Composites of magnesium hydride with catalytic nanoadditives

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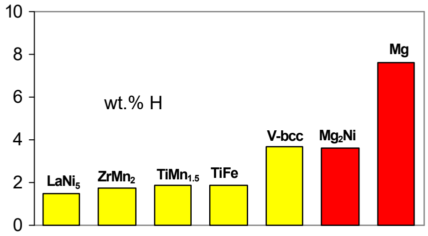
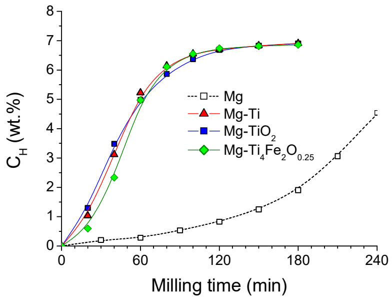
❑ Practical use of magnesium and its alloys in hydrogen storage systems is limited by slow kinetics and elevated temperatures (>300°C) of H_2 absorption-desorption. A lot of recent studies were devoted to the enhancement of these parameters, including preparation of magnesium by reactive ball milling in hydrogen medium (RBM) and modification by different additions, e.g. oxides, intermetallic compounds (IMC), graphite etc [1].



❑ In our previous work we have studied the properties of Mg-based composite materials with two different types of oxides and suboxides: TiO_2 [2], $Ti_4Fe(Ni)_2O_x$ and Zr_3NiO_x [3]. Substantially improvement of hydrogen absorption-desorption properties was demonstrated for the Mg–$Ti(Zr)_4Fe_2O_x$ composites prepared by RBM.



❑ The aim of this work was to study the hydrogen absorption-desorption properties of Mg-based composite materials with the $Dy_{0.5}Nd_{0.5}FeO_3$ oxide as nanoadditive.

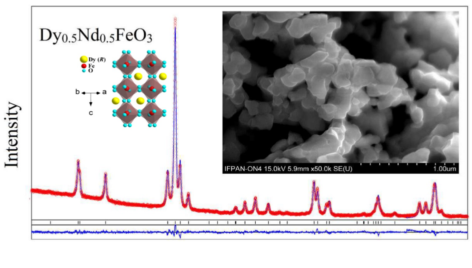
Materials: Mg (99.8 %; ~0.5 mm); intermetallic alloys (arc-melted, annealed); rare earth oxides R_2O_3, $Fe(NO_3)_2x9H_2O$.

Reactive ball milling
Fritsch 6 Pulverisette mill.
milling conditions: P_{H2}=20 bar;
500 rpm; BPR = 60:1

Phase analysis: powder XRD (Cu-Kα), FULLPROF software.

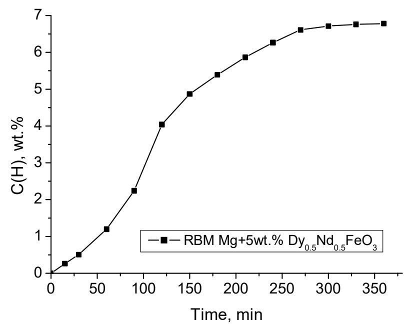
Thermal desorption spectroscopy (TDS): linear heating (2 °C/min.) in a dynamic vacuum from room temperature up to 350-400 °C

❑ Preparation of nanocrystalline powders of $Dy_{0.5}Nd_{0.5}FeO_3$ a low-temperature sol–gel citrate method was used. Rare earth oxide Dy_2O_3, as well as $Nd(NO_3)_2{\cdot}6H_2O$ and $Fe(NO_3)_2{\cdot}9H_2O$ were used as an initial reagents. Neodymium and iron nitrates were dissolved in distilled water, whereas nitrate solutions of Dy prepared by dissolving of oxide in HNO_3. Appropriate amounts of corresponding solutions were mixed on magnetic stirring for 30 min, after that water solution of citric acid (CA) and ethyleneglycol (EG) were sequentially added to the reaction mixture under continuous stirring. The foamy product obtained was finally calcined at 1273 K for 2 h. In such a way single phase nanocrystalline powders of $Dy_{0.5}Nd_{0.5}FeO_3$ were obtained with average grain size of 86 nm [4].

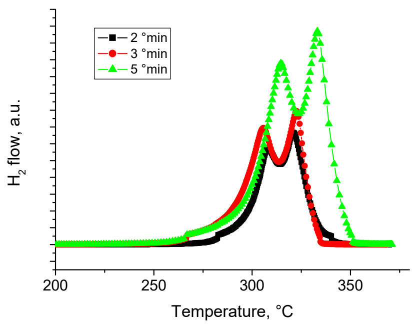


❑ X-ray powder diffraction examination revealed that $Dy_{0.5}Nd_{0.5}FeO_3$ sample synthesized by solid state method adopt orthorhombic perovskite structure isotypic with $GdFeO_3$ (space group Pbnm).

❑ Preparation of magnesium hydride composite by reactive ball milling in hydrogen medium (RBM) (2 MPa H_2 pressure) and modification by additions 5 wt.% nanocrystalline powders of $Dy_{0.5}Nd_{0.5}FeO_3$.



Dependences of the amount of absorbed hydrogen on the time of reactive milling



Plots of vacuum thermal desorption at different heating rates

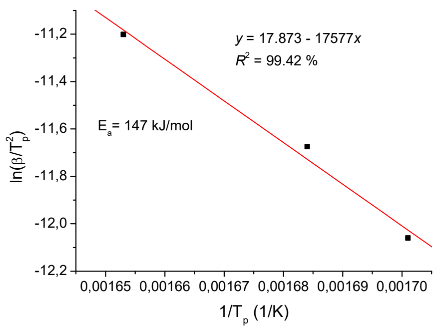
❑ XRD demonstarted that mechanochemical hydrogenation results in complete transformation of Mg into two modifications of MgH_2. Analysis of hydride profile parameters indicates that the size of crystallites is <10 nm.

❑ The first cycle of thermal desorption composite 95wt.% Mg+5wt.% $Dy_{0.5}Nd_{0.5}FeO_3$ is one-stage, maximum hydrogen evolution at 315° C.

❑ At temperatures above 200 ° C, the absorption rate of hydrogen for composite is high - complete saturation with hydrogen (6.5-6.8 wt.% H) occurs within 1 min.

❑ After re-hydrogenation of the composites, the desorption peak position for the 95wt.% Mg+5wt.% $Dy_{0.5}Nd_{0.5}FeO_3$ composite does not change, with hydrogen peaking being split.

❑ The calculated desorption activation energy of hydrogen is 147 kJ / molH_2.



Kissinger curve of hydrogen desorption from the 95wt.% Mg+5wt.% $Dy_{0.5}Nd_{0.5}FeO_3$ hydride composite

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SUMMARY

❑ **Grinding of magnesium composites has revealed the merits of mechanochemical hydrogenation: first, magnesium hydrogenation rate is higher than that with other methods; second, no activation is required; third, 100% Mg ->MgH_2 transformation is reached; and fourth, nanocrystalline material with particles smaller than 0.5 µm is formed.**

❑ **The difference between the desorption activation energies for pure magnesium hydride and the nano-particles composite (TiO_2) is about ~ 200 kJ / mol H_2. However, the $Dy_{0.5}Nd_{0.5}FeO_3$ nanopowders with perovskite structure did not show the expected improvement.**