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Effects of compositions and mechanical milling modes on hydrogen storage properties

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by

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Declaration

I, Zhenguo Huang, hereby certify that the work presented in this thesis is original and was carried out at the Institute for Superconducting and Electronic Materials, the University of Wollongong, New South Wales, Australia. To the best of my knowledge and belief this thesis contains no material previously published or written by another person, except where otherwise acknowledgement and references have been made in the thesis. This work has not been submitted previously, in part or in whole, to qualify for any other degree.

Zhenguo Huang

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Abstract

The objectives of this work are to further enhance the hydrogen storage properties of some promising candidate materials and to investigate the impact of milling mode on the hydrogen storage properties.

$Mg_{1.9}Cu_{0.1}Ni_x$ (x = 1.8, 1.9, 2.0, and 2.1) alloys were synthesized using a high-energy Spex 8000 ball mill. The effects of nickel content on the thermal stability and on the hydrogenation of the alloys are discussed. It was found that the nickel content affects the recrystallization of the predominately amorphous alloys, and as a result, affects the formation of Mg_2NiH_4.

The $Mg_{1.9}Cu_{0.1}Ni_x$ (x = 1.8, 1.9, 2.0, and 2.1) alloys were also investigated with respect to the electrochemical performance. Ni was found to be effective in maintaining the reversibility and discharge capacity of the alloy electrodes.

With the aim of improving the hydrogen cycling properties of magnesium, two types of catalysts were studied. In order to investigate the differences in the catalysis arising from the respective valence states of a transition metal in the oxides, two types of iron oxides, i.e. Fe_2O_3 and Fe_3O_4, were ball milled with Mg in hydrogen using the low-

energy shearing mode of a Uni-Ball-Mill 5, as discussed below. The hydrogen cycling properties of the ball-milled composites were studied. There was little difference in the hydrogen absorption and desorption kinetics of the two composites, which is presumably due to the reduction reaction occurring during hydrogen cycling.

Three carbon allotropes with very different structure, i.e. graphite, carbon black, and multiwalled nanotubes, were also tried as catalysts. Although the graphitic structure experienced the most disruption, graphite showed a noticeable catalytic effect by improving the hydrogen absorption and desorption kinetics of Mg. The possible origins of the enhancement are probed.

In order to investigate the effects of milling energy on the hydrogen storage properties, a special mill was used, the Uni-Ball-Mill 5, which allows the control of the movements of the grinding balls. Two milling modes, a high-energy impact mode and a low-energy shearing mode can be realized through the adjustment of the attached external magnet.

Graphite, a very interesting material for hydrogen storage, was studied in particular. The influence of the different milling modes on the hydrogen absorption and storage capacity is discussed. It was found that there is a strong correlation between the composition of the milled graphite and the milling mode. As a result, different thermal behaviors were observed for the respective samples.

Boron was milled in hydrogen using both low-energy shearing and high-energy impact. The amount of hydrogen trapped during milling is dependent on the milling mode. The thermal behaviors were also different for the respective samples.

Key words: hydrogen storage, ball milling, nanocrystalline, graphite, magnesium, boron, nickel, carbon, catalyst