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# Activation of titanium-vanadium alloy for hydrogen storage by introduction of nanograins and edge dislocations using high-pressure torsion

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## ABSTRACT

Ti–V alloys thermodynamically absorb hydrogen at room temperature, but hydrogenation does not occur practically without a sophisticated activation process. In this study, a nanograined TiV alloy with the supersaturated bcc structure and an ultrahigh density of edge dislocations ( $>10^{16} \text{ m}^{-2}$ ) was mechanically synthesized from Ti and V powders using the high-pressure torsion (HPT) method. The presence of large fractions of grain boundaries and dislocations, as effective pathways for hydrogen diffusion, activated TiV and it absorbed ~4 wt.% of hydrogen at room temperature after an incubation period. The kinetic measurements suggested that the hydrogen absorption in the incubation period is controlled by the slow rate of hydrogen dissociation, while the hydrogenation rate in the latter stage is controlled by diffusion of hydrogen atoms.

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## Introduction

In 1970s, it was shown that single-phase Ti–V alloys with the bcc structure can absorb hydrogen and produce metal hydrides [1]. Following this pioneering work and several other interesting works [2–6], Ti–V-based alloys such as Ti–V–Ni [7], Ti–V–Fe [8], Ti–V–Mn [9] and Ti–V–Cr [10] were

considered as future candidates for solid-state hydrogen storage for stationary applications. Although reversible hydrogen storage capacity for these materials is ~2 wt.% [7–10] and is smaller than those for Mg-based hydrides [11–13] and Li-based hydrides [14,15], they can reversibly absorb and desorb hydrogen at room temperature by addition of a third element [7–10]. One of the main drawbacks of Ti–V-based alloys for hydrogen storage is their difficult

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activation (they are usually activated by exposure to high hydrogen pressures and/or vacuum at high temperatures) [1–10].

There are two main reasons for difficult activation of Ti–V-based materials: (i) the presence of oxide layers on the surface which act as barriers for hydrogen diffusion [16,17], and (ii) high hydrogenation plateau pressures which are usually higher than 1 MPa [1–10]. Despite the difficult activation of these materials, they get fully activated after the first hydrogenation cycles due to the sample pulverization and formation of fresh and oxide-free surfaces which facilitate the hydrogen absorption [1–10]. Moreover, large fractions of lattice defects such as dislocations, which are generated in the first hydrogenation cycles, not only act as pathways for fast hydrogen transport but also facilitate the phase transformation from the metallic phase to the hydride phase in the latter cycles [18,19].

So far, two strategies have been employed to improve the activation of Ti–V-based hydrogen storage materials: (i) addition of elemental additives to the materials such as Cr/Mn/Fe to TiV [17]; and (ii) addition of a second phase to the material to produce interphase boundaries for hydrogen transport [20,21]. It was shown recently that the introduction of large fractions of grain boundaries and cracks, as pathways for hydrogen transport, is an effective strategy to improve the activation of TiFe intermetallics for hydrogen storage [22]. It should be noted that similar to Ti–V-based alloys, TiFe also suffers from difficult activation for hydrogen storage [23–27]. In contrary with the two strategies that are currently used to activate the Ti–V-based alloys, the microstructural modifications, which was employed for activation of TiFe, improve the activation more significantly without any change in the chemical composition. Although microstructural modifications using different processing techniques such as high-pressure torsion (HPT) [28,29], groove rolling [29] and ball milling [30–32] has been successfully applied to activate TiFe, there have been few studies on the effect of lattice defects on the activation of Ti–V-based alloys.

In this study, the HPT method is employed to improve the activation for hydrogen absorption in a Ti–50 at.% V alloy by introducing large fractions of lattice defects such as grain boundaries and dislocations. As recently reviewed in Ref. [33], the HPT method was first introduced by Bridgman in 1935 to investigate the phase transformations and mechanical alloying/reactions in different kinds of materials [34], but the method is currently used as a severe plastic deformation (SPD) technique mainly for grain refinement in metallic materials [35–37]. Although TiV forms a stable TiVH<sub>4</sub> hydride at room temperature which should be heated above 410 K for reversible hydrogen storage [38], the material was intentionally selected in this study because its activation is more difficult than ternary Ti–V-based alloys [7–10]. Since earlier studies on some structural materials showed that the fraction of grain boundaries and the density of dislocations can be significantly enhanced by synthesizing alloys from elemental powders [39,40], the TiV alloy was directly synthesized from the Ti and V powders using the HPT method in this study.

## Experimental materials and procedures

V (99.9%) powders with particle sizes less than 50 μm were mixed with 50 at.% of Ti (99.9%) powders with particle sizes less than 75 μm. The powders were first mixed in dry condition and further homogenized by mechanical mixing in acetone. An HPT facility with 50 tons capacity was used to consolidate the powders, synthesize the TiV alloy with the bcc structure and introduce lattice defects. The facility had one upper anvil and one lower anvil with flat-bottom holes on the surface and the center of each anvil. The diameter of the hole was 14 mm and their depth was 0.4 mm.

HPT was conducted at room temperature under a pressure of  $P = 3$  GPa and shear strain ( $\gamma = 2\pi rN/h$ ,  $\gamma$ : shear strain,  $r$ : distance from disc center,  $N$ : number of turns,  $h$ : disc thickness [35,36]) was introduced by rotating the lower anvil with respect to the upper anvil with a rotation speed of  $\omega = 1$  rpm for  $N = 0$  (pure compression), 1, 10 and 100 turns. The HPT-processed discs were examined using different methods as described below.

First, in order to examine the homogeneity of microstructure along the disc radii, the HPT-processed discs were first polished to mirror-like surfaces and the Vickers microhardness was measured from the disc center to periphery in four radial directions with increments of 1 mm. A load of 500 g for 15 s was applied for each hardness measurement.

Second, in order to evaluate the formation of TiV alloy with the bcc structure, X-ray diffraction (XRD) analyses were performed on disc samples using the Cu  $K\alpha$  radiation with a wavelength of  $\lambda = 0.1542$  nm. Following the XRD analyses, dislocation density  $\rho$ , and crystallite size  $D$ , were calculated from the full width at half maximum of XRD peaks  $\beta$ , using the Williamson–Hall method [41].

$$\frac{\beta \cos \theta}{\lambda} = \frac{0.9}{D} + \frac{2\varepsilon \cos \theta}{\lambda} \quad (1)$$

$$\rho = 14.4 \frac{\varepsilon^2}{b^2} \quad (2)$$

In these equations,  $\varepsilon$  is the lattice strain,  $\theta$  is the Bragg angle and  $b$  is the Burgers vector. The XRD patterns were further analyzed by Rietveld refinement method using the FullProf Suite software [42]. A convolution of Gaussian and Lorentzian functions (“Thompson-Cox-Hastings pseudo-Voigt” function) was employed to measure the lattice parameters, crystallite size, lattice strain and dislocation density [43]. The crystallite size was calculated from the width of Lorentzian function  $H_L(\Delta 2\theta)$ , and the lattice strain was calculated from the width of Gaussian function  $H_G(\Delta 2\theta)$ , using the following equations [43–45].

$$D = \frac{2\lambda}{\pi H_L(\Delta 2\theta) \cos \theta} \quad (3)$$

$$\varepsilon = \frac{H_G(\Delta 2\theta)}{8\sqrt{\ln 2} \pi \tan \theta} \quad (4)$$

The dislocation density was also calculated using Eqs. (2) and (4). For Rietveld analyses, the instrumental resolution was determined using the LaB<sub>6</sub> powders.

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