

## Quaternary Mg-based Transition-Metal Complex Hydrides Produced by Reactive Milling

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In the past, we employed ball milling in a reactive H<sub>2</sub> (or D<sub>2</sub>) atmosphere with the aim of exploring if: i) different transition-metal complex anions, such as [FeH<sub>6</sub>]<sup>4-</sup> and [CoH<sub>5</sub>]<sup>4-</sup>, can coexist in the same crystalline structure and ii) the presence of [FeH<sub>6</sub>]<sup>4-</sup>, [CoH<sub>5</sub>]<sup>4-</sup>, or [NiH<sub>4</sub>]<sup>4-</sup> anions can stabilize the [MnH<sub>6</sub>]<sup>5-</sup> complex, which is observed in Mg<sub>3</sub>MnH<sub>7</sub> prepared at high pressure (2 GPa) and temperature (800 K) [1]. It was found that the quaternary hydride Mg<sub>2</sub>(FeH<sub>6</sub>)<sub>0.5</sub>(CoH<sub>5</sub>)<sub>0.5</sub> forms during reactive milling, confirming that the two different transition metal complex anions [FeD<sub>6</sub>]<sup>4-</sup> and [CoD<sub>5</sub>]<sup>4-</sup> can coexist in the same crystalline structure [2].

In this work, we focus on the Mg-Ni-Co system. Elemental powder mixtures were ball milled in H<sub>2</sub> (or D<sub>2</sub>) at about 50 bar. The pressure and temperature of the vial were followed throughout the milling process and revealed the occurrence of mechanically-activated hydrogen absorption process within the first 10 hours of milling. The structural characterization of the powders was carried out by powder X-ray and neutron diffraction analysis, as well as by vibrational spectroscopy (i.e. IR). The thermal stability and the hydrogen sorption behaviour were investigated by differential scanning calorimetry and thermal programmed desorption. In-situ powder diffraction was carried out to follow the structural changes upon heating and hydrogen desorption.

The quaternary hydrides generally adopt a K<sub>2</sub>PtCl<sub>6</sub>-type structure (space group *Fm3m*) [2,3]. However, diffraction analysis indicates that a tetragonal phase forms in the Mg-Co-Ni-D system. Experimental data suggest that the thermal stability is governed by the relative content of the complex hydride. In addition, solubility gaps in the disordered solid solutions of the transition-metal complex anions in the Mg<sup>2+</sup> sub-lattice were observed.

[1] M. Bortz, B. Berthel, K. Yvon, E.A. Movlaev, V.N. Verbetsky, F. Fauth, J. Alloys Comp. **279** (1998), L8-L10.

[2] S. Deledda, B.C. Hauback, Nanotechnology, **20** (2009) 204010

[3] A. Baum, M. Meyer and L. Mendoza-Zelis Int. J. Hydrog. Energy **33** (2008) 3442-3446.