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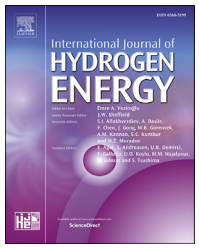

Structural characterization and hydrogen storage properties of MgH_2–Mg_2CoH_5 nanocomposites

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ABSTRACT

Mixtures of XMg–Co containing different amounts of Mg (X = 2, 3 and 7) were reactive milled under hydrogen atmosphere. 2Mg–Co only formed the Mg_2CoH_5 complex hydride, while the mixtures 3Mg–Co and 7Mg–Co formed different contents of Mg_2CoH_5 and MgH_2. Their structural features and hydrogen storage properties were analyzed by different techniques. *In-situ* synchrotron X-ray diffraction, combined with thermal analysis techniques, (differential scanning calorimetry, thermal gravimetric analysis and quadrupole mass spectrometer) was carried out to observe the behavior of the MgH_2–Mg_2CoH_5 mixtures during the first H-desorption. It was found that the presence of the Mg_2CoH_5 complex hydride has a beneficial effect on the first H-desorption of the MgH_2. Additionally, after first desorption, conventional hydrogenation under high pressure and high temperature of 3Mg–Co and 7Mg–Co samples led to the formation of the $Mg_6Co_2H_{11}$ complex hydride. The presence of $Mg_6Co_2H_{11}$ considerably impaired the desorption properties of the nanocomposites.

Introduction

MgH_2 is a promising material for hydrogen storage application because of its considerably high hydrogen storage capacity (7.6 wt.%). Moreover, Mg is a quite abundant element, relatively cheap, and its density is quite low (1.738 g/cm^3), making it an interesting candidate for mobile applications. However, some characteristics concerning hydrogen storage properties of the MgH_2, such as the high temperature needed for H-absorption/desorption (typically above 400 °C for microcrystalline structures) and slow hydrogen absorption/desorption kinetics, are limiting factors for its large usage.

Several approaches have been studied aiming at improving the H-storage properties of the MgH_2, such as the synthesis of MgH_2 with nanocrystalline structures either by high energy ball milling and reactive milling [1–4]; refinement of the

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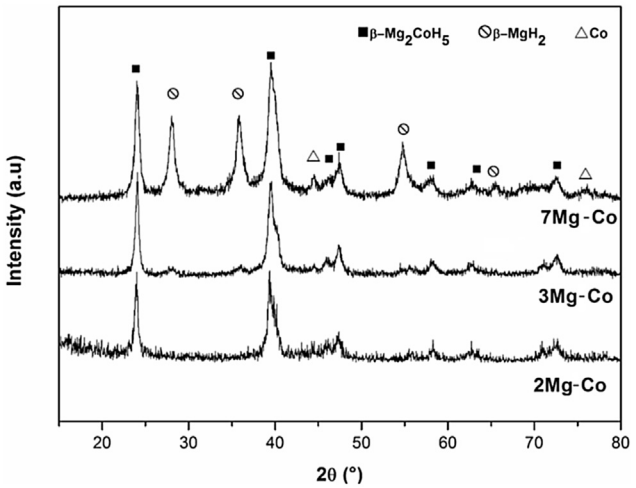

Fig. 1 – XRD patterns of the as-reactive milled 2Mg–Co, 3Mg–Co and 7Mg–Co nanocomposites.

hydride microstructure by severe plastic deformation techniques [5–11]; addition of catalyst or additive elements (for instance, transition metals, fluorides, oxides, etc) [12,13]; and combinations of the previous approaches [10,11,14–21].

Besides the MgH_2 phase, Mg combined with transition metals can form complex hydrides, such as Mg_2NiH_4, Mg_2CoH_5 and Mg_2FeH_6, which are of considerable interest for hydrogen storage because of their high volumetric capacity of hydrogen (97, 125 and 150 g/L, respectively).

Asselli et al. [22] demonstrated that the hydrogen storage properties of MgH_2–Mg_2FeH_6 nanocomposites synthesized by reactive milling are significantly enhanced in comparison with both pure hydrides (also reactive milled). However, a reduction of the hydrogen capacity of the system accompanies the improvement of the hydrogen storage properties.

