Control and Application of Ultrahigh Hydrogen Flux in Materials*⁾

Makoto I. KOBAYASHI[1,2], Yuji HATANO[3], Masanori HARA[3], Yasuhisa OYA[4],
Yuji YAMAUCHI[5], Teppei OTSUKA[6] and Takuya NAGASAKA[1,2]

[1]*National Institute for Fusion Science, National Institutes of Natural Sciences, Gifu 509-5292, Japan*
[2]*The Graduate University for Advanced Studies, SOKENDAI, Gifu 509-5292, Japan*
[3]*Hydrogen Isotope Research Center, University of Toyama, Toyama 930-8555, Japan*
[4]*Graduate School of Integrated Science and Technology, Shizuoka University, Shizuoka 422-8529, Japan*
[5]*Graduate School of Engineering, Hokkaido University, Sapporo 060-8628, Japan*
[6]*School of Science and Engineering, Kindai University, Osaka 577-8502, Japan*

This paper reviews the control and the application of ultrahigh hydrogen flux in materials for fusion reactors and future hydrogen societies. Ultrahigh hydrogen flux can be efficiently formed by the combination of hydrogen plasma exposure and the surface modification method, similar to super-permeation. The paper discusses the possibility of the fabrication of oversaturated hydrogen storage materials and the effective tritium removal from the components using the ultrahigh hydrogen flux.

1. Introduction

In the Deuterium (D)-Tritium (T) fusion reactor, fuel hydrogen isotopes will be in the high-temperature plasma as well as sub-systems for processing under wide ranges of temperatures, pressures, and physical/chemical states. For example, there will be a high temperature burning plasma of hydrogen isotopes at the core region of vacuum vessel [1], liquid phase hydrogen isotopes at the isotope separation processes under the cryogenic temperature [2, 3], and stable hydrides under the ambient temperature in the storage and delivery system [4, 5].

Besides, hydrogen would be a promising energy carrier in future society. Hydrogen is the most abundant element. It can be produced from the various sources. Also, combustion product is water which is free of pollutant. In the hydrogen society, a huge amount of hydrogen will be transported, stored, and consumed.

Hydrogen is the smallest element, and it can easily penetrate into materials. Therefore, hydrogen-material interactions have been studied for the efficient hydrogen control in above systems and industries [6–8]. Based on the understanding of hydrogen-material interaction, various technologies have been developed for the successful handling of hydrogen. Even such successes, there still exists many challenges on the understanding and control of the hydrogen-material interaction under the harsh environments. For example, the interaction between hydro-

gen isotope plasma and metals on the first wall of the fusion reactor is still unclear. It is reported that surface morphology of tungsten drastically changes after the high flux hydrogen isotope plasma exposure [9, 10]. Other reports stated the considerable increase of hydrogen isotope retention in tungsten in the depth region beyond the range of hydrogen isotopes in plasma [11, 12]. For the case of hydrogen related industries, the hydrogen embrittlement has been problematic [13–17]. Hydrogen can dissolve and diffuse into metals in various processes, and the accumulation of hydrogen reduces ductility of metals, finally leading a crack. In the hydrogen society, gaseous hydrogen with a large volume and with a high pressure need to be safely handled and stored. Therefore, the quantitative prediction method for the degradation of the mechanical property of component materials are necessary from the safety hydrogen use in public.

These environments with high pressure gaseous hydrogen or highly dense hydrogen plasma induce an ultrahigh hydrogen flux in materials and will modify material structures and properties by disordered lattice structures or phase transitions of materials due to the introduction of a large amount of hydrogen atoms into the crystal lattice of materials. Therefore, these mechanisms in materials under ultrahigh hydrogen flux should be revealed comprehensively so that the control of materials property is possible in the above future hydrogen systems.

This paper provides a brief review of the mechanisms of hydrogen-material interaction under the existence of ul-

trahigh hydrogen flux in materials. Furthermore, it proposes the control and the application of these phenomena.

