

Transport kinetics of protium and deuterium in titanium: Experiments and modeling

Author names:

Jun Yamazaki, Chihiro Kobayashi, Kengo Nishi, and Katsuaki Tanabe^{*}

Author address:

Department of Chemical Engineering, Kyoto University, Nishikyo, Kyoto 615-8510, Japan

Corresponding author:

^{*}Email: tanabe@cheme.kyoto-u.ac.jp

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Abstract

We conducted absorption experiments on Ti using hydrogen isotopes, protium and deuterium, to gain insights into the kinetics of hydrogen atoms, particularly across the Ti surface. Rather than relying on various surface pretreatments, we identified the initial temperature of Ti in vacuum as the determining factor in achieving a high absorption rate and content. Specifically, we found that the initial Ti temperatures of approximately 900 and 980 °C were optimal for protium and deuterium, respectively, likely due to sufficient removal of the native surface oxide on Ti. The dependence of the absorption rate and amount of hydrogen isotopes on the temperature during absorption was partially explained by the phase transformation and exothermicity of the hydrogenation reaction. Moreover, this dependence strongly indicated the existence of a tunneling transport process. Additionally, we developed a kinetic model for hydrogen isotope transport in Ti to conduct numerical simulations. The absorption curves, calculated using the developed model, closely matched a series of experimental curves obtained at different temperatures. These curves were from an identical set of equations and kinetic parameters for both protium and deuterium. Our numerical kinetic model has the potential to serve as a valuable simulation tool for various applications, such as the design of high-performance hydrogen storage systems and maintenance strategies against hydrogen embrittlement of structural materials.

1. Introduction

The development of precise numerical simulators for hydrogen transport in metals is crucial for various applications, including the design of high-performance hydrogen storage systems [1–5] and preventing hydrogen embrittlement in structural materials [6–8]. Titanium (Ti), its alloys, and hydrides play pivotal roles in a wide range of applications, such as hydrogen storage [9–13] and nuclear power generation [14,15]. For example, the high hydrogen-absorption property of Ti makes it ideal for use in sublimation pumps in hydrogenic vacuum environments and the long-term storage of tritium [16,17]. Ti is also used to increase the absorption and desorption rates of lightweight hydrogen-storage materials as a dopant on their surfaces, as Ti enhances the dissociative adsorption and recombinative desorption of hydrogen molecules [18,19]. In nuclear fission reactors, Ti is employed in condenser tubes due to its mechanical robustness and corrosion resistance against seawater [20,21]. For nuclear fusion reactors, Ti is expected to be used as part of various alloys such as Ti–Zr–Mo, V–Cr–Ti, and Ti–Al–V for blanket materials [22–24]. Ti hydrides are promising for radiation shielding due to their moderating effects on neutron beams [25]. In addition, Ti particles can serve as particulate additives in molten-salt blankets, facilitating tritium absorption and transportation [26,27]. Ti particles can also suppress the corrosion of tubes in fusion reactors through sacrificial reactions with highly corrosive HF and F species [28]. Therefore, it is vital to understand the transport kinetics of hydrogen isotopes in Ti for optimizing these applications. Despite its significance, comprehensive studies on this topic, particularly concerning deuterium, have been limited [29–31]. While the hydrogen–Ti system has been studied for over 50 years, certain critical aspects, such as kinetic modeling for numerical simulation and surface condition/treatment analyses, remain insufficiently studied and understood. Therefore, we focused on addressing these crucial missing technical components

in the hydrogen–Ti system. In this study, we analyzed the kinetics of hydrogen isotope transport in Ti and developed a numerical model that can be utilized for simulations in various applications.

2. Experimental Methods

Figure 1 schematically illustrates the configuration of the experimental system. We measured the rate of hydrogen absorption in Ti using a self-built Sieverts-type apparatus [32]. Ti plates (99.5%) with dimensions of 3 cm × 3 cm × 1 mm served as the samples for hydrogen absorption. It is widely recognized that realizing smooth and reproducible hydrogen absorption in Ti through experimental methods is challenging. This is due to the rapid formation of surface oxides on Ti when exposed to ambient air [33–36]. Upon exposure to oxygen, Ti naturally reacts with oxygen molecules to form a thin layer of Ti oxide on its surface. The oxide layer usually comprises TiO₂ and other oxide phases and is typically less than 10 nm thick. The presence of this oxide layer severely hinders the transport of hydrogen from the gas phase into the bulk Ti. Therefore, in this study, we tested various surface pretreatments on Ti: acetone submergence, hydrofluoric-acid submergence, polishing, annealing, and reduction, for some experimental runs. Figure 2 presents the flow diagram of the experimental process used in this study. For the experimental runs with the acetone submergence pretreatment, the Ti sample was submerged in acetone (99.5%) with ultrasonication for 5 min to remove organic contaminants adsorbed onto the Ti surface. This was followed by a repeated submergence in renewed acetone, and then rinsing in deionized water for 10 s. For the runs with the hydrofluoric-acid submergence pretreatment, the Ti sample was submerged in 10% hydrofluoric acid (46.0%) for 10 s to remove the native oxide layer on the Ti surface. This was followed by a rinse with deionized water for 10 s. For the

polishing pretreatment, both surfaces of the Ti plate were polished with sandpaper until the surface darkness was removed and the metallic luster was exposed, to remove the native oxide layer on the Ti surface. The Sieverts-type apparatus featured a main chamber made of stainless steel with a volume of $1.6 \times 10^3 \text{ cm}^3$, housing the Ti sample. The entire apparatus was then evacuated to a pressure in the range of $3 \times 10^{-5} - 9 \times 10^{-5} \text{ Torr}$. In the annealing pretreatment, the Ti sample was vacuum-annealed using a heater at temperatures ranging from 500 to 900 °C for 30 min, to remove the native oxide layer on the Ti surface. For the runs with the reduction pretreatment, the Ti sample was annealed in 760-Torr hydrogen isotope that was used in the subsequent absorption experiment at the designated temperature for 30 min to remove the native oxide layer on the Ti surface. This was followed by evacuation for 1 h to desorb the hydrogen isotope absorbed during the annealing process. Thereafter, the electric power supplied to the heater was adjusted to achieve the desired Ti sample temperature, ranging from 600 to 1000 °C. This Ti temperature kept for 5 min before the subsequent injection of hydrogen isotope gas is defined as the initial temperature, which is an important factor affecting the hydrogen absorption rate. Either protium (H_2 , 99.999%) or deuterium (D_2 , 99.6%) gas was introduced into the main chamber through a reference chamber with a volume of $1.0 \times 10^3 \text{ cm}^3$ until the pressure reached 760 Torr. The electric power supplied to the heater was immediately set to the designated temperature of the Ti sample for the absorption experiment. As hydrogen was absorbed by Ti, the pressure in the chamber decreased. The pressure and temperature of the gas phase inside the chamber were continuously monitored in real-time to determine the temporal evolution of the hydrogen molar fraction in Ti [32]. Additionally, the temperature of the Ti sample was influenced by the injection of room-temperature hydrogen gas and the absorption enthalpy, particularly during the initial stages of hydrogen absorption. However, it quickly converged to a steady-state value ranging from 400 to 800 °C, defined as the absorption temperature.