Similarly to Mg_2FeH_6, the formation of the Mg_2CoH_5 complex hydride during reactive milling takes place in two steps. Firstly, Mg reacts with hydrogen forming a mixture composed of MgH_2 and Co. Secondly, MgH_2 reacts with Co and hydrogen generating Mg_2CoH_5 [23]. However, it has been reported that, for the same milling parameters, the time needed to complete the reaction of the Mg_2CoH_5 is considerably shorter when compared with the Mg_2FeH_6 [23,24]. In addition, the onset temperature for desorption of the reactive milled Mg_2CoH_5, evaluated by DSC, is around 230 °C whereas for the Mg_2FeH_6 this temperature is around 280 °C [23,24]. Moreover, the nanocrystalline Mg_2CoH_5, synthesized by reactive milling, presents considerably different hydrogen desorption behavior when compared to the Mg_2FeH_6.

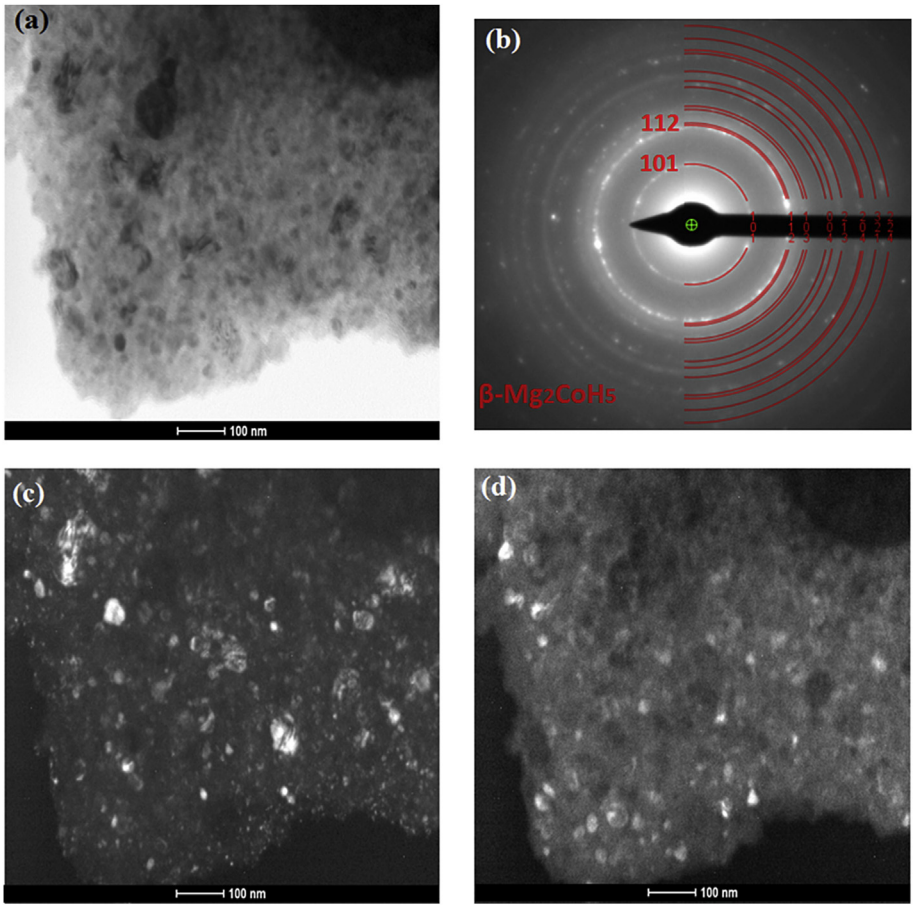

Fig. 2 – TEM images of the as-milled 3Mg–Co. (a) Bright field, (b) Electron Diffraction Pattern (EDP), (c) Dark field using the 101 ring reflections and (d) Dark field using 112 ring reflections of the β-Mg_2CoH_5.