2. Hydrogen-Material Interaction

The schematic image of hydrogen-material interaction is provided in Fig. 1 [18]. Gaseous hydrogen composing hydrogen molecules collide onto the surface of the material. The collision probability depends on the partial pressure of hydrogen molecules. A part of hydrogen molecules is adsorbed on the top-most surface of the material as the physical-adsorption. Physically adsorbed hydrogen molecules are dissociated into two hydrogen atoms to transit to the chemical-adsorption. Then, adsorbed hydrogen atoms penetrate into the sub-surface region of materials. The above processes are reversible with the desorption of hydrogen molecules. Therefore, there should be simultaneous processes of hydrogen absorption and desorption in the system with gaseous hydrogen and materials under the equilibrium. The hydrogen concentration in materials under equilibrium as a function of the partial pressure of gaseous hydrogen can be summarized as the hydrogen solubility [19–21].

In the case of hydrogen ion implantation into the materials, energetic hydrogen ions can directly be injected into the sub-surface. Energetic hydrogen ions should be thermalized in the sub-surface region. Then, hydrogen atoms can be desorbed on the top-most surface by forming hydrogen molecules by the recombination as in the case of gaseous hydrogen exposure.

Solute hydrogen atoms occupy the interstitial posi-

tions of the crystal structure of the material in which electric repulsion by the constituent metal atoms is minimized [18]. Therefore, hydrogen solubility is different in each material. Due to a low potential-well for solute hydrogen in the interstitial positions, solute hydrogen atoms easily change their position by the random walk processes. This migration processes of hydrogen atoms via interstitial positions in the materials are called as diffusion process. The diffusion flux macroscopically depends on the concentration gradient of hydrogen atoms [22]. The diffusion coefficient is the proportional coefficient to correlate the concentration gradient of hydrogen atoms with the diffusion flux.

An important phenomenon caused by the hydrogen transport in materials is hydrogen permeation [23–27]. This event can be occurred when a surface of the materials is exposed to hydrogen. Solute hydrogen atoms on a surface of the materials diffuse into the bulk, and finally reached another surface to release out. The permeation flux depends on the concentration of hydrogen atoms at the surface region of materials, diffusion coefficient, and the material thickness. Hydrogen permeation is a specific phenomenon of hydrogen-material system, and the prediction and the mitigation of permeation flux is of importance in the safety point of view, in particular for the system with tritium [28–30].

Another important phenomenon is hydrogen trapping in the materials. In particular for the group 4 and 5 elements such as Ti, Zr, V, Nb, and Ta, hydrogen can form the hydrides with these elements [31–35]. The forma-
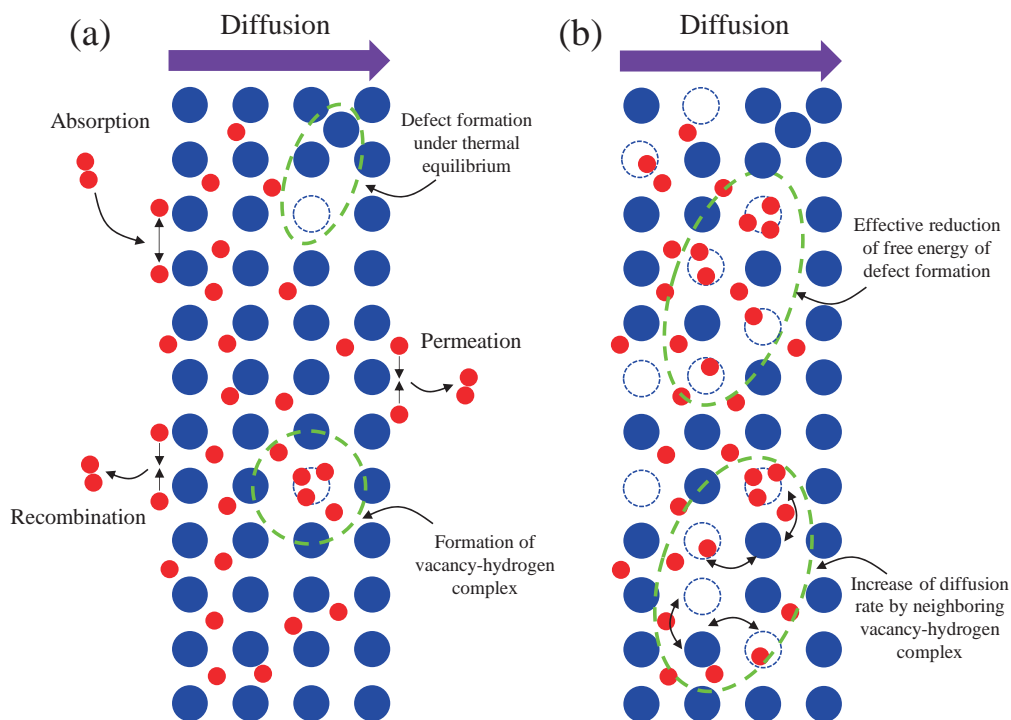

