マテリアル先端リサーチインフラ利用報告書
ARIM User's Report

【Release：2025.07.17】　【Update：2025.07.16】

課題データ / Project Data

課題番号 Project Issue Number	23KU0058
利用課題名 Title	In-situ gas atmosphere transmission electron microscopy of hydrogen de/absorption in TiH_2
利用した実施機関 Support Institute	九州大学 / Kyushu Univ.
機関外・機関内の利用 External or Internal Use	外部利用/External Use
ARIM半導体基盤PF 関連課題 Related to ARIM-SETI	指定なし / No Designation
横断技術領域 Cross-Technology Area	計測・分析/Advanced Characterization
重要技術領域 Important Technology Area	高度なデバイス機能の発現を可能とするマテリアル/Materials allowing high-level device functions to be performed
キーワード Keywords	Hydrogen storage, metal hydrides, titanium hydride, in-situ electron microscopy,電子顕微鏡/ Electronic microscope

利用者と利用形態 / User and Support Type

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利用形態 Support Type	技術補助/Technical Assistance

利用した主な設備 / Equipment Used in This Project

利用した主な設備 Equipment ID & Name	KU-004：広電圧超高感度原子分解能電子顕微鏡

報告書データ / Report

概要（目的・用途・実施内容） **Abstract (Aim, Use Applications and Contents)**	Ti based hydrides have been identified as potential hydrogen storage materials due to their high volumetric H_2 capacities. In addition to the technical advantages, Ti hydrides have relatively low raw material costs as Ti is used as structural material, and it is non-toxic. This experiment studies the desorption and re-absorption of hydrogen in TiH_2 in-situ under transmission electron microscopy (TEM). In-situ TEM observation during hydrogen absorption and desorption are vital in identifying the diffusion pathways of hydrogen and in understanding the fundamental mechanisms of phase nucleation and growth. However, due to the high vacuum environment in TEM, in-situ studies of hydrogen storage materials are often limited to hydrogen desorption only. In this study, in-situ TEM of H_2 absorption of Ti based hydrides which have equilibrium temperatures above 300˚C has been achieved along with in-situ H_2 desorption. It reveals the desorption mechanism of TiH_2 involves the nucleation of Ti at multiple sites in a TiH_2 single crystal, while the absorption process involves the growth of TiH_2 in the existing Ti crystals.
実験 **Experimental**	Sample preparation:Approximately 3 mg of TiH_2 powder (Sigma Aldrich, hydrogen storage grade) was dispersed in 1.5 ml of ethanol in a sample tube by placing in an ultrasonic bath for 10 min. To segregate the finer powder for TEM observation, the suspension was placed in a centrifuge and spun at 3000 rpm for 1 minute. The large particles are segregated at the bottom of the tube and the top 1.2 ml of the suspension was moved to a second tube with a pipette. The fine particles in the second tube were concentrated by spinning the tube at 6000 rpm for 1 minute and removing the top 0.8 ml of the suspension. A small drop of the concentrated fine particle suspension was placed on the Si_3N_4 window on a bottom E-chip (Protochips Atmosphere) using a micropipette. The E-chip was dried in a vacuum chamber overnight, before being assembled on the in-situ heating gas environmental TEM holder. TEM Experiment: The in-situ holder was placed into a JEOL JEM-ARM200CF TEM, operating at an accelerating voltage of 120 kV. Moisture in the assembled sample cell was removed by heating the cell to 100˚C under an Ar atmosphere of 10 kPa at a flowrate of 1 sccm for 1 hour. Images of a selected TiH_2 particle was obtained at 300˚C (Point A), where the deposition of volatile organic compounds is minimal. Electron diffraction pattern (DP) was also obtained to identify the crystal structure of the sample. To perform in-situ hydrogen desorption, the Ar pressure was reduced to 0.5 kPa and the temperature was increased to 650˚C at a rate of 4.8˚C/min. Images and DP of the particle after hydrogen desorption (Point B) was captured. Following this, the temperature was decreased to 450˚C at 60˚C/min. Images and DP was captured again (Point C) before 101.3 kPa H_2 pressure with a flowrate of 0.1 sccm was introduced for in-situ hydrogen absorption. Images and DP of the particle after hydrogen absorption (Point D) was captured.

