Hydrogen desorption of Mg–Mg$_2$Ni hypo-eutectic alloys in air, Ar, CO$_2$, N$_2$ and H$_2$

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ABSTRACT

The hypo-eutectic Mg–Mg$_2$Ni system can be modified by trace elemental additions of Na which change the microstructure and the functional properties of the alloy. The modified microstructure results in improvements to the hydrogen storage properties. In alloys of optimal composition, it has been shown that the reversible storage of 6.5–7 wt% H$_2$ is possible at a rate of reaction that is realistic for industrial applications. This research investigates the release of H$_2$ in air under atmospheric pressure as well as under 0.2 MPa atmospheres of Ar, CO$_2$, N$_2$, and H$_2$. The release kinetics were characterised using in situ crystallographic phase transformation analysis obtained by synchrotron Powder X-ray diffraction (PXRD) at the Australian Synchrotron. The mole fraction of MgH$_2$, Mg, Mg$_2$Ni, and Mg$_2$NiH$_4$ was determined by Rietveld refinement using RIETAN-FP. It was found that the hydrogen release temperature largely depends on the atmosphere.

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1. Introduction

Concern regarding the environment, climate change and our unsustainable use of non-renewable energy sources continues to rise. Hydrogen is a clean energy carrier, and is therefore a means of storing, transporting and delivering energy on-demand from, for example, wind, solar or nuclear energy sources. Energy can be provided through combustion or in a fuel cell, with water vapour as the only emission. The need for a safe, efficient and cost-effective means of hydrogen storage has been identified as one of the key remaining barriers preventing wider use of hydrogen. The automotive sector is the key driver for hydrogen energy, however there are also other large users of hydrogen that can benefit from a new hydrogen storage solution. These include the chemical and metallurgical industries, and also applications such as remote and back-up power, mobile electronics and refuelling infrastructure. It is likely that the requirements for these other applications may differ from those of the automotive sector.

The traditional methods of hydrogen storage are in compressed gaseous or cryogenic liquid form. Safety concerns and weight, volume and processing inefficiencies are amongst the disadvantages of these technologies. Solid hydrogen storage is therefore generally considered to be the future solution. A multitude of different mate-

rials have been shown to store hydrogen [1]. These include metal hydrides, chemical hydrides and carbon-based materials.

A technique of trace element doping to modify the solidification mechanisms of the faceted/non-faceted eutectic Mg–Mg$_2$Ni alloy system has been developed [2]. It was demonstrated that the micro- and nano-structure of cast hypoeutectic Mg–Mg$_2$Ni alloys can be varied by trace additions of Na, Ca or Eu to the liquid prior to solidification. As a result, a reversible hydrogen absorption capability in excess of 90% of the theoretical value of 6.8 wt% under the absorption parameters of 350 °C and 1 MPa for 24 min and subsequent desorption at 0.2 MPa for 24 min after activation has been achieved [3]. The hydrogen absorption kinetics have been dramatically improved under realistic industrial conditions, and the alloys also show no sign of reduced capacity even after 200 hydride/dehydride cycles [4]. The solidification processing route results in a non-pyrophoric material that may be produced in large quantities at comparatively low cost [4]. The exact mechanisms of improved kinetics are still not understood, however, it is expected that the combination of the morphological change and trace element distribution along with possible changes in the density of crystallographic defects and the chemical nature of the modifying additions are all likely to contribute to the unique hydrogen storage properties of modified magnesium based hydrogen storage alloys [5]. It has been found that Mg–Ni alloys in machined 'chips' react with the external atmosphere (air/oxygen) at a slower rate than samples of higher specific surface area such as – powders which are produced by high energy ball milling under inert atmo-

spheres. However, regardless of the sample geometry, alloy surface oxidation of a few nm thickness of MgO is largely unavoidable. MgO may act as a barrier between Mg-hydride, hydrogen gas and Mg_2Ni since its dense crystal structure may limit the diffusion of H_2 molecules. As such, it is important to understand how exposure to oxygen, and other gasses, affects the hydride/dehydride process. This knowledge is also important in understanding how a compromised storage system (due to damage or failure) may affect practical performance or operational safety, as well as give insight into possible hydrogen separation or purification processes. Also, there is no existing research to predict the influence of different operating atmosphere such as Ar or CO_2. This research aims to increase the understanding of hydrogen release behaviour in Mg–Ni alloys under various atmospheric conditions.

To detect the types of phase changes that are occurring during hydride/dehydride reactions, and to clarify the mechanisms of hydriding/dehydriding of each phase, detailed in situ X-ray diffraction (XRD) experiments with heating and a gas flow control unit were conducted using a synchrotron beamline.