3. Theory and Calculation Methods

To analyze the experimental data, we employed our numerical model developed in Ref. 37, with a major modification. Figure 3 illustrates the essential approach of the model for hydrogen transport. In this model, hydrogen molecules in the gas phase are adsorbed onto the Ti surface, simultaneously dissociating into hydrogen atoms. These hydrogen atoms, located at the Ti surface, then diffuse into the subsurface region of Ti and eventually into the bulk region. The subsurface, spanning one or two atomic monolayers directly beneath the surface and possessing distinct characteristics [38–40], is located between the surface and bulk regions of the material. Transition metals with active surface for hydrogen dissociation, such as Ti and Pd, often experience rate-limiting hydrogen transport across the subsurface region, rather than the surface or bulk, in the overall hydrogen transport processes [41,42]. Thus, it is crucial to consider subsurface transport when constructing of kinetic models to accurately simulate net hydrogen transport rates. The mass balances are formulated as follows:

$$X_{max} N_s \frac{d\theta}{dt} = J_{ads} - J_{des} - J_{sb} + J_{bs}, \quad (1)$$

$$X_{max} N_s \frac{d\theta_{ss}}{dt} = J_{sb} - J_{bs} - J_{dif}|_{subsurface}, \quad (2)$$

$$\frac{N_b V_b}{A} \frac{dX}{dt} = J_{sb} - J_{bs}. \quad (3)$$

The maximum molar fraction of hydrogen in Ti, denoted as X_{max} [mol-H/mol-Ti], was set to 3 [37,43–45]. To elaborate, the β phase of Ti has a body-centered cubic structure with two Ti atoms in a unit cell. There are 24 tetrahedral sites on the surface of a unit cell; thus, there are

essentially 12 atoms for the full occupancy of the tetrahedral sites. However, H atoms can occupy at most half of the tetrahedral sites due to the site-blocking effects. Consequently, the maximum possible number of H atoms in a unit cell is six, resulting in $X_{max} = 3$, while it is 1 and 2 for the α and δ phases, respectively. A more detailed rationale is provided in Ref. 37. The areal molar density of the Ti surface is denoted as N_s ($2.16 \times 10^{-5} \text{ mol} \cdot \text{m}^{-2}$ [17]). The coverage fraction, or occupancy, of hydrogen atoms on the Ti surface is represented by θ . The hydrogen fluxes for the surface adsorption and desorption processes are denoted as J_{ads} and J_{des} , respectively. Similarly, the hydrogen fluxes for inward and outward subsurface transport are represented by J_{sb} and J_{bs} , respectively. The coverage fraction of hydrogen atoms on the Ti subsurface is denoted as θ_{ss} . The hydrogen flux for transport in the bulk Ti is represented by J_{dif} . The spatial molar density of the Ti atoms is denoted as N_b ($9.4 \times 10^4 \text{ mol} \cdot \text{m}^{-3}$). The volume and surface area of Ti are represented by V_b and A , respectively. The molar fraction of the hydrogen atoms in Ti is represented by X [mol-H/mol-Ti]. J_{ads} , J_{des} [17], J_{sb} , J_{bs} [41], and J_{dif} can be calculated as follows:

$$J_{ads} = 2S_0 (1-\theta)^2 \frac{P_{H_2}}{\sqrt{2\pi M_{H_2} RT_g}}, \quad (4)$$

$$J_{des} = k_{des}^0 \theta^2 \exp\left(-\frac{E_{des}}{RT_s}\right), \quad (5)$$

$$J_{sb} = k_{sb}^0 X_{max} N_s \theta (1-\theta_{ss}) \exp\left(-\frac{E_{sb}}{RT_s}\right), \quad (6)$$

$$J_{bs} = k_{bs}^0 X_{max} N_s \theta_{ss} (1-\theta) \exp\left(-\frac{E_{bs}}{RT_s}\right), \quad (7)$$

$$J_{dif} = D_H^0 \frac{\partial C(z,t)}{\partial z} \exp\left(-\frac{E_{dif}}{RT_s}\right). \quad (8)$$

S_0 represents the coefficient of hydrogen atoms for sticking to the Ti surface when the surface is not yet covered by hydrogen. P_{H2} represents the hydrogen pressure, M_{H2} is the molar mass, and R represents the gas constant for the ideal gas state equation. T_g and T_s represent the absolute temperatures of the gas phase and solid phase (that is, Ti), respectively. There are three frequency factors involved: k_{des}^0 (for surface desorption) ($2.16 \times 10^8 \text{ mol-H}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$ [17]), k_{sb}^0 (for inward subsurface transport), and k_{bs}^0 (for outward subsurface transport). There are four activation energies for hydrogen: E_{des} (for surface desorption) ($1.17 \times 10^5 \text{ J}\cdot\text{mol}^{-1}$ [17]), E_{sb} (for inward subsurface transport), E_{bs} (for outward subsurface transport), and E_{dif} (for diffusion in the bulk region) ($5.3 \times 10^4 \text{ J}\cdot\text{mol}^{-1}$ [46]). The coefficient for the hydrogen diffusion rate in Ti is denoted as D_H^0 ($9.0 \times 10^{-7} \text{ m}^2\cdot\text{s}^{-1}$ [46]). Finally, $C(z,t)$ represents the spatiotemporal hydrogen concentration in the Ti bulk region, which depends on time (t) and position (z) within the material.

In Eq. 4, S_0 is dimensionless in the SI unit system and can be calculated as:

$$S_0 = 0.0143 \exp\left(-\frac{E_{S_0}}{RT_s}\right), \quad (9)$$

where E_{S_0} ($-1.99 \times 10^3 \text{ J}\cdot\text{mol}^{-1}$ [17,30]) represents the activation energy for adsorption [17,30], which is regressive. For consistency with the experimental situation, P_{H2} is updated in each time step via the following equation of state:

$$P_{H_2} = \frac{n_{H_2} RT_g}{V} = \left\{ \frac{P_{H_2,0} V}{RT_{g,0}} + \frac{(X_0 - X) n_{Ti}}{2} \right\} \frac{RT_g}{V}, \quad (10)$$

where n_{H_2} is the hydrogen amount of substance of hydrogen, V is the volume of the gas phase, $P_{H_2,0}$ is the initial pressure of the hydrogen gas, $T_{g,0}$ is the gas temperature at the initial stage, X_0 is the molar fraction of hydrogen in Ti at the initial stage, and n_{Ti} is the amount of substance of Ti. The value of X obtained from the previous time step was used.

To determine $X(t)$, we numerically solved Eqs. 1–3. For each time step, we updated the spatial profile of $C(z,t)$. In a previous study [37], the quasi-equilibrium assumption was used for hydrogen adsorption and desorption on the Ti surface due to its high surface activity, instead of solving Eq. 1. However, in the present study, we fully solved Eqs. 1–3 without this assumption for generality. We assumed that Ti is a plate with finite thickness and infinite area. We then considered hydrogen transport only in the direction of the plate thickness. The thickness of the Ti plate corresponds to V_b/A in Eq. 3. We used a symmetric boundary condition at the central plane of Ti, located at $z = 0$, which precludes hydrogen flux across this plane. We simulated the absorption of hydrogen from the two surfaces of Ti. We determined the values of k_{sb}^0 , k_{bs}^0 , E_{sb} , and E_{bs} through numerical fitting.

