富山大学研究推進機構水素同位体科学研究センター研究報告 39：25－35，2019.

技術報告

水素雰囲気中性子照射用キャプセルのための材料選択

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Selection of Capsule and Hydrogen Source Materials for Neutron Irradiation under Hydrogen Gas Atmosphere

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(Received May 19, 2020 ; accepted August 7, 2020)

Abstract

Tungsten is a primary candidate of plasma-facing material (PFM) of a future fusion reactor.As PFM, tungsten will be exposed to deuterium-tritium plasma while irradiated with high energy neutrons. Trapping of tritium at neutron-induced defects needs to be understood for accurate evaluation of tritium inventory in a vacuum vessel of a reactor. From these viewpoints, the conceptual design of the capsule to realize neutron irradiation of tungsten in an existing fission reactor in a hydrogen gas atmosphere was proposed in this report. The irradiation conditions were supposed to be

400 ℃ and 0.1 MPa. Vanadium hydride was selected as a hydrogen source from the viewpoint of equilibrium hydrogen pressure, reaction rate and thermal stability. Molybdenum was chosen as the capsule material due to its low hydrogen permeability.

1. Introduction

Tungsten is a primary candidate of plasma-facing material (PFM) of a future fusion reactor because of favorable physical properties such as high melting point and high thermal conductivity [1]. PFM will be exposed to plasma of deuterium (D), tritium (T) and helium under irradiation of high energy (14 MeV) neutrons. Here, D and T are fuel, and helium and neutrons are products of fusion reactions. T is a radioisotope of hydrogen, and therefore the inventory of T in the vacuum vessel of a fusion reactor should be limited to a certain level. Neutron irradiation results in formation of lattice defects via displacement damages. It is known that radiation-induced defects in tungsten act as strong traps against hydrogen isotopes [1-5]. Hence, the inventory of T in tungsten could significantly increase after neutron irradiation.

The effects of neutron irradiation on hydrogen isotope retention in tungsten have been examined by using research fission reactors [2-5]. A significant increase in the hydrogen isotope retention was indeed observed after neutron irradiation. Vacancies and vacancy clusters are considered the main trap sites [5]. In these studies, tungsten specimens were first irradiated with neutrons in a helium gas atmosphere without hydrogen isotopes, and then exposed to D plasma or D_2 gas. Thereafter, deuterium retention was determined by thermal desorption spectrometry or nuclear reaction analysis.

Hautojärvi et al. have examined the growth of vacancy clusters both in hydrogen-free and in hydrogen-doped niobium and tantalum samples damaged with high energy electrons [6]. They reported that the hydrogen can be bound to vacancies and retard vacancy migration. Similar retardation of vacancy migration has been observed also for Fe [7]. Recently, Markelj et al. have performed simultaneous irradiation of tungsten with Wions and D ions and compared the results with those obtained by sequential irradiation with Wions and D ions [8]. They reported that D retention after simultaneous irradiation was larger than that after sequential irradiation with W ions and D ions. These observations indicate that the presence of hydrogen isotopes can affect the development of microstructures upon irradiation. However, neutron irradiation of tungsten in the presence of hydrogen was not carried out, since from a safety point of view it is difficult to introduce a large amount of hydrogen into a nuclear reactor.

It is obvious that the plasma-facing material of a fusion reactor will be irradiated with neutrons under exposure to D-T plasma, i.e. in the presence of hydrogen isotopes. Therefore, it is necessary to develop a technique for irradiating specimens with neutrons in a hydrogen atmosphere.

In this report, a basic concept of an irradiation capsule is proposed to realize safe neutron irradiation in a hydrogen gas atmosphere at a reasonable cost. The proposed capsule contains a metal hydride as a source of gaseous hydrogen. The candidate capsule material is also discussed in terms of hydrogen permeation.

2. Conceptual design of irradiation capsule

Specimens for neutron irradiation should be as small as possible in order to minimize the amount of radioisotopes generated by neutron-induced transmutation. The sizes of specimens used in the previous study [2-5] were 6 mm in diameter and 0.2 or 0.5 mm thick. These specimens were enclosed in a metal capsule in an atmosphere of gaseous helium to prevent oxidation during neutron irradiation and then installed in a research reactor.

During reactor operation, the specimens are heated by absorbing radiation. The specimen temperature is determined by the balance between heating by radiation and heat loss controlled by the transfer of heat from the specimens to the capsule wall and from the capsule wall to coolant water.

