Investigation of Hydrogen Desorption Mechanism in MgH_2-Nb Nanocomposites

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Introduction

Metal hydrides are a promising solution to the storage problem for hydrogen-energy applications since they store hydrogen at low pressure yet have volumetric densities comparable to liquid hydrogen.[1] Another advantage is the fact that hydrogen is released through an endothermic process making hydrogen storage in metal hydrides inherently safe. Magnesium hydride is a particularly interesting prospect due to its high storage capacity per unit weight but it has slow hydrogen sorption kinetics. However, the use of nanocrystalline metal hydrides has brought great improvement.[2] It has been shown that the addition of a low-temperature hydride (i.e., hydride that can reversibly absorb hydrogen at temperatures lower than 80°C) enhances the hydrogen sorption kinetics.[3] However, the exact role of the additive and the mechanism by which hydrogen flows in and out of the hydride still remains unclear.

This report summarizes our investigation of the structure evolution of MgH_2-5at.%Nb nanocomposites during hydrogen desorption using time-resolved x-ray scattering. These results have recently been published in *Phys. Rev. B*.[4]

Methods and Materials

These measurements were performed using a spectrometer optimized for time-resolved x-ray diffraction installed on the side station of the 8-ID beamline. The 2-circle goniometer is equipped with a photodiode linear array detector, which can be used for acquiring powder diffraction measurements as fast as every 5 ms over a range of as much as 20° of 2θ. The setup also allows one to easily switch from the linear array detector to a sensitive point detector in order to measure conventional 2θ powder diffraction patterns. The nanocomposite studied had a composition of MgH_2-5at.%Nb made from a mixture of pure magnesium hydride and niobium powder mechanically milled in a Spex 8000 shaker mill for 20 hours under argon atmosphere.[3] The milled powder was cold pressed into a 1-mm-thick pellet and mounted in a furnace equipped with a Be window covering approximately 200° in 2θ. The furnace was pumped down to a base pressure of 1×10^{-6} Torr prior to heating the sample. The samples were probed with monochromatic x-rays coming off a diamond (111) monochromator at 7.66 keV with a flux of about 5×10^{12} photons per second for a storage ring current of 100 mA.

Results and Discussion

Figure 1 illustrates a typical time-resolved x-ray scattering data set. Figure 1a shows a gray-scale contour plot of the x-ray scattering intensity while the sample was being heated, and Fig. 1b shows the sample temperature as a function of time. The different peaks corresponding to the start and end product are labeled below and above the graph, respectively. Dehydrogenation of magnesium hydride starts at ~370 s, when temperature has reached 275°C, and is completed in less than 100 s. The first striking feature of this data set is the observation of niobium hydride forming a short-lived metastable phase that is maintained for approximately 200 s before finally desorbing into metallic Nb. The second striking feature from this measurement is the fact that the intensity of the β-MgH_2 peaks increases with temperature until the onset of desorption at 370 s. Finally, looking at this image closely also reveals that the β-MgH_2 peaks are slightly moving toward smaller angles as temperature increases, indicating a small change of lattice parameters due to thermal expansion.

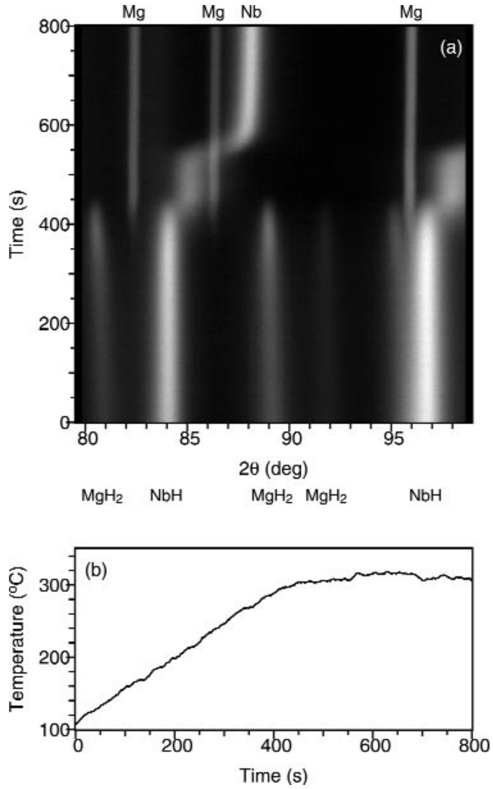

FIG. 1. Time-resolved x-ray scattering data for MgH_2-Nb heated to 583K. (a) Gray-scale contour plot of the x-ray scattering where intensity increases with lighter tones; (b) temperature profile. (Taken from Ref. 5.)

From Fig. 1a it can be seen that there is not a single transition from β-NbH to metallic niobium, and it is evident that all the initial β-NbH phase transforms into a temporary metastable phase, that we shall refer to as NbH_x. Figure 1a distinctively shows that the metastable phase appears simultaneously with metallic magnesium. Metallic Nb does not appear until the β-MgH_2 has completely desorbed, implying that the metastable niobium phase does not spontaneously decay into Nb. Thus it appears that the NbH_x phase is stabilized by the hydrogen flow. Considering this, and the fact that the temperature is constant during the metastable phase decay, a possible explanation for the appearance of the metastable phase could be that the hydrogen released from magnesium hydride is passing through niobium hydride in which hydrogen atoms assume specific locations in the NbH lattice. This would produce a long-range order of hydrogen atoms in the niobium structure before total dehydrogenation which seems to be closely related to the ε-NbH phase. The ε-phase is an ordering of vacancies on a hydrogen sublattice of the β-phase.[5] The niobium nanoparticles may thus act as a gateway for hydrogen flowing out of the magnesium reservoir. Explanations of heterogenous catalytic reaction, such as the spillover effect and gateway models, have been proposed over the years. To our knowledge, this is the first direct evidence of the dehydrogenation mechanism in such composite metal hydrides. This gateway mechanism might also play a role in other cases of heterogenous catalysis.

Acknowledgments

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