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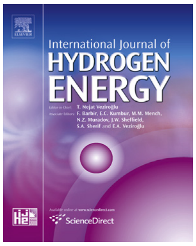

In operando study of TiVCr additive in MgH_2 composites

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ABSTRACT

We report an *in operando* study of the hydrogenation and dehydrogenation of MgH_2–TiVCr composites. The experiment was performed by means of *in situ* synchrotron XRD in order to get insights on the influence of the TiVCr additive on the sorption properties of the MgH_2 based composite. Sequential Rietveld refinement analysis was performed to investigate the structural changes of MgH_2 and of the additive during hydrogenation and dehydrogenation processes. Significant non-monotonic changes in the lattice volume of the $TiVCrH_x$ solid solution were observed concomitantly to the MgH_2 formation or decomposition. These volume changes are assigned to the variation of the hydrogen content in $TiVCrH_x$. These results provide evidence of cooperative effects between the H_2 storage material and the additive.

1. Introduction

Hydrogen is considered as one of the key components of sustainable development owing to high energy density (142 MJ kg^{-1}) and low environmental impact. Introducing this energy vector as a storage means for the leveling-out of power demand over time fulfills the necessity of saving energy, in particular in the case of renewable energy produced by intermittent sources. One of the major issues is to store H_2 safely and efficiently in a reversible hydride. Among the huge number of candidates for solid state storage, magnesium hydride has been studied for decades because of its high hydrogen capacity (7.6 wt.%), the abundance and relatively low cost of Mg, and the non-toxicity to humans and environment [1–4]. The weakness of MgH_2 is a relatively high thermodynamic stability ($\Delta H = -74.5$ kJ/mol) [5] and a slow kinetics of hydrogen sorption. On-going researches directed at the destabilization of magnesium hydride are based on the formation of less thermodynamically stable hydrides of Mg-rich intermetallic compounds [6–9] and on the nanoconfinement of MgH_2 in porous hosts [10,11]. Regarding the kinetics, significant enhancements have been observed on ball milled composites [12–14] with a large variety of additives, such as transition elements [15,16], intermetallic compounds [2,16–18], borides [19], oxides [20–22], and halides [23,24]. The key role of the microstructure of magnesium based

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composites was first reported by Gross et al., who demonstrated that both the reduction of the grain size resulting in an enlarged surface area, and the high degree of dispersion of the additives which act as a catalyst are responsible for enhanced hydrogenation and dehydrogenation kinetics [14,25]. In the case of the Mg/MgH_2 reaction, where the rate limiting step is the metal/hydride interface motion [26], the particles size reduction improves the sorption kinetics through an increased number of hydride nucleation sites located on the accessible surface. Moreover, the presence of the additives is responsible for a lowering of the dissociation energy of the hydrogen molecules and the enhancement of the diffusion rate of dissolved hydrogen atoms along the grain boundaries between Mg and the additives [18,25,27]. Reule et al. reported that optimized composites, in terms of high capacity and fast sorption kinetics, present a typical microstructure where the additive particles are covered by an MgH_2 thin film. In this case, the catalytic effect is mainly due to the MgH_2–additive interface [18]. Magnesium hydride composites with Ti–V based body centered cubic (bcc) alloys as an additive have been successfully implemented in large scale tanks [28,29]. In this type of composites, Yonkeu et al. showed that the hydrogenation kinetics is controlled by a three-dimensional growth of the hydride phase and the diffusion of hydrogen through the hydride phase. In contrast, the dehydrogenation kinetics is governed by the bulk/surface nucleation and two-dimensional growth of the magnesium phase with a constant velocity of the Mg/MgH_2 interface [30]. Yu et al. suggested that the hydrogenated bcc alloy showed superior catalytic properties compared to the quenched bcc alloy in magnesium composites because the hydrogenation induces the formation of micro/nanosized additive particles [31] which greatly enhance the hydrogen atomic diffusivity. Thus, in order to provide insight into the catalytic role of the bcc additive in MgH_2 composites, previous studies have addressed microstructural [18], kinetical [30,32] and thermodynamical issues [16]. In this paper we investigate, *in operando*, the structural evolution of a TiVCr–MgH_2 composite upon hydrogenation and dehydrogenation. The structural and chemical evolution of the composite was studied by using the time resolved and fast acquisition Synchrotron X-Ray Diffraction (Sync-XRD) on the ID15 beamline at ESRF in Grenoble. Structural refinement of the data was performed by means of sequential Rietveld analysis in order to determine the instantaneous behavior of both MgH_2 and the TiVCr additive.

