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# Crucial role of Ce particles during initial hydrogen absorption of AB-type hydrogen storage alloys

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# ABSTRACT

The hydrogen storage behavior and the microstructural features of AB-type  $Ti_{50}Fe_{48}V_2$  hydrogen storage alloys containing a small amount of cerium (Ce) were investigated to understand the effect of Ce addition during initial hydrogen absorption. The initial hydrogen absorption kinetics of the alloys improved significantly at room temperature with Ce addition, which exhibited no significant influence on the pressure-composition isotherms for hydrogen absorption and desorption. Fine spherical particles containing Ce, which were determined to be  $\gamma$ -Ce mixed with cerium oxide, were dispersed in the ordered body-centered cubic TiFe matrix. During the early stage of hydrogen absorption, small cracks were initiated around the Ce particles, likely caused by the volume expansion owing to the formation of  $\epsilon$ -CeH<sub>2</sub>. Subsequently, many large cracks, believed to have formed owing to the hydrogenation of the TiFe matrix, propagated during further hydrogen absorption. Therefore, these Ce particles appear to play a crucial role by providing starting points for the initial hydrogenation, with this mechanism explaining the significant increase in the primary hydrogen absorption kinetics after Ce addition. Notably, some small pits were observed after partial hydrogen absorption, possibly attributed to the hydrogenation of Ce particles underneath the alloy surfaces.

# 1. Introduction

Solid-state hydrogen storage using metal hydrides has been recognized as a safe and efficient method for storing hydrogen owing to its high volumetric density and operation under moderate pressures and temperatures. AB (such as TiFe), AB<sub>2</sub> (such as ZrCr<sub>2</sub>, TiMn<sub>2</sub>, and TiCr<sub>2</sub>), and AB<sub>5</sub> (such as LaNi<sub>5</sub>) type metal hydrides have been investigated as room-temperature hydrogen storage alloys. AB-type alloys exhibit some advantages, such as low material cost [1], high gravimetric density of hydrogen (1.9 wt%) [2], good sorption kinetics [3], and appropriate plateau pressure at room temperature [3,4]. However, the slow and difficult initial hydrogen absorption of the alloys is a major obstacle to their practical application owing to the native passivating surface oxide layers on the alloys. In addition, the initial hydrogen absorption (activation) conditions of the alloys have been considered too extreme for practical applications (such as several cycles at 400  $\,^\circ C$  and 65 bar of hydrogen) [5].

Previous studies suggested various methods for improving the initial hydrogen absorption of AB-type hydrogen storage alloys. For example, surface modification [6,7], ball milling [8–13], plastic deformation [14, 15], and the addition of alloying elements such as transition [16–19] and rare-earth metals [3,20,21] have been reported to mitigate the initial hydrogen absorption problem. In particular, adding a small amount of rare earth metals is considered effective in accelerating the initial hydrogen absorption [3,20,21]. Despite the positive effects of rare-earth element addition, the role of these elements during the initial hydrogen absorption of alloys is still unclear, with only a few studies focusing on the initial hydrogen absorption mechanisms of the alloys.

This study aims to investigate the effect of Ce addition on the hydrogen storage properties of AB-type Ti-Fe-V alloys, focusing on the

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initial hydrogen absorption behavior. We investigated the microstructural features of the alloys during hydrogen absorption using various characterization techniques, such as X-ray diffraction (XRD), scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDS), electron back-scattered diffraction (EBSD), transmission Kikuchi diffraction (TKD), and atomic force microscopy (AFM). In particular, we focused on the microstructural evolution of Ce particles dispersed in the alloys during the initial hydrogen absorption to understand the role of the particles during the initial hydrogenation. We attempted to determine the initial hydrogenation mechanism of the particles in the alloys.

# 2. Experimental details

# 2.1. Synthesis

The starting materials were Ti (RND Korea, 99.995 %), Fe (KRT Lab, 99.95 %), V (KRT Lab, 99.95 %), and Ce (Sigma-Aldrich, 99.9 %). Ce was immersed in anhydrous ethanol and sonicated to remove the mineral oil. Three alloys (Ce-0, Ce-1, and Ce-2) were prepared by arc button melting under an argon atmosphere. Buttons weighing approximately 25 g were remelted at least five times and turned over after each melting cycle to maximize compositional homogeneity. Zirconium was used as a getter to minimize oxygen contamination during melting. Parts of the as-cast button alloys were sealed using a quartz tube and then annealed at 1000 °C for 7 d under vacuum to homogenize the as-cast button alloys. The composition of the annealed alloy samples was analyzed using inductively-coupled plasma mass spectrometry. Table 1 lists the compositions of the annealed alloys employed in this study. The base alloy composition was Ti<sub>50</sub>Fe<sub>48</sub>V<sub>2</sub> (at%), with a small amount of Ce added to the base alloy (0, 0.80, and 1.27 at% in Ce-0, Ce-1, and Ce-2, respectively).

