INFLUENCE OF NANOSTRUCTURED ADDITIVES $(Fe,Co,Ni)_xO_y$ ON THE MECHANOCHEMICAL HYDROGENATION OF Mg

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Nanostructured $(Fe, Co, Ni)_xO_y$ additives were synthesized from Fe-Co-Ni-Al alloys by leaching. The Mg-based composites were obtained by reactive ball milling in a hydrogen atmosphere. This report presents the experimental results to show the catalytic effect of nanostructured additives on the mechanochemical synthesis of Mg-based hydride composites. Their hydrogen sorption properties will be compared. Hydrogen generation in the process of hydrolysis reactions in $MgCl_2$ solutions will be presented for the selected samples.

Keywords: magnesium hydride, hydrogen sorption, hydrogen generation, hydrolysis

Magnesium hydride is a promising material for hydrogen storage [1] and generation due to its high hydrogen capacity (7.6 wt %) and low cost. However, its practical use is limited by slow sorption-desorption kinetics, high operating temperatures and pressures (>300 °C, 5…10 MPa), activation challenges, and poor cyclic stability. Mechanochemical ball milling with catalytic additives [2, 3] has proven effective in producing nanostructured MgH_2-based composites with uniformly dispersed catalysts and a high density of structural defects, which enhance sorption rates and lower activation barriers.

This report will present the experimental results about the synthesis of nanostructured $Fe_{100-x}(Co, Ni)_xO_y$ additives by leaching method [4]. The influence of these additives on the mechanochemical synthesis of hydride composites and their hydrogen sorption capacities will be demonstrated and discussed. It was shown that the use of this catalytic additives is an effective way to obtain composites based on MgH_2 with dual applications: for hydrogen storage and for obtaining hydrogen by hydrolysis.

The starting components for the preparation of hydride composites were magnesium powder (particles size 0.08…0.125 mm, 99.0%) and 10 wt% Fe, Co, Ni, $Fe_{100-x}Co_xO_y$ and $Fe_{100-x}Ni_xO_y$ powders obtained by leaching. The starting materials (Fe, Co, Ni and Al, 99.5%) were alloyed by arc melting to obtain aluminides. The resulting alloys were mechanically ground in a pounder and treated with 5 mol/l NaOH solution at 20°C. Then, the precipitate was washed three times with an alkaline solution at 70°C until the gas release is completely stopped. The resulting precipitate was washed 5 times with distilled water until a neutral pH value was reached and dried at room temperature.

The composites were prepared by reactive ball milling in hydrogen using Fritsch Pulverisette-6 planetary mill. Composites were analyzed using XRD

(Rietveld refinement) and SEM-EDS. Crystallite size was calculated using the Scherrer equation. The kinetics of hydrolysis was studied under pseudoisothermal conditions with using distilled water and $MgCl_2$ solutions of different concentrations.

It was demonstrated that (Fe, Co, Ni)$_x$O$_y$ additives shortened hydrogenation time and modified powder microstructure. The crystallite sizes of the main phases in the $Fe_{100-x}Co_xO_y$ were in range from 3.3 to 6.6 nm, and for $Fe_{100-x}Ni_xO_y$ – from 2.8 to 4.3 nm as well. These results indicate that the powders obtained by leaching are nanostructured. Phase analysis of all studied composites revealed the formation of a mixture of two magnesium hydride modifications: α-MgH_2, γ-MgH_2 and MgO (5…8 wt%) were also detected in all composites. The presence of pure magnesium correlates with the hydrogenation results: 15-20 h of milling doesn't result in complete conversion of magnesium to hydride. The synthesized composites were tested in hydrolysis reactions. Hydrogen generation in $MgCl_2$ solutions will be presented for the selected samples.

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