Fig. 1　Schematic images of hydrogen-material interaction (a) under the ambient hydrogen exposure condition and (b) with ultrahigh hydrogen flux. The red filled circles and blue filled circles indicate hydrogen and metal atoms, respectively.

tion of hydrides can usually be proceeded without activation processes because the heat of solution of hydrogen in these materials are negative value, therefore the reaction is exothermic.

Hydrogen trapping is also occurred at the irradiation defects in materials. Defects intrinsically exist in materials. Also, energetic particles such as radiation can induce the irradiation defects in materials. It is reported that vacancies, which is a vacant lattice point in the crystal structure of the material, can be a strong trapping site for hydrogen. Diffusing hydrogen atoms are stabilized in a vacancy to form a vacancy-hydrogen cluster [36–38]. Moreover, multiple hydrogen trapping in a vacancy is reported [39–43].

The important fact is that the formation energy of vacancy-hydrogen cluster in the material is much lower than the formation energy of vacancy [44, 45]. This indicates that in the material with solute hydrogen atoms, the vacancy concentration can be higher than that in the material without hydrogen. This effect becomes significant in the material under the ultrahigh hydrogen flux. In such a condition, the excess concentration of hydrogen will be introduced into the interstitial sites of the material, leading to a high concentration of vacancy-hydrogen complex. On the other hand, the diffusion process of the constituent atoms of the material should proceed by switching the position with neighboring constituent atoms [22]. This process can easily occur when the neighboring position is vacancy. Therefore, high concentration of vacancy-hydrogen complex in the material should lead the higher diffusivity of the constituent atoms of the material [46]. This consequently results in the drastic modification of material structure. The significantly high vacancy concentration has been observed by high-temperature and high-pressure hydrogen gas exposure to Ni, Pd, Cr, and so on as a superabundant vacancy formation [44, 45, 47–49]. The vacancy concentration reached up to 30 at.% in those research. The superabundant vacancy contains hydrogen atoms in them. Therefore, the material with ultrahigh hydrogen flux should possess oversaturated hydrogen concentration compared to the material under the ambient condition due to its modified crystal structure with superabundant vacancy.

3. Control of Ultrahigh Hydrogen Flux in Materials

As mentioned above, the ultrahigh hydrogen flux in the material should induce the drastic modification in the structure and the hydrogen trapping capacity of the material. This phenomenon is attractive for not only the scientific point but also the application point of view for hydrogen society. In this section, the method to induce ultrahigh hydrogen flux in materials is discussed.

One of the methods is hydrogen gas exposure under the high-pressure and high-temperature condition. According to the van't Hoff equation [31, 32], the solute hydrogen concentration in the material can increase with increasing temperature. Additionally, the solute hydrogen concentration can increase with elevated partial pressure of hydrogen gas according to Sievelt's law [28]. Previous studies on the superabundant vacancy formation adopted high-pressure gaseous hydrogen exposure around 5 GPa using an exclusive anvil to ensure the safety in high-pressure [50, 51].

