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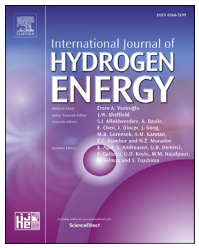

Effect of cold rolling on the structure and hydrogen properties of AZ91 and AM60D magnesium alloys processed by ECAP

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ABSTRACT

This investigation was conducted to evaluate the effect of cold rolling on the structure and hydrogen properties of two magnesium alloys, AZ91 and AM60D, after processing by equal-channel angular pressing (ECAP). The results show that the use of cold rolling after ECAP significantly increases the preferential texture for hydrogenation and increases the potential for the use of these alloys as hydrogen storage materials. The ECAP was performed through two different numbers of passes in order to give different grain sizes and both materials were subsequently cold-rolled through the same numbers of passes for a comparison of the hydrogenation absorption. It is shown that the hydriding properties are enhanced by an (0001) texture which improves the kinetics primarily in the initial stages of hydrogenation. The results demonstrate that optimum sorption properties may be acquired through a combination of fine grains and appropriate texture.

Introduction

It is now well established that increasing global warming due to gaseous greenhouse emissions is seriously affecting the environmental and political climates. Thus, it is becoming clear that there is a very significant demand for alternative fuels. Under these conditions, hydrogen arises as an option of clean energy in which water is the sole sub-product after burning. Despite this attraction, there are several

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shortcomings in the current technology for hydrogen storage and the solutions to these problems present serious challenges in terms of safety, energy density, efficiency and cost.

Considering their volumetric capacity and safety, metal hydrides appear to be adequate and magnesium is a strong candidate for a hydrogen storage system because it has a high hydrogen storage capacity (7.6 wt% hydrogen), reasonable cost and, in the form of bulk metal, a good safety record [1,2]. To date, a number of hydrides based on magnesium or intermetallic compounds [3] have been fabricated. Nevertheless, magnesium metal possesses unsatisfactory hydrogenation properties wherein the kinetics of hydrogenation–dehydrogenation are remarkably slow with the reactions occurring only at very high temperatures [4,5]. These poor kinetics are mainly due to the low diffusivity of hydrogen in the magnesium hydride [4,5] and in practice the presence of surface oxide layers may delay or even hamper hydrogen penetration into the bulk [6,7].

Several efforts have been dedicated to improving the kinetics through, for example, surface oxidation control [8,9], surface modification [10], particle size reduction [4–7,11–15] or the addition of different catalysts [7–9,16–22]. A recent review summarized the use of metal hydrides material for solid-state hydrogen storage applications [23].

It is reasonable to anticipate that a reduction in grain size to the nanometer range may substantially improve the diffusion and thermodynamic sorption properties in magnesium and this may be achieved most readily through the application of severe plastic deformation (SPD) [24–34] since SPD processing is capable of producing Ultra Fine Grained (UFG) or nanocrystalline materials from conventional coarse-grained bulk metals. This high microstructural refinement is achieved by deformation under a high hydrostatic pressure and at relatively low deformation temperatures [35–37].

The most common and efficient type of SPD is equal-channel angular pressing (ECAP) [36] in which numerous light metal alloys have been processed to achieve exceptional grain refinement. Furthermore, several studies report the use of ECAP in Mg and its alloys for the improvement of their sorption properties and their structural cycling stability where these superior properties are attributed both to the presence of defects in the structure and to the microstructural refinement [24,25].

Additionally, ECAP may produce textures that improve the H-sorption properties [31,33,34]. Thus, a recent study examined the influence of preferential orientation in the enhancement of kinetics in the sorption properties of Mg and Mg alloys and the (0001) texture was shown to be beneficial for the absorption of hydrogen in bulk materials processed by ECAP [31,33] and by a combination of ECAP and cold rolling [34]. However, in the two former studies [31,33] the grain size was about 1 μm and in the latter study it was in the range of tens of micrometers [34] so that it was difficult to specifically identify the effect of texture. In all the cases, the samples were left in air to analyze the effect of oxidation and therefore the sample thicknesses were different.

In the AZ31 [31] and ZK60 [33] alloys and commercial purity (CP) Mg [34], the (0001) preferential texture showed its potential by improving the kinetics (by 3.5 times faster on average), absorption and desorption capacities and the resistance to oxidation. For these materials, the times for activation were reduced on average from ~2250 min to ~660 min and the shapes of the first absorption curves were typical for a nucleation and growth diffusion-controlled reaction of the hydride phase.

The present investigation was initiated specifically to investigate the evolution of the hydrogen sorption kinetics of two magnesium alloys (AM60D and AZ91) with grain sizes in the submicrometer range. Different materials were produced with distinct amounts of a second phase and different misalignments of the (0001) plane with the (0001) pole. For these experiments, all samples had the same thickness and they were polished immediately prior to hydrogenation. These steps were taken to better evaluate the effect of grain size and texture, thereby demonstrating any effect of the synergism between them, together with the influence of any deleterious second phases on the sorption properties.

Experimental materials and procedures

Experiments were conducted using two commercial coarse-grained magnesium alloys, AM60D and AZ91, supplied by Rima Industrial S/A (Brazil) in the form of ingots. The initial grain sizes in the ingots were similar and ~900 μm. The chemical compositions of these alloys (in wt%) were 5.8%Al, 0.1%Zn and 0.3%Mn for AM60D and 8.4%Al, 0.4%Zn, and 0.3% Mn for AZ91 with the balance as Mg. Thus, it is possible to produce different amounts of second phase in the different samples and thereby analyze their effect on the hydrogenation behavior. The alloys were solution heat treated (24 h at 425 °C) and then hot extruded to reduce the initial grain size and improve the grain refinement by ECAP. After extrusion, round rods were produced and inspection showed the grain sizes in the as-extruded condition were ~25 and ~60 μm for the AM60D and AZ91 alloy, respectively.

Billets were cut from the rods with lengths of ~60 mm and these billets were processed by ECAP 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 $\Phi = 90°$ and an angle at the outer arc of curvature of the two parts of the channel of $\Psi = 20°$. These angles produce a strain of ~1.1 on each separate passage through the die [38] and repetitive pressings were performed using route Bc in which the billet is pressed through the die after rotation by 90° in the same sense (either clockwise or counterclockwise) between each pass [39].

All billets were pressed at 573 K but AM60D was pressed for 2 passes to give a total strain of ~2.2 and AZ91 was pressed for 8 passes to give a total strain of ~8.8. The temperature during processing was maintained constant to within ±2 K. Following ECAP, the processed samples were cut parallel to the pressing direction to reveal the longitudinal plane and then inserted between two AISI 304 stainless steel plates and subjected to 20 passes of cold rolling (CR) using a duo-reversible FENN conventional rolling facility with a 50% reduction in each pass. This procedure gave a final thickness of ~200 μm for all samples.

The hydrogen absorption properties were measured in a Sieverts-type apparatus where the samples were

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