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Regular Article

Impact of severe plastic deformation on microstructure and hydrogen storage of titanium-iron-manganese intermetallics

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ABSTRACT

$TiFe_{1-x}Mn_x$ intermetallics ($x = 0$, 0.15 and 0.3) were severely deformed by high-pressure torsion (HPT) to enhance their activation and air resistivity for hydrogenation. While the as-cast ingots hardly absorbed hydrogen ($TiFe_{0.7}Mn_{0.3}$ exhibited slow activation after an incubation period), the HPT-processed samples absorbed hydrogen quickly at room temperature even after air exposure. The improvement of hydrogen storage performance was due to the formation of lattice defects and amorphous regions, which act as channels for hydrogen diffusion. Rietveld analyses and first-principles calculations showed that Mn addition expands the lattice and reduces the hydride formation energy, and thus decreases the hydrogenation/activation pressure.

Metal hydrides are potential candidates for the safe storage of hydrogen under low pressure [1]. During the last few decades, Ti-based hydrides have received considerable attention as candidates for hydrogen storage in stationary applications, where the gravimetric capacity is of less importance compared with the mobile applications [2]. Ti can absorb 4% of hydrogen in the form of TiH_2 but TiH_2 desorbs hydrogen only at elevated temperature [2].

In 1974, Reilly and Wiswall reported that the addition of Fe to Ti and the formation of TiFe intermetallics is a pathway to reduce the dehydrogenation temperature to room temperature [3]. Reilly and Wiswall reported that TiFe, which has a B2 structure, suffers from two main drawbacks [3]. First, TiFe is easily oxidized in the atmosphere and thus it does not absorb hydrogen without activation treatment under high temperature and high pressure. Second, the hydrogenation pressure of TiFe is rather high for hydrogen storage applications (>1 MPa). In 1978, Johnson and Reilly found that the addition of Mn to TiFe is a viable approach to improve the activation and reduce the hydrogenation pressure [4]. Despite the positive effect of Mn addition on the activation of TiFe, it was reported that Ti-Fe-Mn intermetallics may still need an activation treatment, especially when the amount of Mn is small or when a second phase is not formed [5–7].

The current authors recently found that microstructural modification through the application of severe plastic deformation (SPD) is an effective strategy to fully activate pure TiFe [8], Ti-V alloys [9] and Mg_2Ni intermetallics [10]. In this study, three TiFe-based intermetallics (TiFe, $TiFe_{0.85}Mn_{0.15}$ and $TiFe_{0.7}Mn_{0.3}$) are processed by SPD through application of the high-pressure torsion (HPT) method [11,12], and the simultaneous effects of Mn addition and microstructural modification on activation, hydrogenation thermodynamics and hydrogenation kinetics are investigated. The effect of Mn addition on the hydrogenation thermodynamics is also examined using density functional theory (DFT).

Ingots of TiFe, $TiFe_{0.85}Mn_{0.15}$ and $TiFe_{0.7}Mn_{0.3}$ with dimensions of $2 \times 4 \times 11$ cm^3 were used in this study. Discs with 10 mm diameter and 0.8 mm thickness were cut from the ingots and processed by HPT at room temperature under a pressure of 6 GPa for 10 turns with a rotation speed of 1 rpm. The samples were first examined by X-ray diffraction (XRD) using Cu Kα radiation. In order to calculate the lattice parameters, the XRD patterns were analyzed by Rietveld method using FullProf Suite software [13,14]. Second, the densities of ingots were examined using the Archimedes method. Third, thin samples taken from 3.5 mm away from the disc center were prepared with a focused-ion-beam (FIB) system, followed by ion milling and plasma

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trimming. Transmission electron microscopy (TEM) was performed at either 200 or 400 keV for microstructure observation and for recording selected-area electron diffraction (SAED) patterns. Fourth, the samples were stored for 7 months in an air atmosphere and later examined using hydrogen pressure-composition isotherms (PCI) and hydrogenation kinetics using a Sieverts-type gas absorption apparatus at 303 K. Crushed pieces of ingot with 0.3–0.8 mm sizes and two pieces of HPT-processed discs were used for PCI measurements. The samples were evacuated by a rotary pump at 303 K for 2 h before the PCI measurements.

For calculation of hydride formation energy, the all-electron basis projector-augmented-wave (PAW) method [15] was used in the framework of DFT using VASP (Vienna Ab-initio Simulation Package) code [16,17] within the generalized gradient approximation in the Perdew-Burke-Ernzerhof form [18]. A plane-wave energy cut-off of 400 eV was applied for the calculations.

In order to examine the effect of Mn addition on the formation energy of TiFe-based hydrides, the energy of $TiFe_{1-x}Mn_x$ intermetallics and $TiFe_{1-x}Mn_xH_2$ hydrides ($x = 0, 0.083, 0.166$ and 0.25) were calculated. The intermetallics and hydrides had the CsCl-type cubic structure (space group: *Pm*-3 m) and orthorhombic structure (space group: *Cmmm*), respectively [19]. The calculations were performed for the constructed supercells of intermetallics ($2 \times 2 \times 3$) and hydrides ($1 \times 1 \times 3$). The Brillouin zones were modeled using $12 \times 12 \times 8$ and $7 \times 8 \times 6$ meshes for the $TiFe_{1-x}Mn_x$ intermetallics and $TiFe_{1-x}Mn_xH_2$ hydrides, respectively. The structural forces were minimized in the intermetallic and hydride structures by relaxing the cell parameters and atomic positions, while the initial symmetry of the structure was kept. The formation energy of $TiFe_{1-x}Mn_xH_2$ hydrides, ΔE_f, was calculated as:

$$\Delta E_F = E_{Hyd} - E_{Int} - E_{H-H} \tag{1}$$

where E_{Hyd} and E_{Int} are the energy of hydrides and interntermetallics, respectively, and $E_{H\text{-}H}$ is the energy of one hydrogen molecule.