# 2.2. Microstructural characterization

The alloy samples were pulverized and characterized by XRD using a Bruker D8 Advance diffractometer with Cu Ka radiation. The phase constitution of the samples was quantified by Rietveld refinement using the DIFFRAC TOPAS software (version 5). The microstructures of the alloy samples were observed using field-emission SEM (Inspect F50, FEI Company) with EDS (X-Flash, Bruker Nano GmbH) and EBSD (e-Flash HR, Bruker Nano GmbH). The EBSD samples were prepared using an Ar ion milling system (IM5000CTC, Hitachi ). The EBSD results were analyzed using EBSD data reprocessing software (OIM Analysis, EDAX). In addition, TKD was conducted using a sample prepared using a focused ion beam (FIB, Nova 600 NanoLab, FEI) to analyze the second-phase particles in the samples. Kelvin probe force microscopy (KPFM) was performed using a commercial AFM (NX10, Park Systems) equipped with a lock-in amplifier (SR830, Stanford Research Systems) [22,23]. Conductive PtIr-coated tips (ATEC-EFM, Nanosensors) were used for the KPFM measurements. During KPFM analysis, the tip was raised to a lift height above the sample, and electrical excitations of 2 V<sub>rms</sub> and 32 kHz were applied to the tip.

able 1	
Composition of the prepared alloys (at%; the values in the brackets are in wt%)	))

Alloy	Ti	Fe	v	Ce
Ce-0	50.7	46.5	2.8	-
	(47.0)	(50.3)	(2.7)	
Ce-1	50.47	46.4	2.33	0.80
	(46.13)	(49.47)	(2.27)	(2.13)
Ce-2	50.57	46.00	2.17	1.27
	(45.83)	(48.67)	(2.13)	(3.40)

# 2.3. Measurement of hydrogen storage properties

The hydrogen storage properties of the annealed alloy samples were determined by measuring the initial hydrogen absorption kinetics using Sievert's apparatus and pressure–composition isotherms (PCIs) using an automatic high-pressure volumetric analyzer (Particulate Systems). During the initial hydrogen absorption of the samples, the pressure was monitored for up to 120 h at 30 °C and 30 bar. Before the PCI measurement, the samples were activated under the following steps: each sample was broken into a few millimeter pieces in air, with 0.5–2 g of each sample immediately charged into a stainless-steel reactor. The reactor was evacuated until the pressure decreased to approximately 1  $\times$  10<sup>-5</sup> bar and 30 bar hydrogen was applied for 30 min for activation. The reactor was then evacuated for 1 h to remove the absorbed hydrogen from the activation. The PCI curves were then measured at 30 °C and up to 70 bar of hydrogen.

# 3. Results

Fig. 1a shows the initial hydrogen absorption profiles of the alloy samples at 30 °C. The pressure decrease in the profiles indicates the hydrogen absorption by the alloy. Adding V to the TiFe alloys enabled the hydrogenation at 30 bar of hydrogen (Ce-0), whereas a pure TiFe alloy hardly absorbs hydrogen at higher hydrogen pressures [24]. Moreover, Ce addition significantly accelerates the hydrogen absorption kinetics of the Ce-1 and Ce-2 samples. The PCI curves for hydrogen



**Fig. 1.** (a) Hydrogen pressure profiles of the Ce-0, Ce-1, and Ce-2 alloy samples during initial hydrogen absorption at 30  $^{\circ}$ C and that of a pure TiFe alloy, and (b) PCI curves of the Ce-0, Ce-1, and Ce-2 alloy samples at 30  $^{\circ}$ C.

absorption and desorption of the three alloys at 30 °C exhibit no significant difference (Fig. 1b). The hydrogen capacity up to 70 bar is approximately 1.9 wt% hydrogen, higher than that of conventional AB<sub>5</sub>-type LaNi<sub>5</sub> alloys (1.5 wt% hydrogen) [2], with good reversibility for both the absorption and desorption. Two-stage desorption plateau behavior is observed for all the alloys, whereas the plateau pressure for hydrogen absorption and desorption is between 1 and 10 bar. This two-stage behavior is associated with the sequential formation of TiFeH monohydride and TiFeH<sub>2</sub> dihydride [25].