結果と考察
Results and Discussion

TEM image of the as-received TiH_2 particle shows it is covered by an oxide skin of approximately 20 nm in thickness. At 300˚C (Point A), the sample comprises of two single crystal particles, matching that of cubic δ-TiH_2. As temperature increased to 600˚C (Point B), hydrogen begun to desorb from the TiH_2 particle with the following transformation sequence: Dehydrogenation of δ-TiH_x → transformation of δ-TiH_x to β-TiH_x → dehydrogenation reaction of β-TiH_x → transformation of β-TiH_x to α-Ti → dehydrogenation of the α-Ti. The concentric DP shows the particle becomes polycrystalline during the desorption process, with lattice parameters matching that of α-Ti and β-TiH_x.
As the temperature was decreased to 450˚C no obvious change was observed at Point C (Fig. 2). When a hydrogen pressure of 101.3 kPa was introduced (Point D), hydrogen absorption is expected to follow the reverse sequence to the desorption process. The crystallites grew into facetted grains at the end of the hydrogen absorption. The DP confirms that the particle remained polycrystalline.
The technique elucidated the formation of Ti nano-crystallites during hydrogen desorption, indicating that Ti nucleates at multiple sites in the TiH_2 single crystal. This was followed by the growth of facetted TiH_2 from the existing nano-crystalline Ti during the H_2 absorption process.

図・表・数式 1
Figures, Tables and Equations 1

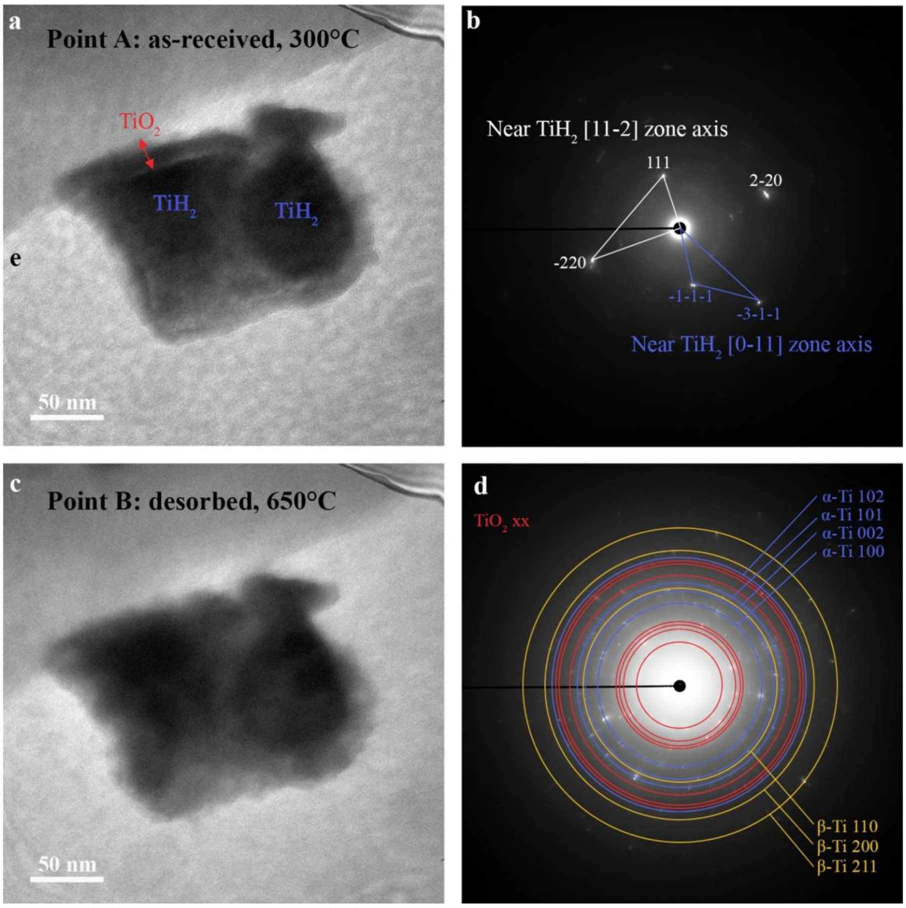
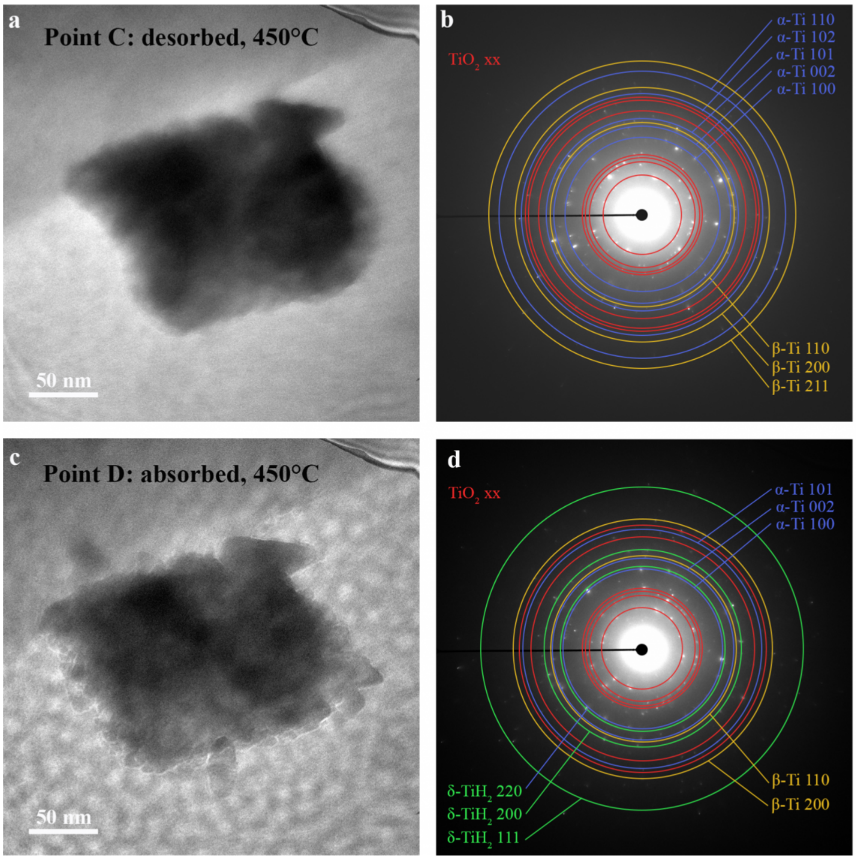