The conceptual design of the capsule for neutron irradiation in an atmosphere of

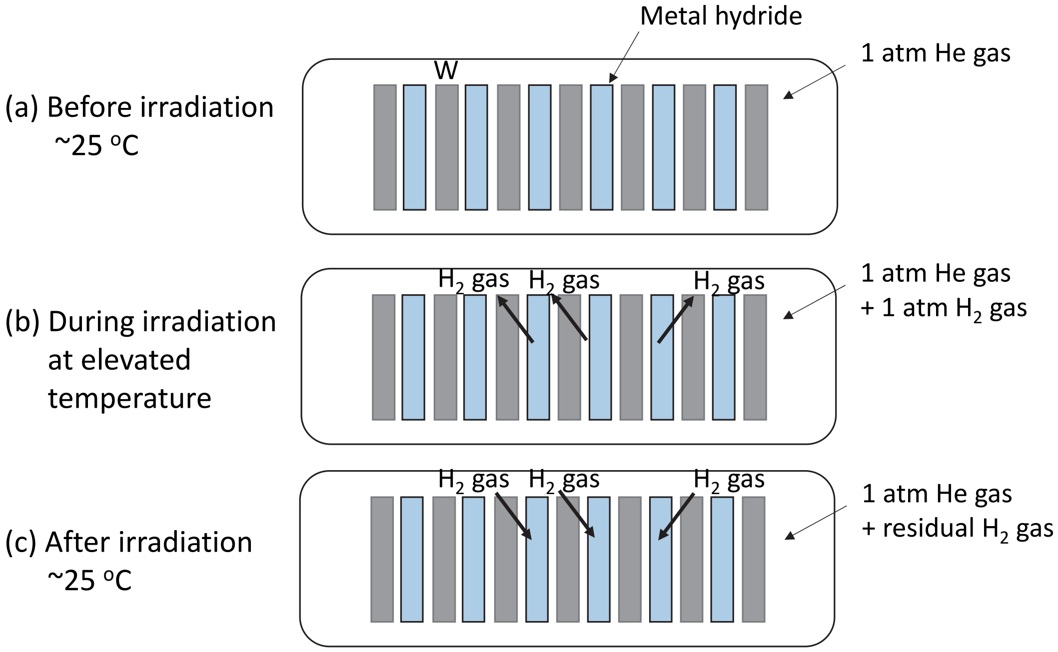

Fig. 1. Conceptual design of irradiation capsule to realize neutron irradiation of tungsten specimens in a hydrogen gas atmosphere. Hydrogen gas is reversibly supplied and absorbed by a metal hydride.

gaseous hydrogen is shown in Fig. 1. Initially, hydrogen is stored in metal hydride disks with a size similar to the size of the specimens, as shown in Fig. 1(a). The operation of the reactor leads to an increase in the temperature of both specimens and metal hydride disks. Hydrogen gas is released with increasing temperature of metal hydride, and the partial pressure of hydrogen gas in the capsule becomes constant if the temperature of the hydride reaches a stable value and equilibrium is attained between the hydrogen gas and the metal hydride (Fig. 1 (b)). When cooling after the completion of neutron irradiation, hydrogen gas is absorbed by the metal hydride and therefore the partial pressure of hydrogen gas in the capsule decreases, as shown in Fig. 1 (c). Therefore, the capsule can be opened safely.

Typically, metal hydride in powder form is used to supply hydrogen to increase the reaction rate by increasing the surface area and reducing the diffusion distance. However, metal hydride becomes radioactive after neutron irradiation via transmutation. Powdered radioactive material has a higher risk of contamination. Therefore, it is better to use bulk and reliable metal hydride in the form of, for example, thin disks or wires.

3. Metal hydride

The requirements for metal hydride are listed below.

(1) High thermal stability; the melting point of the metal hydride and the metal itself should be sufficiently higher than the irradiation temperature. The vapor pressure of metal should be low enough at the irradiation temperature to prevent reaction with tungsten specimens.

(2) High reaction rate with hydrogen; as discussed in the previous section, it is better to use bulk material rather than powder. In order to realize sufficiently high rates of

hydrogen desorption and absorption, large hydrogen diffusivity is required for the metal hydride. As reported in [9], metals with a body-centred cubic (bcc) structure has a greater diffusion ability of hydrogen than metals with face-centred cubic (fcc) and hexagonal close-packed (hcp) structures. In addition, the reaction rate on the surface should be sufficiently high.

(3) The appropriate value of the heat of hydride formation or hydrogen solution; the equilibrium pressure of hydrogen gas is determined by the heat of hydride formation if the hydride retains its structure at the irradiation temperature. If the hydride phase decomposes into the solid solution phase at the irradiation temperature, the equilibrium pressure is controlled by the heat of the hydrogen solution and the fraction of hydrogen in the metal. It is expected that tungsten will be used in the range between the ductile-brittle transition temperature (DBTT, ~300 ℃) and the recrystallization temperature (~1300 ℃). The trapping of a hydrogen isotope by a radiation-induced defect is an exothermic reaction and, therefore, more significant at lower temperatures. Therefore, irradiation tests at 300–400 ℃ are a priority. The metal hydride should have an equilibrium pressure of about 0.1 MPa (1 atm) in this temperature range with a moderate hydrogen content (for example, [H]/[M] ~ 0.1). The hydrogen content should not be too high because metal hydride can be brittle with high hydrogen content.