The XRD patterns of the alloy samples are shown in Fig. 2. The major phase is determined to be the TiFe phase with an ordered body-centered cubic (BCC) structure (CsCl structure), whereas a small amount of the  $\gamma$ -Ce phase with a face-centered cubic (FCC) structure is observed in the Ce-1 and Ce-2 samples. In the Ce-0 sample, a small amount of Ti<sub>2</sub>Fe with a cubic structure is observed. Furthermore, we conducted XRD analysis on the fully hydrogenated Ce-2 sample (Fig. 2d). This result indicates that the Ce phase hydrogenated into  $\varepsilon$ -CeH<sub>2</sub> after hydrogen absorption. TiFeH (monohydride) and TiFeH<sub>2</sub> (dihydride) are not observed after hydrogen absorption because they tend to easily decompose into TiFe under air at room temperature [25]. However, CeH<sub>2</sub> is a stable hydride under the same conditions [26]. Table 2 lists the phase compositions of the XRD patterns quantified by the Rietveld refinement. The amount of Ce phase in the Ce-1 and Ce-2 samples was 1.5 and 3.3 wt%, respectively, and the amount of CeH<sub>2</sub> in the Ce-2 sample after hydrogen absorption is similar to that of the Ce phase in the Ce-2 sample.

Fig. 3 shows the SEM-BSE images of the annealed alloy samples. Dark phases with a size of 3–20  $\mu$ m are observed in the Ce-0 sample, which appears to be Ti<sub>2</sub>Fe as observed in the XRD pattern (Fig. 2a). However, bright spherical particles with a size ranging from hundreds of nm to 10  $\mu$ m are observed in the Ce-added samples, Ce-1 and Ce-2. These white particles appear to be the Ce phase observed in the XRD patterns (Fig. 2b and c) because phases with high atomic weights tend to be bright in the BSE images. Considering the compositional differences between the three alloys, the presence of the Ce particles appears to be responsible for the significant increase in the initial hydrogenation kinetics of the Ce-1 and Ce-2 samples compared with that of the Ce-0 sample (Fig. 1a). The number density of the Ce particles in the Ce-2 sample is slightly higher than that in Ce-1, which may explain the better kinetics of the Ce-2 sample than that of the Ce-1 sample.

The SEM-EDS-EBSD analysis results for the Ce-2 sample prepared by ion milling are shown in Fig. 4. The images in Fig. 4b and c appear to be slightly expanded in the vertical direction because the sample was tilted



Fig. 2. XRD patterns of the (a) Ce-0, (b) Ce-1, and (c) Ce-2 alloy samples, and (d) Ce-2 alloy sample hydrogenated for 40 h at 30  $^\circ$ C and 30 bar of hydrogen.

#### Table 2

Phase constitution of the annealed Ce-0, Ce-1, and Ce-2 alloy samples calculated by the Rietveld refinement and that of the Ce-2 alloy sample hydrogenated for 40 h at 30  $^{\circ}$ C and 30 bar of hydrogen (wt%).

Alloy	TiFe	Ti <sub>2</sub> Fe	Ce	CeH <sub>2</sub>
Ce-0	97.6	2.4	-	-
Ce-1	98.5	-	1.5	-
Ce-2	96.7	-	3.3	-
Ce-2 after hydrogenation	96.7	-	-	3.3



Fig. 3. SEM-BSE images of the (a) Ce-0, (b) Ce-1, and (c) Ce-2 alloy samples.

by 70° for the EDS and EBSD measurements. Ce particles of various sizes are observed in the SEM image, with few particles located along the grain boundaries (Fig. 4a). The Ce EDS maps of the two large particles indicate that the overall Ce concentration is high (approximately 80 at %) even though the concentration is low (approximately 50 at%) in the



Fig. 4. (a) SEM image, (b) EDS Ce mapping, and (c) EBSD phase map of the Ce-2 alloy sample prepared by ion milling.

small central region of the upper particle (Fig. 4b). As shown in Fig. 4c, the EBSD analysis reveals that the matrix phase is the TiFe phase and the particles consist of Ce and CeO<sub>2</sub>, corresponding to the low-Ce concentration region, even though the analysis quality is poor even after the ion milling treatment. Considering the large regions of high Ce concentration in the particles, it can be concluded that the particles primarily

consist of a metallic Ce phase and a small amount of  $CeO_2$ .

