts of the channel of $\Psi = 20^\circ$. These angles produce a strain of ~0.8 on each separate passage through the die [43] and repetitive pressings were performed using route A in which the billet is pressed through the die without any rotation between each pass [44].

In this investigation, the billets were pressed under conditions in terms of the numbers of passes and processing temperatures such that the samples were able to achieve high numbers of ECAP passes with little or no grain growth. Specifically, AZ31 alloy was pressed for two passes at 473 K and a subsequent two passes at 443 K to give a total of 4 passes and a strain of ~3.2. Each processing temperature was maintained stable so that it was within an error range of $\pm 2^\circ$. For changes in the processing temperature after every two passes, the processing was conducted after the ECAP die achieved a constant temperature within $\pm 2^\circ$. The samples were kept at room temperature until the die achieved a stable processing temperature.

Following ECAP, the processed samples were cut in two directions: (i) perpendicular to the pressing direction to give the cross-sectional plane and (ii) parallel to the pressing direction and perpendicular to the upper surface of the billet to give the longitudinal plane. For both sections, pieces were prepared having mean thicknesses of about 0.3 mm.

To evaluate the effect of thickness on the hydrogen absorption, some additional experiments were conducted using commercial coarse-grained magnesium supplied by Baofull Trading Co. (Liuzhou, China) in the form of an ingot having an