4. Results and Discussion

Figure 4 displays typical protium absorption curves for various Ti surface pretreatment conditions. The temperature labelled for each condition indicates the initial temperature for protium absorption. The absorption temperature was all about 600 °C. Unexpectedly, compared to the absorption curve for an initial Ti temperature of 940 °C, those

for all the other runs with lower initial temperatures were significantly lower, regardless of the surface pretreatment condition. The significantly lower protium absorption curves can presumably be attributed to the native surface oxide on Ti, which can act as a potential barrier to hydrogen transport, as mentioned earlier. These results suggest that the setting of initial Ti temperature might be deterministically more important than the Ti surface pretreatment conditions. Therefore, we carried out further protium absorption experiments at various initial temperatures. Figures 5 and 6 plot the dependence of the initial protium absorption rate and protium molar fraction in Ti (in mol-H/mol-Ti) at 1 h, respectively, on the initial Ti temperature for various Ti surface pretreatment conditions. These plots clearly reveal a threshold at approximately 870 °C for both significantly higher absorption rate and absorption fraction. In other words, regardless of the surface pretreatment condition, a sufficiently high initial temperature, above about 870 °C, is likely to be the determinative factor to secure a high protium absorption rate and fraction amount. This situation likely occurs because such a high temperature leads to the removal of the native surface oxide on Ti via a certain mechanism. Two possible processes were considered for the removal of the surface oxide: the dissociation of the oxide at the vacuum/oxide interface and the dissociation of the oxide at the oxide/Ti interface, followed by the subsequent diffusion of the oxygen atoms into the bulk region of Ti. However, the first mechanism is unlikely to work under the conditions of our experiments. This is because the dissociation partial pressure of TiO_2 is known to be 4×10^{-29} Pa at 850 °C [47], which is extremely small compared to the chamber pressure of approximately 1×10^{-3} Pa when the chamber was vacuumed. Conversely, the second mechanism becomes observable as a macroscopic change on a practical time scale at 800 – 900 °C [47–49], which is consistent with the results of our experiments. Therefore, in the current experiments, the disappearance of the oxide on the Ti surface, which obstructs hydrogen transport, through the second mechanism involving oxide decomposition and subsequent oxygen diffusion into the Ti bulk due to the increased initial Ti temperature, was

considered to have improved the protium absorption rate and absorption fraction. Based on these results, the initial Ti temperature for the following protium absorption experiments was set to 900 °C. For experimental simplicity and reproducibility, the Ti surface pretreatment was omitted.

For the deuterium absorption experiments, we only tested the reduction method as the Ti surface pretreatment. This is because we observed in the previous protium experiments that the conditions of the Ti surface pretreatment did not substantially affect the absorption rate and amount. Instead, the crucial factor appeared to be the initial Ti temperature. Figure 7 presents the typical deuterium absorption curves with and without the reducing Ti surface pretreatment at various initial Ti temperatures. The absorption temperature was all approximately 700 °C. Similar to the case of protium absorption, there might exist a certain threshold in the initial temperature range between 900 and 1000 °C that removes the native surface oxide on Ti, which acts as a barrier to deuterium transportation, thus enhancing deuterium absorption in Ti. Therefore, we performed deuterium absorption experiments at various initial Ti temperatures, focusing on this temperature range. Figures 8 and 9 show the dependence of the initial deuterium absorption rate and deuterium molar fraction in Ti (mol-D/mol-Ti) at 1 h, respectively, on the initial Ti temperature with and without Ti surface pretreatment. From these plots, no clear dependence trend of the initial deuterium absorption rate on the initial Ti temperature was observed (Fig. 8). However, the 1-h deuterium molar fraction in Ti was observed to become maximal at about 980 °C (Fig. 9). Based on these results, the initial Ti temperature for the following deuterium absorption experiments was set at 980 °C. Again, the Ti surface pretreatment was omitted for experimental simplicity and reproducibility.

Figure 10 presents the protium and deuterium absorption curves at various absorption

temperatures. The initial Ti temperature was 900 and 980 °C for the protium and deuterium absorption experiments, respectively. No Ti surface pretreatment was performed. Incidentally, the equilibrium molar fractions of approximately 1.8 reached for both protium and deuterium in Ti at absorption temperature of 500 °C corresponds to a hydrogen storage of approximately 1900 atm based on the volume of Ti. For both protium and deuterium, the absorption rate and equilibrium molar fraction in Ti were higher at lower absorption temperatures. Furthermore, it is evident that the absorption rate is higher for protium than for deuterium across all experimental absorption temperatures of 500, 600, and 700 °C. In addition, the difference in the equilibrium molar fractions in Ti between protium and deuterium was greater at higher absorption temperatures. In the following section, we discuss the origin of these observed trends.

The observed trend of higher hydrogen absorption rates and equilibrium molar fraction in Ti at lower absorption temperatures for both protium and deuterium can be explained by considering the thermodynamics of the hydrogenation of Ti. The smaller equilibrium absorption in Ti at higher temperatures is simply attributed to the fact that the hydrogenation of Ti is an exothermic reaction. In other words, the equilibrium tends toward the reactant side at higher temperatures, and thus, the amount of Ti hydride product decreases. The trend of the absorption rate being lower at higher temperatures may be explained similarly. For example, the hydrogen absorption rate is proportional to the difference between the hydrogen pressure in the chamber and its equilibrium value particularly when the dissociative surface adsorption of hydrogen is the rate-determining process [50]. As described above, the equilibrium molar fraction of hydrogen in Ti decreases at higher temperatures. Therefore, at higher temperatures, the hydrogen pressure in the chamber at equilibrium increases and the difference between the actual and equilibrium pressures decreases, as does the absorption rate. In contrast, in the experiments conducted at far lower hydrogen gas

pressures, the absorption rate and equilibrium content were higher at higher temperatures, presumably due to the smaller effect of the aforementioned pressure difference [34]. By this mechanism, the absorption rates of protium and deuterium, as observed in Fig. 10, tends to be lower at higher temperatures. Notably, this inverse temperature dependence of hydrogen absorption rate was also experimentally observed for a Mg–Ni alloy [50].

The difference in the absorption rate into Ti of protium and deuterium is considered to stem mainly from their mass difference. Graham's law states that the diffusion rate of a gas is inversely proportional to the square root of the molar mass of its particles. This relationship is also observed in the widely recognized formula for the diffusion coefficient in Knudsen diffusion. Owing to such an influence of the mass difference between the hydrogen isotopes, the higher absorption rate of protium compared to deuterium, as shown in Fig. 10, can be explained.

The observed trend, where the difference in the equilibrium molar fraction in Ti between protium and deuterium was larger at higher absorption temperatures, is considered to arise from the dependence of the crystalline phases formed on different temperatures. In the common pressure–concentration–temperature diagram of protium in Ti [44], Ti with absorbed protium up to the vicinity of equilibrium takes the δ phase at 500 and 600 °C, and the β phase at 700 °C around 1 atm, corresponding to our experimental condition of the hydrogen isotope gas phase. Notably, β -Ti and δ -Ti have body-centered and face-centered cubic structures, respectively. Body-centered cubic structures have shorter inter-atomic distances than face-centered cubic structures, and these structures undergo different hydrogen transport processes in Ti. In a face-centered cubic structure, hydrogen atoms are transported to overcome potential barriers via thermal activation. In a body-centered cubic structure, the tunneling transport process often occurs due to the lower potential barriers for shorter Ti–H

(D) inter-atomic distances. Since the tunneling transport process exhibits a large isotope dependence on the activation energy, the suppression of the equilibrium absorption amount in Ti for deuterium relative to protium is considered to increase at higher temperatures, as observed in Fig. 10 [51].