Cathodic hydrogen charging is also an option for hydrogen introduction into the material [52, 53]. In this method, the sample material is used as the cathode, and immersed into the solution with electrolyte. For example, the sulfuric acid diluted by water is usually used as the solution. Then, electrolysis operation produces protons on the surface of the sample. Applied voltage attracts protons into the sample, therefore, hydrogen can be introduced into the sample material. Due to the vaporization of the solution, the maximum operation temperature must be below the boiling temperature of the solution.

Plasma exposure is the method to introduce hydrogen into materials [54–56]. The sample material is mounted in the chamber under vacuum. The sample temperature can be controlled by the heating system such as ohmic heater. Then, low pressure hydrogen gas is introduced into the chamber. The gas was heated by some methods, such as RF heating, to excite the hydrogen molecules into the plasma. The hydrogen ions in plasma are accelerated by the bias voltage applied on the sample. The plasma exposure has been developed for the plasma-wall interaction experiments for fusion reactor. The hydrogen flux of more than $10^{24}\,\mathrm{m^{-2}\,s^{-1}}$ has been achieved [57]. Heating of the sample by the plasma becomes significant with increasing hydrogen flux due to the energy deposition of plasma into the surface region of the sample. Therefore, an active cooling on the rear surface of the materials is necessary, although a significant temperature gradient between the surfaces should be formed.

As reviewed for various methods of ultrahigh hydrogen flux formation in materials briefly, there are several issues in the conventional methods to be adopted on the wide scientific research and applications. For example, the hydrogen gas exposure under high-temperature and high-pressure condition needs the exclusive devices with a strict safety regulation. Additionally, the operation temperature must be high. The high flux hydrogen plasma exposure method also needs the exclusive devices to realize a highly dense plasma. The precise temperature control is difficult due to the localized energy deposition from the plasma into the shallow surface region of the material. In the cathodic hydrogen charging, the control of material surface should be difficult due to a direct immersion into the electrolyte solution. Also, the operation temperature range is limited due to the electrolyte solution as liquid. According to the review, here we propose the combination of hydrogen plasma exposure and the surface modification method for the ultrahigh hydrogen flux formation in materials.

The combination of hydrogen plasma exposure and the surface modification has been examined for the research of super-permeable membrane [58–60]. In such research, the direct recovery of fuel hydrogen isotopes at the divertor of fusion reactor was investigated. Materials such as Nb, V were used as they possess high hydrogen solubility and an intrinsic oxide layer on the surface. During hydrogen plasma exposure, hydrogen atoms are introduced into the sub-surface of the sample. Without the surface oxide layer, major part of hydrogen can release out from the incident surface by the recombination, because the incident range of hydrogen atoms is nanometer order in the plasma exposure with low bias voltage. On the surface of Nb, V, and other group 4 elements, the oxide layer naturally forms and works as a potential barrier for migration of hydrogen atoms in the material. By such an effect, hydrogen atoms should lose the freedom to migrate to the incident surface. Consequently, most of hydrogen atoms penetrates in the material and releases from the rear surface. This effect is called as a hydrogen super-permeation. The hydrogen super-permeation could achieve $\sim100\%$ permeation efficiency, which is defined as the ratio of the permeated hydrogen flux to the incident hydrogen flux, although a conventional plasma driven permeation for W, Cu, and other materials could show the permeation efficiency around $10^{-3} \sim 10^{-5}$ [61, 62].

The hydrogen super-permeation is caused by the surface impurity layer as the potential barrier for hydrogen migration. The distribution of hydrogen concentration at the interface of two layers can be given as the chemical potentials of hydrogen in each layer being equivalent. Compared to materials with high hydrogen solubility, materials with low hydrogen solubility exhibit a significant increase in the chemical potential of hydrogen, even at low hydrogen concentrations. Therefore, the hydrogen super-permeation should be likely seen in the combination of the bulk material with high hydrogen solubility and the surface layer with low hydrogen solubility. On the other hand, a significant increase of hydrogen permeation flux could be observed in the case of tungsten [63], which possesses quite low hydrogen solubility, during hydrogen isotope and impurity mixed plasma exposure. This indicates the hydrogen permeation flux in various materials can be controlled by the surface layer as well.