2. Experimental details

The powders, MgH_2 (purity 98%) and 10 wt.% TiVCr ($Ti_{0.5}V_{1.9}Cr_{0.6}$ + 4 wt.% Zr_7Ni_{10} activating phase) were milled under Ar atmosphere in a Fritsch Pulverisette 5 planetary mill. WC balls and jars were used with a ball-to-powder ratio close to 1:20. A milling period of 60 min was applied with a rotational speed of 200 rpm. The handling of all powders was done in a glove box containing argon with O_2 and H_2O contents <1 ppm. *In situ* Sync-XRD measurements were performed at high energy (~90 keV) on the ID15 beamline at ESRF. The composite was introduced under the shape of compressed pellets in a 3 mm inner diameter sapphire capillary. The capillary was connected to a dedicated High-Pressure High-Temperature gas loading system fitted to an X-ray transparent furnace. The latter enables accurate sample temperature control during the diffraction experiment. The Pixium 4700 flat-panel detector was used with an exposure time of 1.6 s at a frequency of 5 s. A lead mask was specially designed and applied on the detector surface to shield the diffraction signal of the sapphire capillary. The beam size illuminating the sample was 0.3 × 0.3 mm^2. The exact wavelength, $\lambda = 0.1423(31)$ Å, was determined by using CeO_2 as a calibration reference. The diffraction pattern was obtained by radial integration of the raw image corrected from polarization and detector efficiency.

Fig. 1 describes the values of temperature and pressure during the *in operando* experiment. The experiment was composed of the following 4 sequences: (1) dehydrogenation of the fresh composite. The sample was heated up on a ramp of 20 °C/min up to 470 °C under a 2 bar argon flow (from pattern #1 to pattern #128). (2) Rehydrogenation at constant pressure and decreasing temperature. A pressure of 10 bar of hydrogen was applied in the fixed volume of the capillary and the tubing toward it and the sample was cooled down at a rate of 5 °C/min (from pattern #129 to #1240). (3) Dehydrogenation at constant pressure and increasing temperature. Once the temperature of 100 °C was reached, the atmosphere pressure was set to a continuous 2 bar Argon flow and the temperature was raised at a rate of 5 °C/min (from pattern #1241 to #2172) and, (4) cooling down of the dehydrogenated sample. Once the

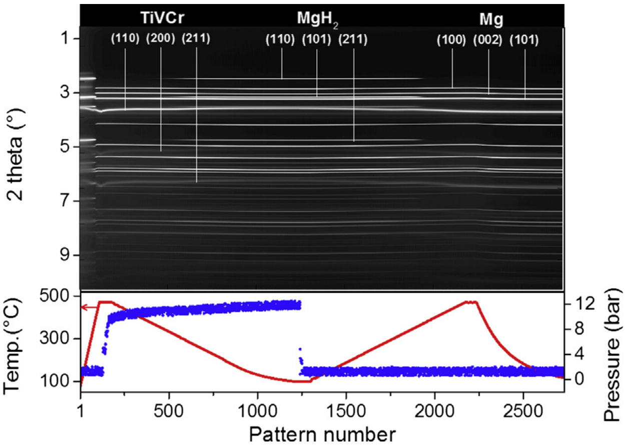

Fig. 1 – *In situ* Sync-X-Ray diffraction performed on TiVCr–MgH_2 composite at the wavelength of $\lambda = 0.1423$ A, the brighter the higher diffracted intensity (top) and experimental conditions (bottom). The sample temperature and pressure evolution are plotted as red line and blue dot respectively. Due to an inopportune synchrotron beam loss, the diffractograms collection was interrupted at pattern #128 during 30 min during the first high temperature dwell (meanwhile the temperature was maintained at 470 °C and the atmosphere was an Argon flow). It is the reason why the first dehydrogenation of the composite is only partially represented in the contour plot diagram. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)