Fig. 1. (a) TEM image and (b) electron diffraction pattern of an as-received TiH2 powder (Point A). (c) TEM image and (d) electron diffraction pattern of the TiH2 powder after H2 desorption (Point B).

図・表・数式 2 Figures, Tables and Equations 2	 Fig. 2. (a) TEM image and (b) electron diffraction pattern of an TiH_2 powder at Point C. (c) TEM image and (d) electron diffraction pattern of the TiH_2 powder after H_2 absorption (Point D).
その他・特記事項（参考文献・謝辞等） Remarks(References and Acknowledgements)	X.F. Tan would like to acknowledge Japan Society for the Promotion of Science (JSPS) Postdoctoral Fellowship for Research in Japan (Standard) (No. P22739) for the financial support and the Australian Academy of Science for the facilitation of the JSPS Fellowship. Xin Fu Tan,"Improving Metal Hydrides to Diversify Energy Storage and Transportation”, The 14th HOPE Meeting with Nobel Laureates, Tsukuba, Japan, 27 Feb – 3 Mar 2023[poster]

成果発表・成果利用 / Publication and Patents

DOI（論文・プロシーディング） DOI (Publication and Proceedings)	
口頭発表、ポスター発表および、その他の論文[1] Oral Presentations etc.	Xin Fu Tan, Youichirou Kawami,Yuma Hamano,Tomokazu Yamamoto,Kazuhiro Nogita,Kazuhiro Yasuda"In-situ gas atmosphere transmission electron microscopy of hydrogen de/absorption in TiH2",13th Asia Pacific Microscopy Congress,Brisbane, Australia, February 5, 2025[oral]
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特許登録件数 Number of Registered Patents	0件