In Fig. 11, we replot the experimental protium absorption curves from Fig. 10 as dots to enhance clarity. In addition, the solid lines in Fig. 11 represent the numerically simulated protium absorption curves at various temperatures using our kinetic transport model. The fitting parameters were: $k_{sb}^0 = 6.26 \times 10^{-1} \text{ s}^{-1}$, $k_{bs}^0 = 1.28 \times 10^{-2} \text{ s}^{-1}$, $E_{sb} = -74.8 \text{ kJ} \cdot \text{mol}^{-1}$, and $E_{bs} = -108 \text{ kJ} \cdot \text{mol}^{-1}$. E_{sb} and E_{bs} are the activation energies for diffusion across the subsurface region and are typically positive in the case of hydrogen diffusion, overcoming the potential barriers by thermal activation. However, the negative values of E_{sb} and E_{bs} determined by numerical fitting indicate the possibility that hydrogen diffusion in the subsurface region occurs through tunneling rather than overcoming the inter-site potential barriers. Incidentally, the crossover of the simulated curves for 500 and 600 °C at approximately 11 min is attributed to the mechanism wherein the absorption rate is kinetically higher, but the equilibrium hydrogen fraction is lower at higher temperature. Figures 12 and 13 depict the potential diagrams for hydrogen transport for positive and negative values of E_{sb} and E_{bs} , respectively. In the case of positive E_{sb} and E_{bs} , the values correspond to the height of the potential barriers that hydrogen atoms must overcome during diffusion [17,52]. However, for negative E_{sb} and E_{bs} , their absolute values can be regarded as the depth of the potential valleys between the surface and subsurface regions. In this situation, the surface and subsurface sites do not locate at an energetic local minimum, which may be related to the zero-point energies and tunneling transport of hydrogen atoms between these levels [51]. Similarly, Fig. 14 presents the replotted experimental deuterium absorption curves, accompanied by the curves calculated from our numerical transport model. The fitting parameters were: $k_{sb}^0 = 21.4 \text{ s}^{-1}$,

$k_{bs}^0 = 2.12 \text{ s}^{-1}$, $E_{sb} = -42.0 \text{ kJ}\cdot\text{mol}^{-1}$, and $E_{bs} = -64.2 \text{ kJ}\cdot\text{mol}^{-1}$. The values of the activation energies E_{sb} and E_{bs} for protium and deuterium determined by the numerical fitting in Figs. 11 and 14, respectively, are summarized in Table 1. As observed in Figs. 11 and 14, our numerical kinetic model of hydrogen transport in Ti moderately reproduced a series of experimental absorption curves at various temperatures. It used an identical single set of equations and kinetic parameters for both protium and deuterium, demonstrating the utility of the model, for instance, predicting the accumulation of hydrogen isotopes in structural materials for the prevention and maintenance against embrittlement. Finally, Table 2 summarizes the research conducted in earlier studies on the transport kinetics of hydrogen isotopes in Ti and the current study.

5. Conclusions

In this study, we conducted experiments involving the absorption of protium and deuterium in Ti to investigate the kinetics of hydrogen atoms, particularly across the Ti surface. Although we performed a series of surface pretreatment tests, our findings revealed that the initial temperature of Ti in vacuum predominantly determined the success or failure of smooth, fast absorption and high equilibrium molar fraction in Ti. Specifically, the initial Ti temperatures of approximately 900 and 980 °C were optimal for protium and deuterium, respectively, presumably due to sufficient removal of the native surface oxide on Ti. The observed dependence of the absorption rate and eventual content of hydrogen isotopes in Ti on the absorption temperature was partially explained by considering the phase transformation and exothermicity of the hydrogenation reaction. However, it strongly suggested the existence of a tunneling transport process of hydrogen atoms. In addition, we developed a kinetic model for hydrogen isotope transport in Ti for numerical simulations. The

calculation results based on our model reproduced a series of experimental absorption curves at various temperatures using an identical set of equations and kinetic parameters for both protium and deuterium. Our numerical kinetic model can be a useful simulation tool for Ti-related material applications, including the design of high-performance hydrogen storage systems and the maintenance against hydrogen embrittlement of structural materials. In the present study, our model is designed for one-dimensional transport within a single flat metal body, as we employed plate-shaped Ti samples for convenience and analysis. For spherical metal particles, similar to many practical hydrogen storage materials, one can simply replace Eq. 8 with the polar-coordinate form of the diffusion equation [53], as we calculated in Refs. 41 and 42. In future studies, we plan to extend our model to higher-dimensional, complex shapes for broader applicability.

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.

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Figure and Table Captions

Figure 1: Schematic illustration of the configuration of the experimental system.

Figure 2: Flow diagram of the experimental process in this study.

Figure 3: Conceptual schematic diagram of our calculation model for hydrogen transport in titanium. J_{ads} and J_{des} are the hydrogen fluxes for the surface adsorption and desorption processes, respectively; J_{sb} and J_{bs} are the fluxes for the migration of hydrogen from the surface to the subsurface, and from the subsurface to the surface, respectively; J_{dif} is the hydrogen flux for diffusion in the bulk region; and θ and θ_{ss} are the fractional coverages at the surface and subsurface, respectively.

Figure 4: Typical protium absorption curves for various Ti surface pretreatment conditions. Each label indicates the Ti surface pretreatment condition and the initial temperature for protium absorption. The absorption temperature was about 600 °C.

Figure 5: Dependence of the initial protium absorption rate on the initial Ti temperature for various Ti surface pretreatment conditions.

Figure 6: Dependence of the protium molar fraction in Ti (in mol-H/mol-Ti) at 1 h on the initial Ti temperature for various Ti surface pretreatment conditions.

Figure 7: Typical deuterium absorption curves with and without the reducing Ti surface pretreatment for varied initial Ti temperature. The absorption temperature was about 700 °C.

Figure 8: Dependence of the initial deuterium absorption rate on the initial Ti temperature with and without the Ti surface pretreatment.

Figure 9: Dependence of the deuterium molar fraction in Ti (in mol-D/mol-Ti) at 1 h on the initial Ti temperature with and without the Ti surface pretreatment.

Figure 10: Protium (solid curves) and deuterium (dotted curves) absorption curves for various absorption temperatures. The initial Ti temperature was 900 and 980 °C for the protium and deuterium absorption experiments, respectively. No Ti surface pretreatment was carried out.

Figure 11: Experimental (dots) and numerical (lines) protium absorption curves for various absorption temperatures.

Figure 12: Schematic diagram of the spatial potential energy profile for hydrogen transport in the cases of positive values of E_{sb} and E_{bs} .

Figure 13: Conceivable schematic diagram of the spatial potential energy profile for hydrogen transport in the case of negative values of E_{sb} and E_{bs} .

Figure 14: Experimental (dots) and numerical (lines) deuterium absorption curves for various absorption temperatures.

Table 1: Summary of the values of activation energies, E_{sb} and E_{bs} , for protium and deuterium determined by numerical fitting in Figs. 10 and 13, respectively.

Table 2: Summary of the research contents conducted in the earlier studies on the transport kinetics of hydrogen isotopes in Ti and our present study.