# 4. Discussion

The TKD and EDS results for the Ce-2 sample are shown in Fig. 5. Phase identification of significant areas of the Ce particles was possible



Fig. 5. (a) SEM image, (b) TKD phase map, and (c) EDS elemental map of a Ce particle in the Ce-2 alloy sample with a thickness of approximately 50 nm prepared by FIB.

by TKD measurements. The TKD phase map confirms that the particles primarily consisted of the Ce phase surrounded by the TiFe matrix phase (Fig. 5b). The EDS mapping results of the same location indicate that the concentration of oxygen in the particles is as high as that of Ce. According to the phase diagram of the Ce-O system [27], the particles in the Ce-2 sample with this high concentration of oxygen should exist as liquid cerium and α-Ce<sub>2</sub>O<sub>3</sub> during the heat treatment at 1000 °C. However, crystalline cerium oxide phases were not observed in the XRD results of both Ce-1 and Ce-2 samples (Fig. 2), although a very small amount of crystalline CeO<sub>2</sub> was detected by the EBSD analysis (Fig. 4). Therefore, it is likely that amorphous cerium oxide, which is not detected by XRD, as well as  $\gamma$ -Ce supersaturated with oxygen formed in the particles during rapid cooling after the heat treatment at 1000 °C. In fact, Pan et al. [28] reported the presence of amorphous Ce<sub>2</sub>O<sub>3</sub> inclusions in a ferritic stainless steel, which was furnace-cooled from 1600 °C. The unidentified regions in the particles analyzed by EBSD/TKD might correspond to amorphous cerium oxide. If the particles were fully cerium oxides, they would not be easily hydrogenated into CeH<sub>2</sub> during hydrogen absorption, as observed after hydrogen absorption of the Ce-2 sample (Fig. 2d). For example, the Gibbs free energy change for the hydrogenation of CeO<sub>2</sub> at room temperature was determined to be significantly higher than 389 kJ mol<sup>-1</sup> [29].

$$CeO_2 + 3 H_2 \rightarrow CeH_2 + 2 H_2O \tag{1}$$

Naturally, surface oxide layers would also form on the Ce particles located on the alloy surfaces, when the samples are exposed to air. Nevertheless, the Ce particles might be relatively easily hydrogenated [30], because it has been quite well known that the surfaces oxide layers formed on metallic Ce do not exhibit a passivating feature [31,32].

SEM-BSE images of the Ce-2 sample partially hydrogenated at 30 °C and 30 bar were investigated (Fig. 6) to understand the effect of the Ce particles on the early stage of the hydrogen absorption of the alloys. Small cracks that appeared to originate from the particles are observed in the Ce-2 sample hydrogenated for 1.5 h (Fig. 6a). Crack formation during hydrogen absorption appeared to be caused by volume expansion owing to the hydrogenation of Ce into CeH<sub>2</sub>, reaching approximately 17 %. The strong hydrogen affinity of Ce appears to cause the hydrogenation of Ce particles earlier than the TiFe matrix [3], despite the high oxygen concentration in the particles. Several long cracks are observed in the TiFe matrix and around the particles for the sample hydrogenated for 12 h (Fig. 6b and c); several small cracks are also observed inside some of the particles in Fig. 6c. The matrix cracks appear to be caused by volume expansion owing to the subsequent hydrogenation of the TiFe matrix, i.e., the formation of TiFeH and TiFeH<sub>2</sub>, reaching approximately 12 % and 17 %, respectively, with respect to the TiFe phase. Therefore, it can be concluded that the Ce particles play a crucial role during the initial hydrogen absorption of the alloys by providing the starting points, where cracks are initiated owing to the formation of CeH<sub>2</sub>. These initial cracks around the particles contributed to the exposure of fresh surfaces of the TiFe matrix without passivating oxide layers, considered major obstacles to the initial hydrogen absorption of AB-type hydrogen storage alloys. Subsequently, the TiFe matrix is hydrogenated by the hydrogen supplied through the fresh surfaces, and the hydrogenation of the TiFe phase to TiFeH or TiFeH2 also leads to new cracks. The repetition of this process accelerates the propagation of several cracks and hydrogen absorption. This mechanism may explain why Ce addition significantly increases the hydrogen absorption kinetics of the alloys. Fig. 7 shows a schematic of the hydrogen absorption mechanism of the allovs.