According to Fick's diffusion equation [22], it is considered that the high permeation flux under hydrogen super-permeation can be achieved due to high hydrogen concentration at the sub-surface of the materials. Thus, the combination of hydrogen plasma exposure and surface modification methods, such as hydrogen super-permeation, can effectively generate ultrahigh hydrogen flux in materials compared to conventional plasma exposure methods. Moreover, the highly efficient formation of ultrahigh hydrogen flux in materials helps to minimize temperature increases compared to conventional plasma exposure, which often requires active cooling of the sample. This leads the

capability of a precise temperature control and in-situ hydrogen permeation measurement, which expand the window to investigate the material development and precise analyses under ultrahigh hydrogen flux.

4. Application of Ultrahigh Hydrogen Flux in Materials

In the above section, the control method of the ultrahigh hydrogen flux in materials was proposed based on the analogy of the hydrogen super-permeation. In this section, the possible applications of ultrahigh hydrogen flux in the materials are proposed.

4.1 Oversaturation hydrogen storage materials

One of the issues on the hydrogen as an energy carrier is its large volume when it is used as gas phase. Hydrogen storage materials have been developed as a compact hydrogen storage method in which hydrogen is stored in metals as hydrides such as VH_2, TiH_2, and MgH_2. Hydrogen storage materials with high stability, desirable hydrogen absorption/desorption temperature, and low equilibrium pressure have been developed so far [31–35]. However, the development of the material with high hydrogen weight density is still challenging for mobility field such as electric vehicles [64]. The hydrogen containing compounds such as AlH_3, $LiBH_4$, and $LiAlH_4$, are also attractive due to their high hydrogen weight density [65]. However, the synthesis processes for these materials are complicated [66, 67]. Therefore, the mass production of these materials is challenging.

The application of ultrahigh hydrogen flux in the materials can be a solution of this challenge. High concentration of hydrogen in the material promotes the formation of vacancy-hydrogen complex, and results in the drastic change of material structure. These materials with high concentration of vacancy-hydrogen complex would have a high hydrogen weight density. In fact, the material with superabundant vacancy after high-pressure and high-temperature hydrogen exposure showed additional hydrogen desorption peaks compared to the same material with conventional hydrogen gas exposure [45]. In fact, experiments, where hydrogen isotope ion implantation experiments into some metal materials, indicated quite high hydrogen concentration [68]. In particular for Zr, whose hydride under ambient pressure usually is the composition of ZrH_2, showed H/Zr~5 [69].

The high hydrogen concentration in the material induced by the ultrahigh hydrogen flux can also contribute to the fabrication processes of hydrogen containing compounds. For example, AlH_3 is attractive materials due to its high hydrogen content (10.1 at.%). However, its fabrication processes are complicated, consisting of organic reactions using ethers and several reagents [66, 67]. It is known that the hydrogen gas exposure into Al powder can-

not form AlH$_3$. However, recent experiments using high-temperature and high-pressure hydrogen gas exposure into metal Al showed that a direct formation of AlH$_3$ can be possible [70]. This result indicates that the high hydrogen concentration in Al is of critical importance on the formation of AlH$_3$. Compared to high-temperature and high-pressure hydrogen gas exposure, the combination of hydrogen plasma exposure and the surface modification method can induce ultrahigh hydrogen flux in lower temperature. Therefore, the materials with high hydrogen content, which can be decomposed in high-temperature condition, can be investigated.

