

Kinetic behavior of MgH₂-transition metal composites: towards hydrogen storage

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Hydrogen as an energy vector represents great potential, due to its high gravimetric density and low mass, as well as the fact that combustion does not emit harmful chemical byproducts. Hydrogen has the highest energy density per unit mass compared to any other fuel but a rather low energy density per unit volume. Further, hydrogen storage is a key technology for developing a hydrogen and fuel cell-based economy [1]. Metal hydrides as alternative hydrogen carriers have a wide range of performance parameters such as operating temperature, sorption kinetics, activation conditions, cyclic options, and equilibrium hydrogen pressure. These parameters can be improved or adjusted to meet the technical requirements of different applications. The most commonly used method for hydride destabilization is nanostructuring by mechanical milling which leads to a reduction in the particle and crystallite size of the MgH₂ powder. Nanostructuring is often combined with catalyst addition and composite formation [2,3]. The most of research is focused on the morphological, structural, and thermodynamic effects typical for long milling times, while in this work we have followed the changes taking place under short milling times. The thermal stability of magnesium hydride is related to - changes in the crystallites and powder particle size. The analysis also considered the changes in activation energy. MgH₂-M composites were prepared by mechanical milling of the as-received MgH₂ powder (Alfa Aesar, 98% purity) with the addition of 2 and 5 wt.% of M (M= V, W, Mo). Mechanical milling was performed in a SPEX 5100 Mixer Mill using 8mm diameter milling ball. Samples were milled for 15-45 minutes under the inert atmosphere of argon and a ball-to-powder ratio 10:1 Figure 1. shows the kinetic curves obtained for composites with 5wt% of vanadium. To investigate the desorption process in detail, different models of solid-state kinetics were used as implemented in the code developed in our group. The rate-limiting step of the desorption reaction was determined using the iso-conversional kinetic method due to better accuracy of obtained apparent activation energies. As shown in Table 1 a decrease in apparent activation energies has been observed. It is obvious that the sorption kinetics is affected by material preparation because the reactivity of magnesium with

hydrogen is strongly modified by changes in several surface parameters that govern the chemisorption, the dissociation of molecular hydrogen, and hydride nucleation.

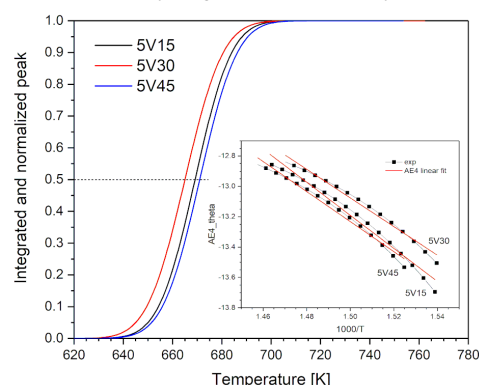


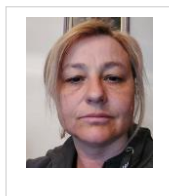
Figure 1. Kinetic curve for MgH₂-5% V nanocomposites mechanically milled for 15, 30 and 45 minutes. Inserted figure: From $\ln g(\theta) = f(1/T)$ the best fit of experimental data is obtained for nucleation.

Table 1. Thermodynamics and kinetics parameters of MgH₂-V composites

Sample	HT (°C)	E _{app} (kJ/mol)	VHT (°C)	E _{ACT} (kJ/mol)
5V15	396.12(6)	90(1)	469.9(6)	60.3(2)
5V30	392.01(4)	78(1)	452.4(7)	61.5(7)
5V45	398.03(4)	82(1)	-	-

References

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