PCI results at 303 K are shown in Fig. 1 for (a) $TiFe_{0.85}Mn_{0.15}$ and (b) $TiFe_{0.7}Mn_{0.3}$ samples before and after processing by HPT. Since the PCI results for TiFe after processing by HPT were reported elsewhere [8], they were not included in Fig. 1. It is apparent that similar to TiFe, the Ti-Fe-Mn intermetallics without processing by HPT do not absorb hydrogen. However, both samples are significantly activated after processing by HPT and readily absorb ~1.7 wt.% of hydrogen from the first hydrogenation cycle even after storage in the air for 7 months. Close inspection of Fig. 1 shows that the first and second plateau pressures (corresponding to $TiFe_{1-x}Mn_xH$ and $TiFe_{1-x}Mn_xH_2$ hydrides, respectively) decrease with increasing Mn fraction, which is consistent

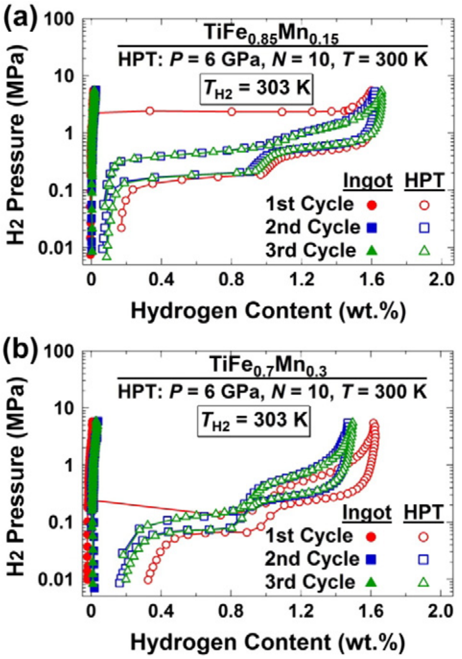

Fig. 1. PCI measurements at 303 K for (a) $TiFe_{0.85}Mn_{0.15}$ and (b) $TiFe_{0.7}Mn_{0.3}$ samples before (ingot) and after processing by HPT.

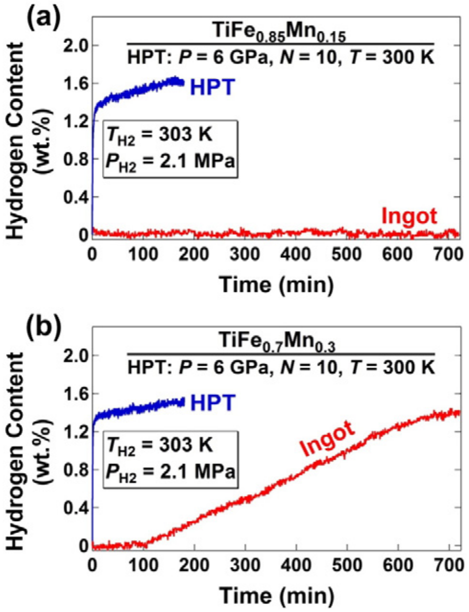

Fig. 2. Variation of hydrogen content against hydrogenation time at 303 K under initial hydrogen pressure of 2.1 MPa for (a) $TiFe_{0.85}Mn_{0.15}$ and (b) $TiFe_{0.7}Mn_{0.3}$ samples before (ingot) and after processing by HPT.

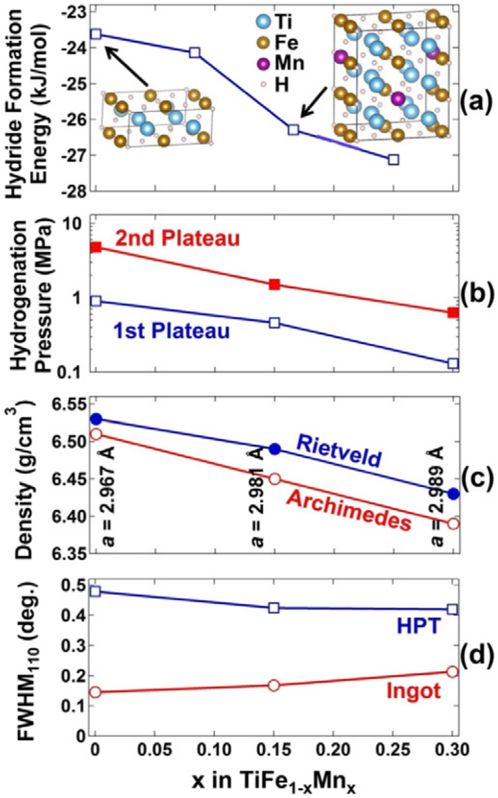

Fig. 3. Effect of Mn content on (a) theoretical hydride formation energy, (b) equilibrium hydrogen absorption pressure, (c) bulk density and lattice parameter, and (d) FWHM for (110) XRD peak in $TiFe_{1-x}Mn_x$ samples.