Figures

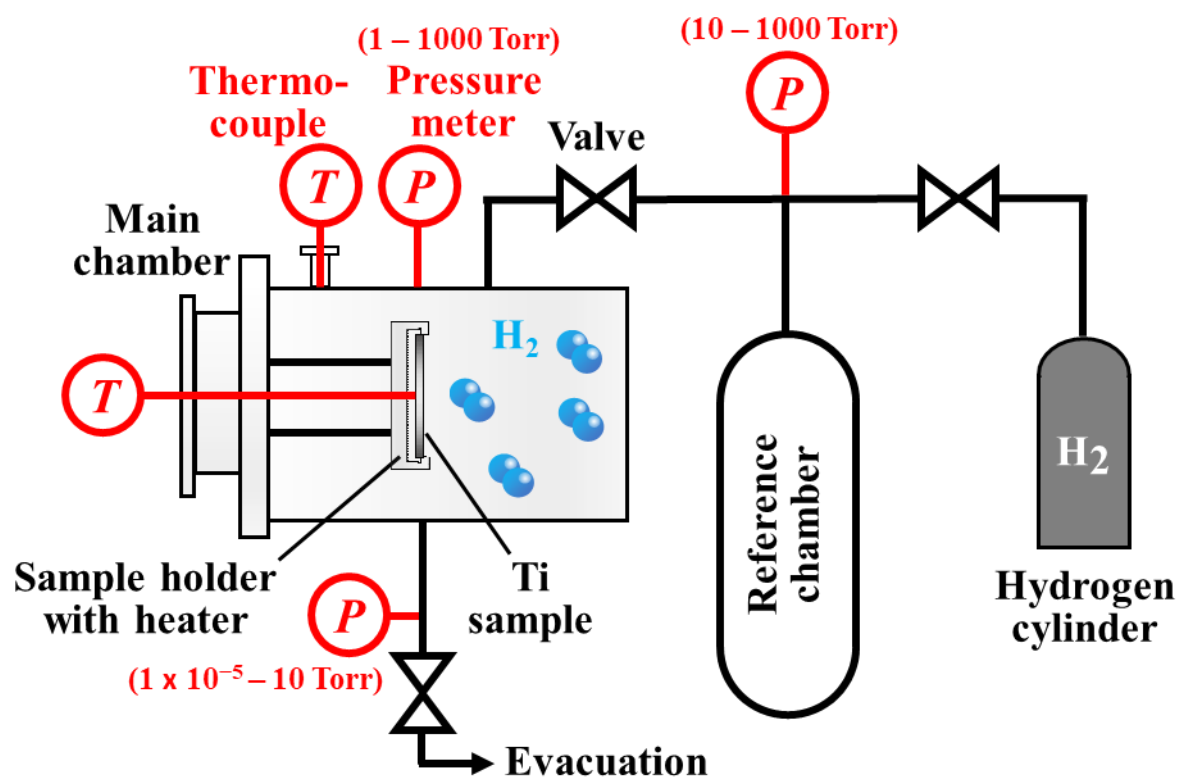


Fig. 1

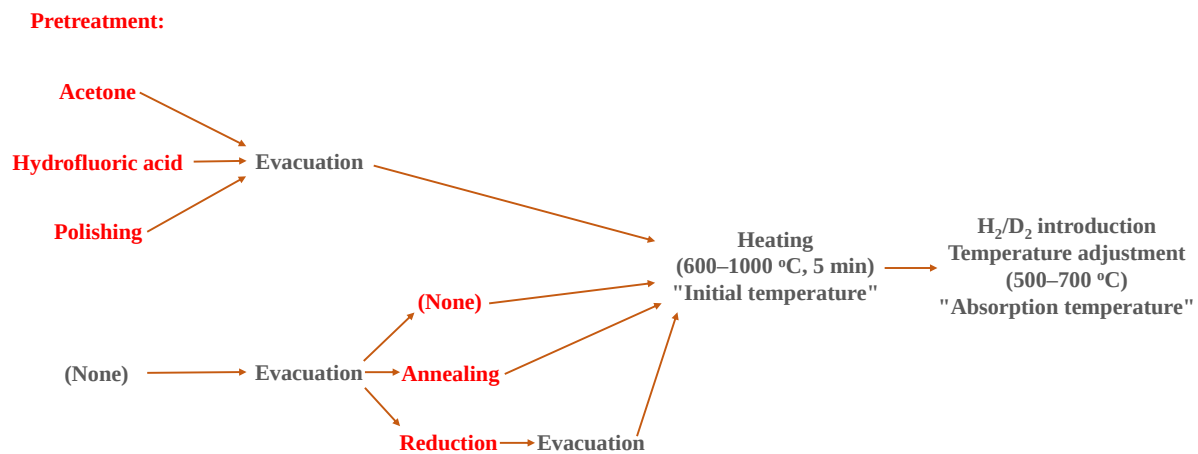


Fig. 2

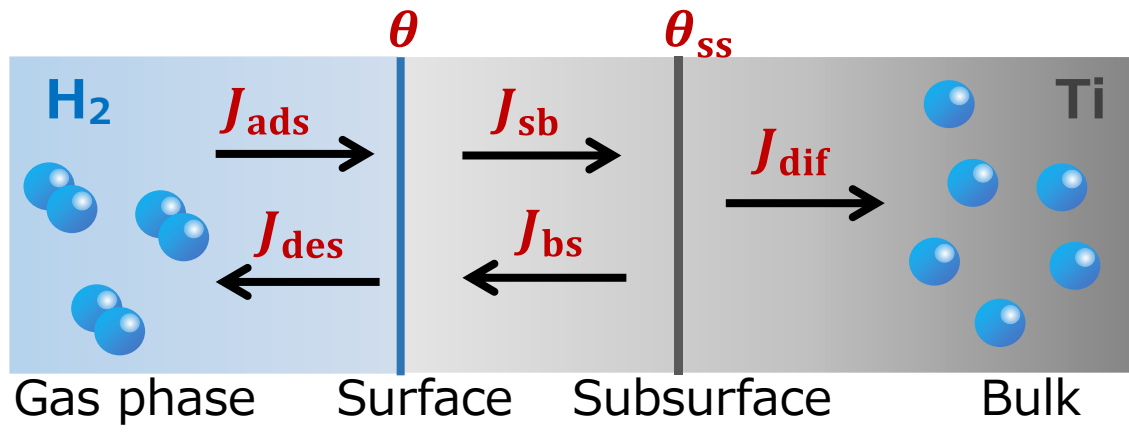


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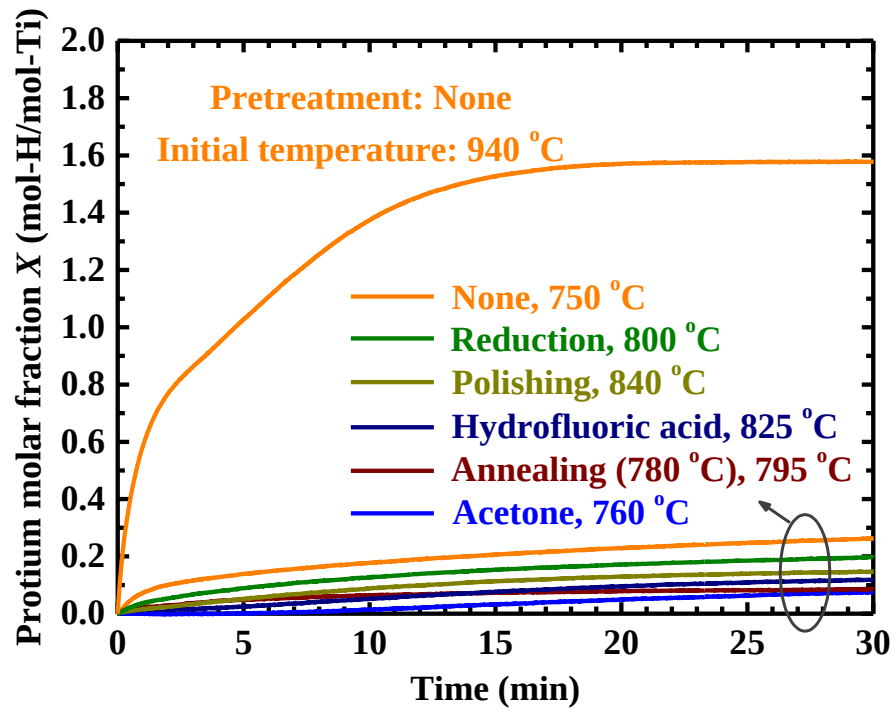


