Synthesis, structural characterization and H-sorption properties of Mg$_2$FeH$_6$-based nanocomposites processed by reactive milling

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Abstract – The direct synthesis of magnesium complex hydride Mg$_2$FeH$_6$ was carried out by high-energy ball milling under hydrogen atmosphere (reactive milling) from 2Mg – Fe mixtures. The starting Fe was used in the conditions granulated and as powders and theirs effects on the formation and H-sorption properties are reported. Transition metals fluorides were also added as additives and theirs effects on H-sorption properties of Mg$_2$FeH$_6$ are presented. Structural analysis was carried out by X-ray diffraction (XRD), transmission and scanning electron microscopy (TEM and SEM), and the thermal analysis by differential scanning calorimetry (DSC).

Magnesium is an attractive material to hydride forming due to several advantages, such as its high gravimetric density of H$_2$ (7.6 wt. %), its abundance on the Earth and its low cost. However, its main drawbacks are its high stability and low hydrogen sorption kinetics. In this context, the magnesium complex hydrides appear as an interesting alternative, compromising hydrogen capacity for better absorption – desorption kinetics. In this compounds group, the Mg$_2$FeH$_6$ presents the highest know volumetric density of 150kg of H$_2$/m$^3$, nevertheless, as Mg and Fe do not form any intermetallic compound, the hydride phase is difficult to synthesize. At first, sintering processes of Mg and Fe powders under H$_2$ were used to obtain Mg$_2$FeH$_6$ [1], but high pressures, elevated temperatures and several days were required.

A processing route to diminish these severe conditions is the high-energy ball milling of precursory metallic powders, furthermore, a direct synthesis of hydride can be obtained when a hydrogen pressure is applied (Reactive Milling – RM) [2]. This mechanically activated method can reduce the grain and particles sizes to the nanometric scale and improve H-sorption kinetics of hydrides.

In the present work, the compound Mg$_2$FeH$_6$ was synthesized from a 2Mg+Fe mixture in a single process by reactive milling (RM) under hydrogen atmosphere at room temperature. The complex hydride was prepared from Mg powder and granulated (1-2 mm) or powdered Fe using a planetary mill. Transition metals fluorides were added to study theirs effects on H-sorption properties of Mg$_2$FeH$_6$.

The phase evolution during different milling times (from 3 to 72h) was investigated by X-ray diffraction (XRD) technique. The dehydrogenation behavior of the so-formed metal hydride was investigated by differential scanning calorimetry (DSC). Scanning (SEM) and transmission electron microscopy (TEM) have been carried out to correlate the structural characteristics of the as-milled materials to the decomposition behaviors.

The use of powdered iron as starting material promoted conversion to complex hydride at shorter milling times than when granulated iron was used. On the other hand, the DSC analysis show a decrease in temperature of release of hydrogen for the as-milled 2Mg+Fe (Fe granulated) mixtures. Moreover, in milling time longer than 48 hours, Mg$_2$FeH$_6$-based nanocomposites exhibited an increase in the temperature of hydrogen desorption, even containing higher proportions of Mg$_2$FeH$_6$ and lower agglomeration level. This behavior is attributed to a catalytic effect of the Fe on the mixture. Similar catalytic effect was reported to MgH$_2$ [3], where Fe had an effect on the thermal stability of MgH$_2$ and acted as catalyst in the desorption process.

References