2. Experimental

2.1. Alloys and hydrogen up-take

The alloys investigated were based on the hypoeutectic Mg–14 wt%Ni composition. Alloys were produced by first melting industrial purity magnesium under an SF_6 atmosphere in an electric resistance furnace. Industry grade nickel powder was then added and stirred into the melt, and the melt was held for 30 min at 750 °C to

ensure full dissolution of the addition. Following this for selected samples, 1000 ppm of elemental Na was added to the melt. After homogenisation, the liquid was cast into cylindrical steel moulds preheated to 250 °C with cavity dimensions of diameter 20 mm and height 200 mm.

To prepare samples for hydrogen absorption they were machined to fine chips in air using a drill press. The unreacted chips were of the order of 0.1 mm thick and a few mm in length. Sorption testing was conducted using an automated gravimetric testing apparatus (Technosystem Ltd. PCTM-5000A) using laboratory grade high purity H_2 gas (99.98% purity). The apparatus levitates approximately one gram of sample material and directly records the weight change using a balance. The details of this machine are described elsewhere [6]. Activation properties were measured under a temperature of 350 °C and pressure of 2 MPa. The samples used in the subsequent experiments were 'hydrided', effectively holding hydrogen in solid form within the alloy.

2.2. In situ XRD experiments

The samples were crushed in an agate mortar to obtain powder for the X-ray diffraction (XRD) experiments. The samples were powdered and loaded into a quartz capillary sample cell (0.7 mm in diameter) in preparation for exposure to temperatures between 26 and 520 °C in the Powder Diffraction beam line within a gas flow cell at the Australian Synchrotron. XRD measurements were performed using 15 kV in the 2θ range 10–70° to obtain peak counts. Samples were kept at 26 °C (room temperature) for 10 min then 10 min for measurement (total 20 min) then heated using a hot-air stream from 26 to 500 °C at a rate of 6 °C/min. The samples were maintained at each experimental temperature for 10 min for stabilisation purposes followed by 10 min for data collection. The wavelength of each of the experiments are slightly different depending on the exact acceleration voltage, therefore for calibration, a Si standard (NIST640C) cell was measured at room temperature for 5 min for each condition. The phase identification of each component was estimated using X-ray peak data obtained from the sample at each temperature using the analysis software (EVA, Bruker-AXS, Germany) along with reference details for Mg and MgH_2. Rietveld refinement
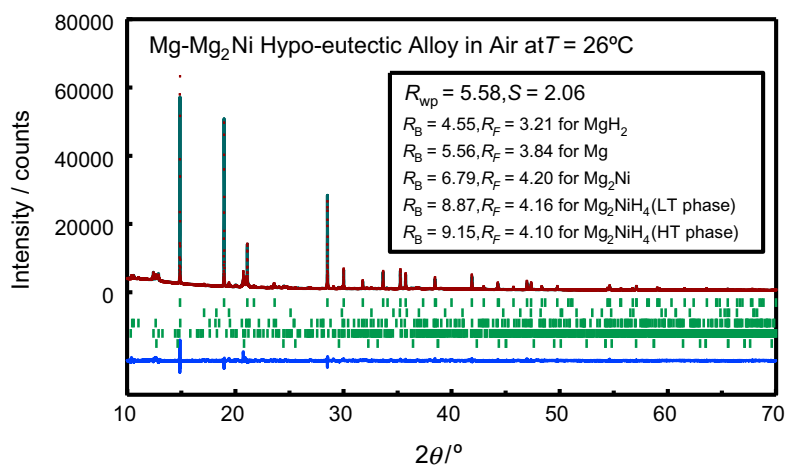

Fig. 1. An example of the Rietveld refinement for samples tested in-air, at 26 °C.

Table 1
Experimental conditions and the Rietveld refinement parameter R_{wp} for each condition.

Air, 0.1 MPa Wave length: 0.82706 (Å)		Ar, 0.2 MPa Wave length: 0.82729 (Å)		CO_2, 0.2 MPa Wave length: 0.82729 (Å)		N_2, 0.2 MPa Wave length: 0.82729 (Å)		H_2, 0.2 MPa Wave length: 0.77350 (Å)	
T (°C)	R_{wp}	T (°C)	R_{wp}	T (°C)	R_{wp}	T (°C)	R_{wp}	T (°C)	R_{wp}
26	5.58	26	5.82	26	5.82	26	5.82	30	8.84
248	5.67	280	5.25	220	3.82	220	8.52	202	6.64
280	5.65	310	6.50	235	3.62	235	9.23	230	8.23
311	5.71	340	8.16	265	3.33	265	9.90	260	6.90
341	5.94	370	7.63	295	3.21	295	9.13	289	8.75
371	6.45	400	7.84	320	3.57	320	9.80	329	8.04
400	9.06	430	8.28	350	4.06	350	12.08	359	9.74
430	9.49	460	9.15	380	3.67	380	15.09	380	11.61
460	8.85			410	3.80	410	14.7		
				440	4.05	440	15.26		
				480	4.63	480	15.66		
				500	4.72	500	13.42		