Notably, some pits with a size of  $5-20 \ \mu\text{m}$  are occasionally observed in the Ce-2 sample partially hydrogenated for 2.5 h. SEM images of the sample titled  $70^{\circ}$  clearly exhibit the morphology of these pits (Fig. 8). Fine particles, assumed to be CeH<sub>2</sub>, were observed at the center of the pits. Similar to the SEM images, a pit is observed in the AFM topography image (Fig. 9a). The height of the pit is significantly lower than that of



**Fig. 6.** (a) SEM image of the Ce-2 alloy sample hydrogenated for 1.5 h at 30  $^{\circ}$ C and 30 bar of hydrogen, and (b) low, and (c) high magnification images of the Ce-2 alloy sample hydrogenated for 12 h under the same conditions. The black and red arrows indicate the cracks initiated at the particles and the particles containing several cracks, respectively.







**Fig. 8.** (a) SEM image of pits formed in the Ce-2 alloy sample hydrogenated for 2.5 h at 30  $^{\circ}$ C and 30 bar of hydrogen, which was tilted 70 $^{\circ}$ , and (b) magnified image of the white rectangular box in (a).

the TiFe matrix (approximately 800 nm). Notably, two distinct signal levels were clearly visible in the surface potential (Fig. 9b). In particular, the pit center clearly exhibited a higher surface potential, indicating that CeH<sub>2</sub> was located at the pit center. It is difficult to understand why these pits were formed during hydrogen absorption of the alloy, possibly associated with the hydride formation of the Ce particles underneath the alloy surfaces, which is promoted by the hydrogen supplied through the



**Fig. 9.** (a) AFM topography, (b) KPFM surface potential image of the pit in the Ce-2 alloy sample, and (c) area line profiles of the height and surface potential obtained from the rectangular boxes in (a) and (b).

cracks propagated from the surfaces during hydrogen absorption. Volume expansion owing to hydride formation underneath the surfaces may induce significant stress that can partially tear out the surfaces, eventually leaving pits on the surfaces.

# 5. Conclusions

The hydrogen-storage behavior and microstructural features of ABtype  $Ti_{50}Fe_{48}V_2$  hydrogen-storage alloys containing small amounts of Ce were investigated. Ce addition significantly improved the hydrogen absorption kinetics of the alloys at room temperature in situations where slow and difficult initial hydrogen absorption is known to be a significant drawback of AB-type hydrogen storage alloys because of their passivating surface oxide layers. In addition, fine spherical particles were dispersed in the TiFe matrix of the alloys containing Ce, which were determined to be  $\gamma$ -Ce with an FCC structure mixed with cerium oxide by XRD and SEM-EBSD-TKD analyses. The Ce particles appeared to play a crucial role by providing starting points for the initial hydrogen absorption of the alloys. During the early stage of the hydrogen absorption, the Ce particles were hydrogenated into  $\varepsilon$ -CeH<sub>2</sub> earlier than the TiFe matrix, initiating small cracks around the particles owing to the volume expansion of the hydride formation, which reached approximately 17 %. These cracks appeared to contribute to the subsequent hydrogenation of the TiFe matrix by exposing the fresh alloy surfaces to hydrogen. It was observed that several large cracks formed and propagated, likely owing to the volume expansion of the matrix hydrogenation during hydrogen absorption. This mechanism appeared responsible for the significant increase in the hydrogen absorption kinetics of the alloys containing Ce. In addition, small pits were occasionally observed with particles at their centers in the partially hydrogenated alloy sample. The formation of these pits appeared to be associated with the hydrogenation of Ce particles to CeH<sub>2</sub> underneath the alloy surfaces, although the formation mechanism is not yet clearly understood.

#### **CRediT** authorship contribution statement

Taejun Ha: Methodology, Formal analysis, Writing – original draft. June-Hyung Kim: Methodology, Formal analysis, Writing – original draft. Changhyo Sun: Methodology, Formal analysis. Young-Su Lee: Conceptualization, Writing – review & editing. Dong-Ik Kim: Methodology, Formal analysis. Jin-Yoo Suh: Conceptualization, Writing – review & editing. Jae-il Jang: Writing – review & editing. Joonho Lee: Writing – review & editing. Yunseok Kim: Supervision, Writing – review & editing. Jae-Hyeok Shim: Conceptualization, Supervision, Writing – review & editing.

# **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

# Data availability

Data will be made available on request.

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