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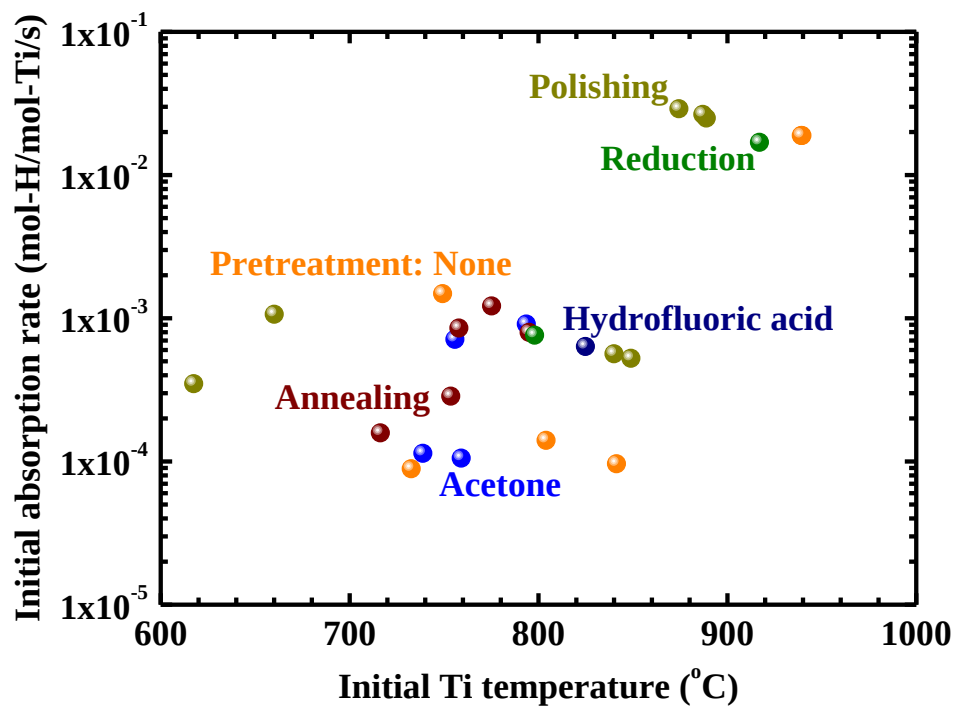


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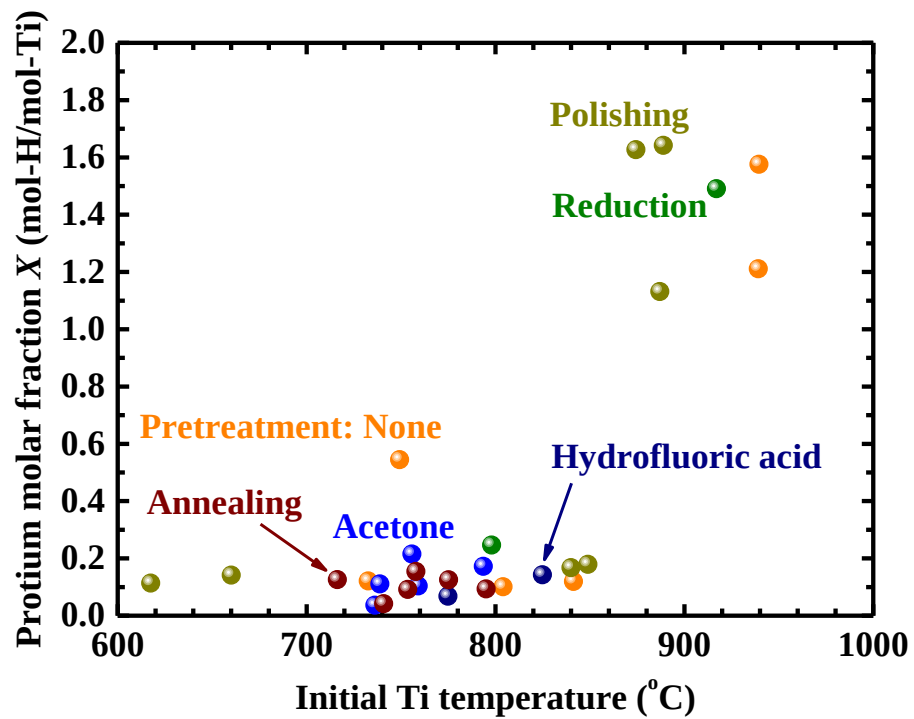


Fig. 6

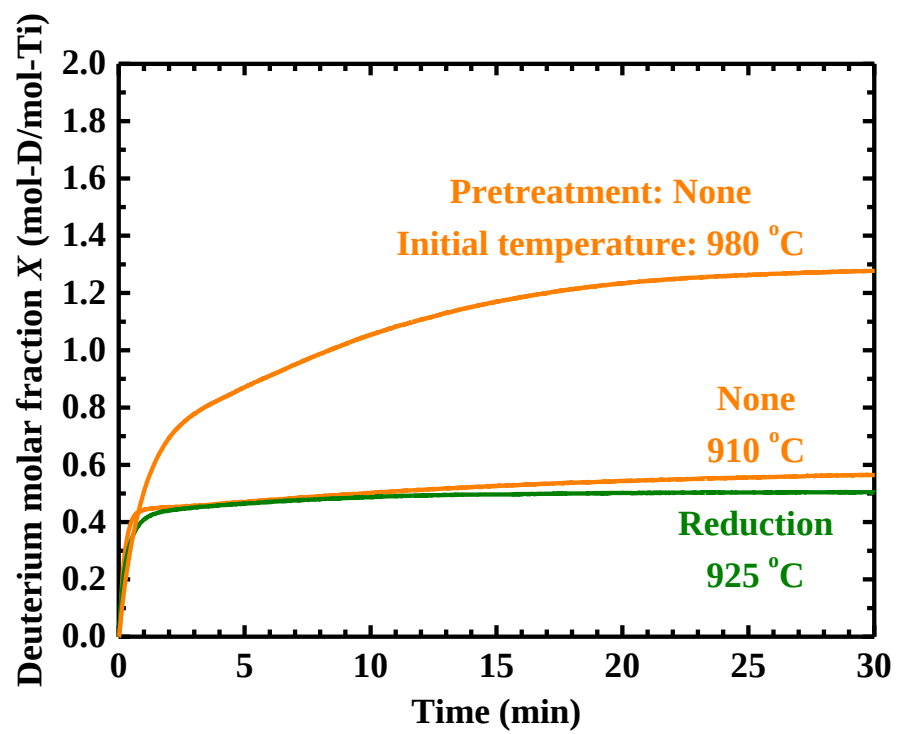


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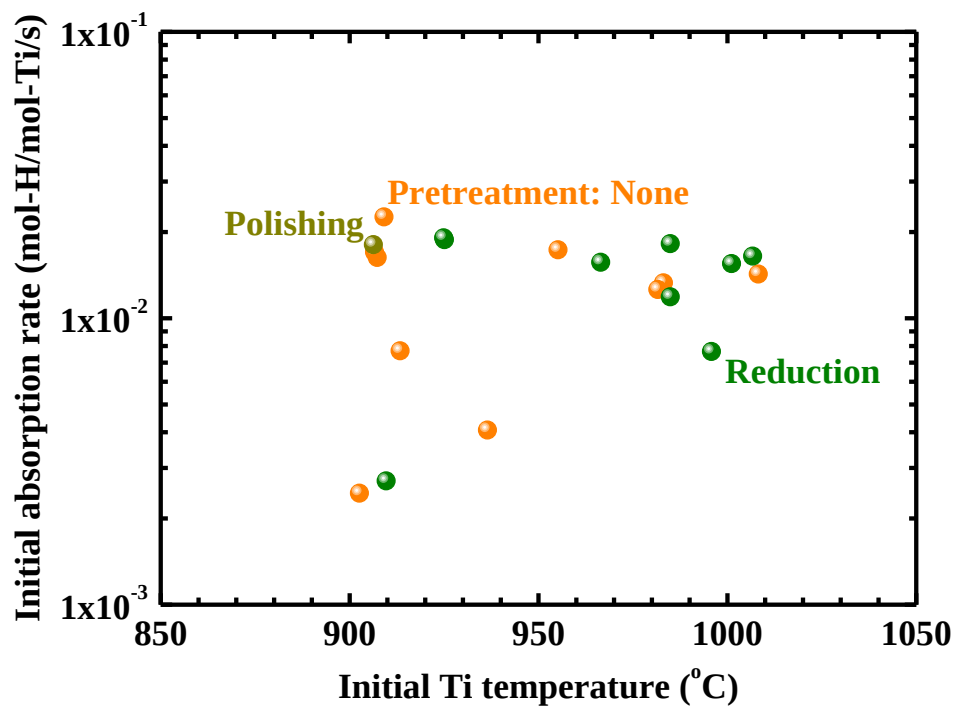