The metals of group 5 (vanadium, niobium and tantalum) and group 6 (chromium, molybdenum and tungsten) have a bcc structure and preferred thermal properties. However, group 6 metals do not form a hydride, and the hydrogen solubility is very low [10]. Thus, group 5 metals appear to be the best candidates. In a previous study [11], we examined the surface reaction rates of hydrogen gas for vanadium, niobium and tantalum and found that vanadium has the highest desorption and absorption reaction rates among these metals. In addition, it is known that the highest surface reaction rate can be obtained by heat treatment at 400–700°C by dissolving the oxide layers in the bulk without surface segregation of other elements such as sulfur [12].

According to the pressure-composition isotherms of the V-H system [13], the hydride phase decomposes into the solid solution phase at ~200 °C. An equilibrium pressure of about 0.1 MPa at 400°C is achieved at the fraction of hydrogen atoms to vanadium atoms [H]/[V] ~ 0.3. Therefore, vanadium hydride with a hydrogen content of [H]/[V] ~ 0.3 seems to be a good source of hydrogen.

The number of vanadium hydride disks required to supply hydrogen gas was calculated assuming an irradiation capsule with inner volume of 2 cm^3 and containing 20 tungsten specimen disks. Exposure to D plasma after neutron irradiation (sequential experiment) showed that the fraction of D in tungsten can reach 1 at.% due to trapping at radiation-induced defects [2-4]. If tungsten specimen disks absorb hydrogen to a comparable fraction during neutron irradiation in a hydrogen gas atmosphere, the required amount of hydrogen for filling the capsule with 0.1 MPa H_2 gas at 400 °C is 3.6×10^{-4} mol H (3.0×10^{-4} mol H in tungsten and 6×10^{-5} mol H in a gas phase as H_2 molecules). The vanadium hydride disk of the same size as the tungsten disk, and with a fraction of hydrogen [H]/[V] = 0.3, contains 5.0×10^{-4} mol H. The change in the hydrogen fraction in the vanadium hydride disks should be reduced to minimum to maintain a constant partial pressure of hydrogen gas. A set of 10 disks of vanadium hydride serves this purpose if the loss of hydrogen due to permeation through the capsule wall is negligible (see the next section).

4. Capsule material

The damage rate by neutron irradiation is relatively low. Consequently, it takes a relatively long time to accumulate damage to a level relevant to fusion conditions. For example, it usually takes about 1 month to reach a damage level called 1 displacement per atom (dpa) corresponding to the level at which each tungsten atom in the bcc lattice is displaced from its original position 1 time as a result of collision with neutron. Therefore, if the capsule material has high permeability at the irradiation temperature, a significant amount of hydrogen may be lost from the capsule.

The material of the capsule should have a sufficiently high mechanical strength and corrosion resistance against cooling water at the expected irradiation temperature. Consequently, austenitic stainless steels, nickel-based alloys and molybdenum-based alloys may be candidates.

If the diffusion process of hydrogen in a metal is the rate-limiting step, the permeation rate J can be expressed as follows:

$$J = -D\frac{C_i}{d} = -D\frac{K_S}{d}P^{0.5},$$

where D is the diffusion coefficient, C_i is the hydrogen concentration in the subsurface region of inner wall of the capsule, d is the thickness of the wall, K_S is the solubility of hydrogen, and P is the partial pressure of hydrogen in the capsule. From the diffusivity and solubility data reported in [14], the permeation rate in type 316L stainless steel at 400 °C is evaluated to be 4.3×10^{-12} mol $\mathrm{m}^{-1}\,\mathrm{Pa}^{-0.5}\,\mathrm{s}^{-1}$. If the diameter and length of the capsule are 8 mm and 50 mm (surface area is 1356 mm^2), the wall thickness is 1 mm, the partial pressure of hydrogen is 0.1 MPa and the irradiation time is 30 days (2.6 Ms), then 5×10^{-3} mol H will be lost during irradiation by permeation. The amount of hydrogen lost is significant compared to the value mentioned in the previous section.

Data for a nickel-based alloy (Inconel 625) yielded a comparable value of the hydrogen permeation. On the other hand, the permeability in molybdenum was evaluated to be 2.2×10^{-13} mol m^{-2} $Pa^{-0.5}$ s^{-1}; this value was 20 times lower than that for type 316L stainless steel due to lower hydrogen solubility. Hence, the amount of hydrogen that can be lost by permeation is also less by an order of magnitude. It was therefore concluded that molybdenum and molybdenum-based alloys are the best candidate of capsule material.

5. Summary

A conceptual design of a capsule for neutron irradiation of tungsten in hydrogen gas atmosphere is proposed. The irradiation conditions are supposed to be 400 ℃ and 0.1 MPa. Vanadium hydride is selected as the hydrogen source from the viewpoint of the equilibrium hydrogen pressure, reaction rate and thermal stability. Molybdenum is selected as the capsule material due to its low hydrogen permeability.

Acknowledgements

This study has been supported in part by JSPS KAKENHI Grant Number 18H03688 and JP20H02661.

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