Characteristics of Titanium Sponge for the Storage of Hydrogen Isotopes: I. Activation Process

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Abstract: Tritium, a radioactive isotope of hydrogen, is removed from heavy water at a TRF (Tritium Removal Facility). Titanium sponge has been selected as a suitable material for tritium immobilization. The purpose of this study was to determine the optimum activation procedure for the storage of tritium in the WTRF. The influence of each different variable, such as the activation temperature, time, and pressure, on the hydriding properties of the titanium sponge was investigated. We found that 400°C is the minimum activation temperature of the titanium sponge for the hydriding reaction; we chose 500°C to be the activation temperature. The activation procedure, which is determined for other experiments, involves heating for two hours at 500°C while maintaining a minimum vacuum of $1.0 \times 10^4$ torr.

Keywords: hydrogen isotopes, titanium sponge, activation

Introduction

There are two types of nuclear power plant in Korea: the Pressurized Water Reactor (PWR) uses light water as a coolant and the CANadian Deuterium Uranium-Pressurized Heavy Water Reactor (CANDU-PHWK) uses heavy water as the primary coolant and moderator. As a result of neutron capture, deuterium in heavy water is partially converted to tritium. Tritium is a radioactive isotope of hydrogen that decays to $^3$He with a half-life of 12.3 years by emitting a low-energy beta particle. Substantial quantities of tritium are produced by neutron activation of the deuterium in the reactor core and, subsequently, the tritium concentration in the heavy water systems tends to increase to the equilibrium values as the reactor ages.

The presence of tritium in the heavy water systems of CANDU reactors is a major source of operator exposure to radiation. To minimize this exposure, Korea Hydro & Nuclear Power constructed a Tritium Removal Facility (TRF) for the Wolsong Nuclear Generating Station that will remove tritium from heavy water and concentrate it to $\text{T}_2$ gas. This plant is expected to produce high purity tritium (> 99.0% isotopically pure). The recovered tritium must be safely packaged for long-term storage. The radiological hazard of tritium in the form of $\text{T}_2$ is several orders of magnitude smaller than it is in the water form. For this reason, tritium in the form of hydrogen, which would be the product of the tritium recovery plant, can be immobilized as a metal tritide and then stored in a container. The immobilization of tritium gas can be achieved by reacting it with a suitable metal to form a solid metal hydride (tritide). The properties of metal hydrides that make them suitable for tritium storage include the ability to bind tritium strongly at normal storage temperatures and pressures, their easy preparation, and the ability to recover the tritium if necessary [1-3]. Sponge-type titanium metal has been selected as the long-term storage material for the recovered tritium at the Wolsong Tritium Removal Facility (WTRF).

Tritium metal usually does not react with hydrogen at room temperature because its surface is covered with a protective layer of oxide, but heating it at a high temperature under vacuum conditions can activate it. The activation procedure causes the dissolution of the oxide into the bulk of the sponge so that clean titanium surfaces are available for hydriding [4,5].

The theoretical bases for the activation process of titanium metal to produce a hydride are well known, but
it is necessary to acquire more comprehensive information of the activation process to apply the titanium sponge as a practical tritium storage material. This paper provides a summary of the engineering data regarding the activation process of titanium sponge metal for the storage of tritium. The purpose of this study was to determine the optimum activation procedure for the storage of the tritium in the WTRF. This paper investigates the influence of variables such as the activation temperature, time, and pressure on the hydriding properties of the titanium sponge.

**Experimental**

The sponge form of titanium metal is used, instead of massive solid bars, because of its large available surface area. Powders are not used because of safety concerns regarding the easy dispersion of small metal tritide particles. The titanium sponge we used (2-1.2 mm in diameter) was obtained from Aldrich Chemicals and used directly without any further cleaning process. Analysis results provided by the supplier showed that the main metal impurities are Fe (1460 ppm), Mg (307 ppm), Cr (141 ppm), and Ni (130 ppm), but chlorine is known to be one of the major impurities of titanium sponge [6]. High-purity hydrogen (99.999%) was used after passing it through moisture and oxygen traps. Since the chemical properties of tritium (T₂) are virtually identical to those of hydrogen (H₂) and deuterium (D₂), this work was conducted using hydrogen.

The metal hydrides were prepared by a direct combination of the metal and hydrogen using a stainless-steel system designed for hydriding reaction [7]. The whole system was made of stainless steel; base vacuum pressures of < 1 × 10⁻⁶ torr were attained using a turbo molecular pump and a mechanical pump. Reference volumes of 0.5 and 2 L were used to calibrate the volumes of the system and the hydriding vessels, respectively. The experimental data were monitored on-line using Labview software. After activating the sponge surface by vacuum annealing, we measured the pressure of the hydrogen gas in a known volume; this gas reacted directly with the sponge initially at room temperature. The amount of gas adsorbed can be determined volumetrically by PVT measurements. A small experimental reaction vessel was prepared, using a Stainless Steel 316 pipe, to investigate the characteristics of the hydriding reaction between the titanium sponge and hydrogen isotopes.

**Results and Discussion**

**Hydriding Profiles in the Titanium Sponge Bed**

Titanium sponge (ca. 15 g) was loaded into the experimental vessel, which was then evacuated by turbo molecular pump at room temperature. When the pressure of the vessel was < 1 × 10⁻⁶ torr, the vessel was heated to 500°C under vacuum for 2 h. The pressure and temperature during activation of the experimental vessel, as a function of time are shown in Figure 1. This figure shows that the maximum pressure occurred near 200°C and that the pressure decreased at higher temperatures. When the vessel temperature reached 400°C, the pressure of the system was near zero. Although the system was maintained under vacuum by a rotary pump, the occurrence of the rise in pressure in the vessel indicates that a large amount of volatile impurities were vaporized. This phenomenon suggests that the vaporizing speed of volatile impurities was faster than the constant rate of the pumping speed at temperatures between 100 and 300°C. The volatile impurities vaporized from the sponge would cause problems during a long tritium immobilization process.

After the activated titanium sponge was cooled slowly to room temperature, it was loaded to a hydrogen fill pressure of 600 torr from a 10-L volume tank. The variations in the pressure and temperature in the vessel and of the hydrogen content of the titanium (atomic mole ratio of hydrogen to titanium, H/Ti) are shown in Figure 2. When the hydrogen was introduced into the vessel, the

![Figure 1. Activation of titanium sponge.](image1)

![Figure 2. Hydriding profiles of titanium sponge.](image2)