Fig. 8

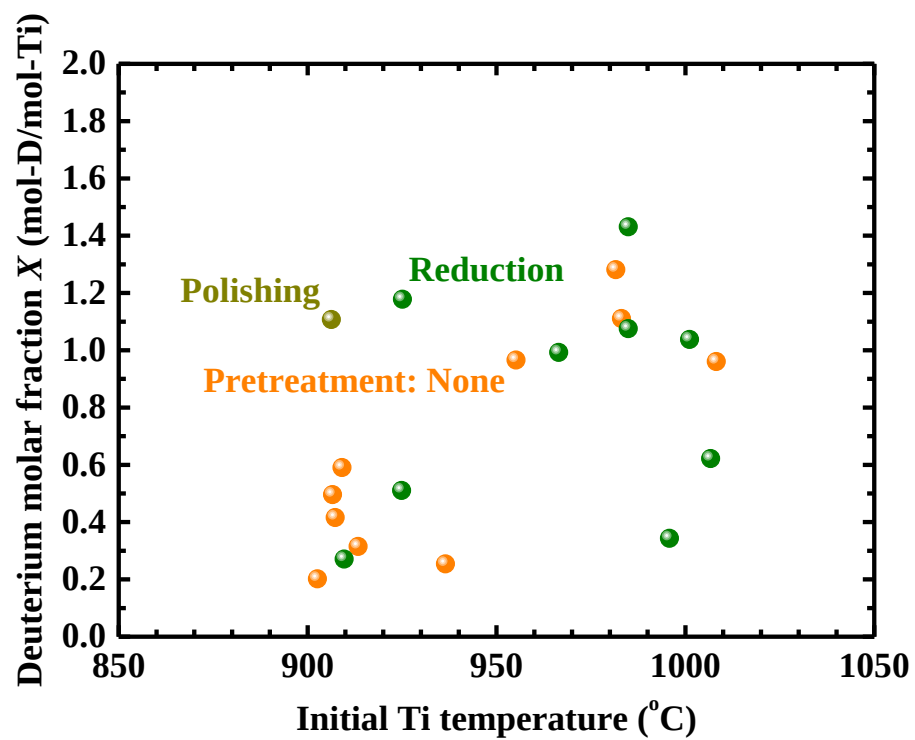


Fig. 9

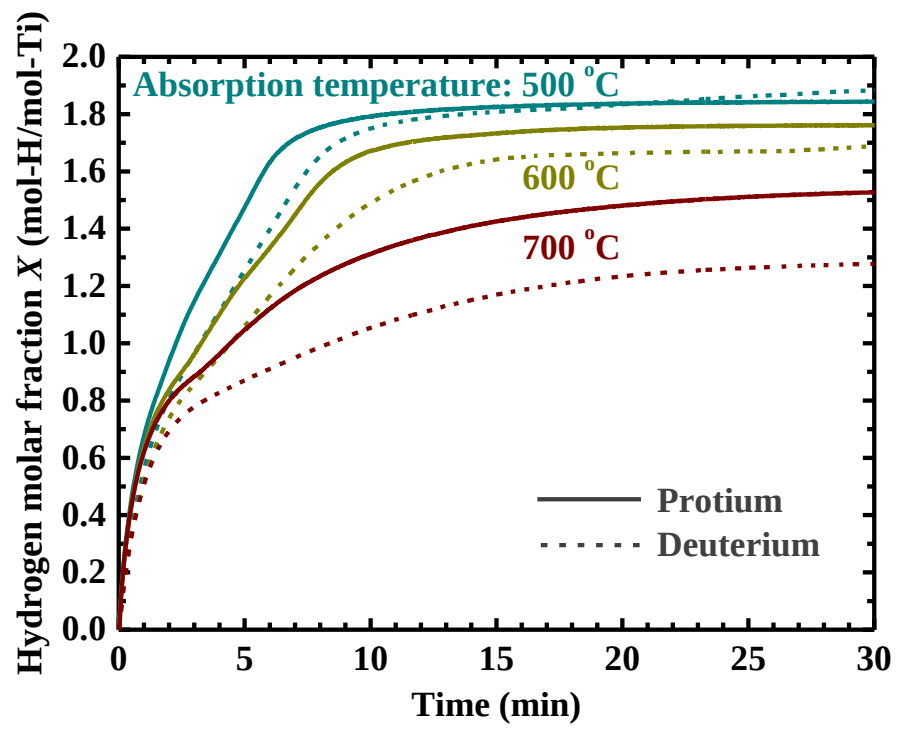


Fig. 10

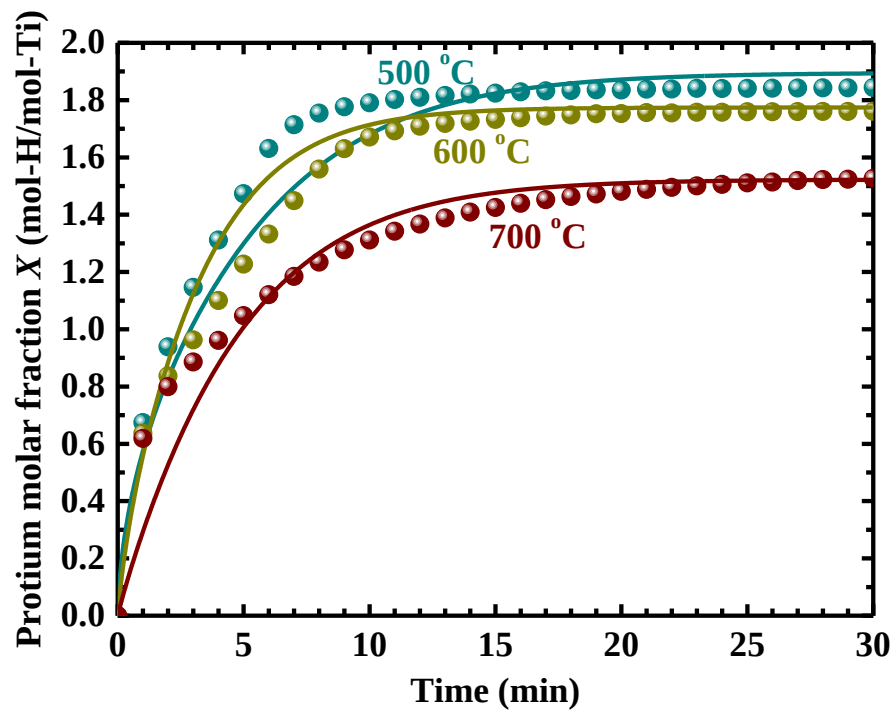


Fig. 11

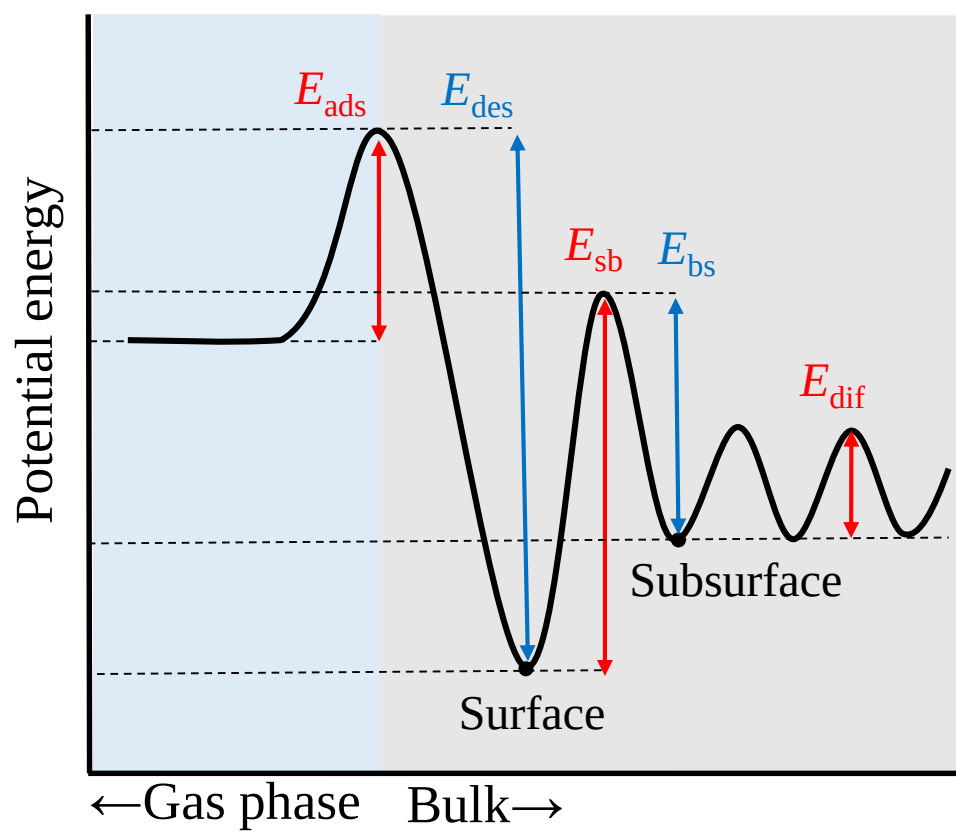


Fig. 12

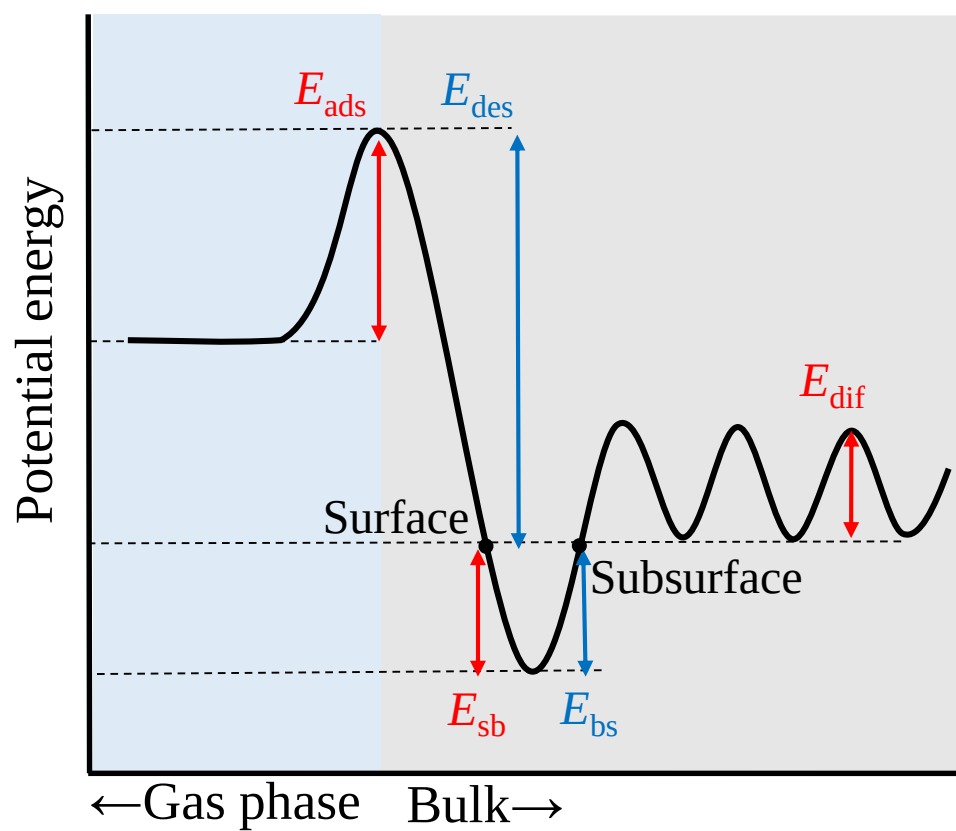


Fig. 13

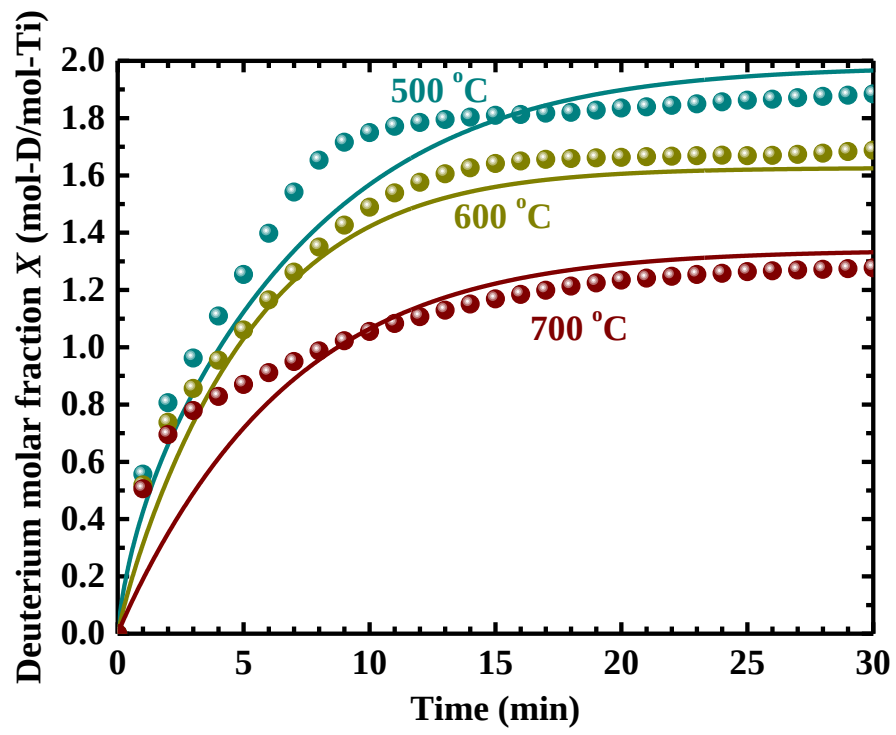


Fig. 14

	E_{sb}	E_{bs}	
Protium	$-74.8 \text{ kJ}\cdot\text{mol}^{-1}$	$-108 \text{ kJ}\cdot\text{mol}^{-1}$	Fig. 11
Deuterium	$-42.0 \text{ kJ}\cdot\text{mol}^{-1}$	$-64.2 \text{ kJ}\cdot\text{mol}^{-1}$	Fig. 14

Table 1

	Protium	Deuterium	Experimental	Modeling	Surface condition variation	Temperature	Pressure
Brown <i>et al.</i> ^[17]	○			○		250 – 500 °C	2 – 60 Torr
Elsworth <i>et al.</i> ^[29]	○	○	○			–190 – 20 °C	5×10^{-8} Torr
Harra ^[30]	○	○		○		–200 – 20 °C	Not shown
Stuhr <i>et al.</i> ^[31]	○		○	○		500 – 700 °C	3 bar
Johnson ^[33]	○		○	○		400 – 800 °C	0.004 – 2.0 Torr
Hirooka <i>et al.</i> ^[34]	○		○			450 – 800 °C	100 Torr
Wipf <i>et al.</i> ^[35]	○	○	○	○		–35 – 0 °C	Vacuum
Naito <i>et al.</i> ^[52]	○	○	○	○		900 – 1200 °C	Not shown
This work	○	○	○	○	○	500 – 700 °C	250 – 900 Torr

Table 2