These facts indicate the ultrahigh hydrogen flux introduction into the material is the promising method to induce an oversaturation hydrogen storage material with high hydrogen weight density. Although these materials with high hydrogen weight density would be formed under ultrahigh hydrogen flux, they become unstable or metastable after the flux decreases. If the phase change proceeds rapidly and hydrogen releases quickly, these materials are not suitable for hydrogen storage materials. However, it can be considered that the surface impurity layer formed to induce the ultrahigh hydrogen flux in the materials works as the potential barrier for hydrogen desorption, therefore the hydrogen desorption would be declined. Thanks to such slow processes, it can be expected that hydrogen storage can be practically possible. These effects of the surface impurity layer to stabilize unstable or metastable hydride can also be found in AlH$_3$, which successfully demonstrated a long hydrogen storage [66, 67].

4.2 High efficiency tritium decontamination

In components used in the D-T fusion reactor, tritium can be retained. It is considered that the retained tritium can be released out during the maintenance work of the components, and can result in an occupational exposure. Also, tritium can quickly release when the physical/chemical conditions drastically change. The accidents such as LOVA (Loss of vacuum accident) or LOCA (Loss of coolant accident) can give the physical/chemical parameter changes on the components such as temperature and surface chemical states [71, 72], and tritium release by these events will increase the hazard of the accident. Therefore, an active decontamination method of tritium from components is desired.

Various tritium decontamination methods such as the hydrogen isotope exchange method [73, 74], heating [75], and etching by chemicals [76] were investigated. In the actual reactor condition and for the efficient energy consumption and a practical work condition, heating of components with large volume is not suitable. Hydrogen isotope exchange method and etching using chemical substances such as acids are effective only on the surface region of the components. Tritium in the component is usually trapped in some trapping sites such as irradiation defects, and re-

tained in the bulk of the components, therefore the methods implementing only on the surface region are not effective.

To construct the high efficiency tritium decontamination method for the components, the ultrahigh hydrogen flux by the hydrogen super-permeation can be a solution. The hydrogen isotope migration in the materials can be expressed as the following equations.

$$\frac{\partial C_{H,m}(x,t)}{\partial t} = D \frac{\partial^2 C_{H,m}(x,t)}{\partial x^2}$$
$$- \left(-k_{dt,H} C_{H,t}(x,t) + k_{t,H} C_{H,m}(x,t) \right.$$
$$\left. \times \left[\frac{\psi(x,t) - (C_{T,t}(x,t) + C_{H,t}(x,t))}{\rho(x,t)} \right] \right)$$
$$+ S_{H,m}(x,t)$$
$$\frac{\partial C_{T,m}(x,t)}{\partial t} = D \frac{\partial^2 C_{T,m}(x,t)}{\partial x^2}$$
$$- \left(-k_{dt,T} C_{T,t}(x,t) + k_{t,T} C_{T,m}(x,t) \right.$$
$$\left. \times \left[\frac{\psi(x,t) - (C_{T,t}(x,t) + C_{H,t}(x,t))}{\rho(x,t)} \right] \right).$$

These are one-dimensional NcNabb-Foster based simultaneous equations for hydrogen isotopes [77]. Here, $C_{H,m}$ is the mobile hydrogen concentration, $C_{H,t}$ is the trapped hydrogen concentration, $C_{T,m}$ and $C_{T,t}$ are the concentrations of mobile and trapped tritium, respectively. The parameters of D, k_{dt}, k_t are the diffusion coefficient, detrapping rate constant and trapping rate constant, respectively. The trapping of hydrogen isotopes at the trapping sites, whose concentration is ψ, is considered here. The parameter of ρ indicates the density of constituent atoms at the lattice points of the material.

Using these equations, the efficiency of removal for tritium retained in tungsten as a model material was evaluated. It was assumed that tritium is trapped in vacancies in tungsten with the thickness of $10\,\mu$m. The initial concentration of tritium and vacancies are 1 at.% throughout the entire bulk of the tungsten, and the detrapping activation energy was assumed to be 2.05 eV according to Ref. [78]. There are three conditions in the simulation. The first condition is with only heating at 700 K which is around the expected temperature of the first wall of the D-T fusion reactor due to the decay heat [79]. The second one is with heating at 700 K and with hydrogen ion irradiation. The third one is with heating at 700 K and with hydrogen super-permeation. The depth profile of trapped tritium concentrations after elapsing for 1000 s under the above three conditions are displayed in Fig. 2. The first condition only with heating at 700 K showed a slight decrease of tritium concentration at the surface region. The decrease of tritium concentration is caused by the detrapping and diffusion processes of tritium to release out from the tungsten surface by heating. Although tritium in the vacancies can be detrapped at this temperature, detrapped tritium can be quickly re-trapped by unoccupied vacancies during diffu-
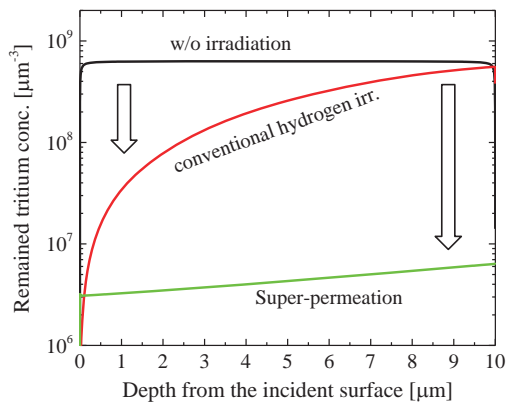
Fig. 2   The depth profiles of retained tritium concentrations after three types of tritium removal treatments. The hydrogen ion flux of 10^{22} m^{-2} s^{-1} were assumed.

sion process, consequently the tritium removal is not significant. The result in the second condition showed a significant decrease of tritium concentration from the incident surface toward the bulk region. In this condition, hydrogen atoms were introduced into the tungsten, and occupied vacancies. Due to the decrease in the concentration of unoccupied vacancies, the possibility for diffusing tritium to be trapped by vacancies can decrease, resulting in a quick release of tritium after detrapping. Even the promotion of effective tritium diffusion by the introduction of hydrogen, this method would not be effective on the deep bulk region as found in Fig. 2, where the tritium concentration near $10\,\mu$m hardly changed. This is caused by the release of induced hydrogen at the incident surface, which limits the increase in the hydrogen concentration at the sub-surface region.

The third condition showed a quite low retained tritium concentration throughout the entire bulk of the tungsten. Unlike to the second condition, the incident hydrogen atoms are refrained to be released out from the incident surface in the super-permeation. Therefore, ultrahigh hydrogen flux can be formed throughout the bulk of the tungsten, resulting in the effective removal of tritium from the tungsten.

5. Summary

In this paper, the influence of ultrahigh hydrogen flux in the materials are discussed. The control method and the application of ultrahigh hydrogen flux were proposed. The contents of this paper can be summarized as follows.

- Hydrogen can be trapped by vacancies intrinsically exist in the material or are induced by radiation, forming vacancy-hydrogen complexes.
- In the second bullet point, consider rephrasing it as: "Ultrahigh hydrogen flux promotes the formation of vacancy-hydrogen complexes in the materials. As a result, the diffusion rate of constituent atoms signif-

icantly increases, leading to a drastic change in the material's structure.
- Ultrahigh hydrogen flux can be efficiently achieved using an analogous method to hydrogen super-permeation. In this process, a surface thin impurity layer acts as a potential barrier, restricting hydrogen migration to the incident surface. Consequently, the hydrogen concentration at the sub-surface of the material significantly increases, inducing the ultrahigh hydrogen flux.
- The ultrahigh hydrogen flux can induce oversaturated hydrogen-containing structures in the material. Although these structures may be unstable or metastable under ambient conditions, the surface impurity layer acts as a potential barrier for hydrogen migration, stabilizing the structures for long-term storage.
- Efficient tritium removal from components in the fusion reactor can be achieved through the use of ultrahigh hydrogen flux. The introduced hydrogen atoms occupy trapping sites for hydrogen isotopes, such as vacancies, thereby increasing the effective tritium diffusion rate.

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