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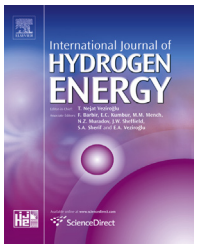

Thermal desorption of tritium and helium in aged titanium tritide films

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ABSTRACT

Titanium films were deposited onto molybdenum substrates and then converted into titanium tritides ($TiT_{1.5-1.8}$) films inside a tritiding apparatus loaded with pure tritium gas. Evolution of tritium and helium in the titanium tritide films over a period of four years was investigated using a thermal desorption technique, together with X-ray diffraction analysis. Results showed that desorption profiles of the tritium varied significantly with the evolution of He contents. Apart from the primary peak from tritium desorption located at a temperature between 610 and 840 K, another higher temperature tritium desorption peak (at ~950 K) was observed, attributed to damages in the lattice structures induced by generation of ^{3}He bubbles. Release of helium in the tritide film became significant after a long term aging process (i.e., after a few years). Depending on the amount of the ^{3}He bubbles generated due to the decay of tritium, spectra of the thermal helium desorption showed five peaks in the range from room temperature to ~1750 K, corresponding to different states of helium evolution during aging of the titanium tritide films. The amounts of helium desorption in different stages were estimated, and the dissociation energy of helium from different trap states as a function of the aging duration was obtained.

Introduction

Tritium (T), an isotope of hydrogen (H), is one of essential elements for future thermo-nuclear energy production [1]. However, due to its high mobility and radioactivity, a safe and cost-effective means for a long-term storage of the tritium is urgently needed. Storage of tritium as a tritide with a low equilibrium pressure is regarded as a safe and efficient method [2]. Titanium has often been selected as one of the good candidates for the long term storage of tritium because of its low cost and key advantages, such as stability in air, high storage capacity, low storage pressure and acceptable helium retention rate [3].

Tritium decays with a 12.32 year half-life into ^{3}He ($T \rightarrow {}^3He + \beta^- + \bar{\nu}$), most of which is retained in the metal tritides [1]. Recoil energy of the ^{3}He in this decay process is quite small, i.e., ~1.03 eV, and is insufficient to cause any damage to the lattice of the tritide [4]. The ^{3}He, which is highly insoluble, will immediately diffuse into the lattice of the tritide and aggregate together to form bubbles inside the tritides. The He bubbles as well as the diffused He in the lattice could induce

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strain in the metal and alter thermodynamics of tritium absorption/desorption [5,6]. They could also form trapped tritium in the lattice which is difficult to be thermally desorbed, and thus result in changes in mechanical properties of the tritides, causing void swelling, low temperature intergranular embrittlement, surface roughening and blistering of the components, etc. [7–9]. This phenomenon is often called 'aging' and has been receiving significant scientific interests [1].

Even though the ^{3}He can be kept in the titanium tritides for several years, significant release of the ^{3}He could occur when the atomic ratio of ^{3}He to titanium in the titanium tritides, i.e., $^3He_{gen}$/Ti, reaches to a critical value of ~0.23 to ~0.30 [4–6,10]. This stage is well-known as the 'accelerated release' stage. With further aging, the ^{3}He starts to be released at a rate equal to (sometimes even higher than) the generation rate, which is often called the 'free-release' stage [4–6,10]. It is of great scientific interest to investigate the formation, growth and evolution of the ^{3}He bubbles, and quantify the rate and extent of ^{3}He release in the aged metal tritides, as the sudden release of retained He could cause disasters due to integrity failure of the pressure vessel.

Thermal desorption of hydrogen or deuterium (D) from the Ti has been extensively studied [11–27]. Hydrogen isotopes were reported to desorb at a maximum rate at a high temperature above 689 K with two main peaks, i.e., at a high temperature (~813 to ~1043 K) and at a low temperature (~689 to ~813 K) [28,29], but there are apparent discrepancies of the results reported in different papers [11,12,16,23]. Shoulder peaks, both at main desorption peaks at different temperatures were often reported, and Malinowski et al. reported that a dual peak spectrum changed into a single broad peak after a long term exposure of the Ti hydride into the air [27]. Desorption of the deuterium and tritium from the aged bulk titanium tritides at the 'free-release' stage has been examined using both thermal desorption (TD) and isotope exchange chemistry [5,6]. Results showed that hydrogen heels were significant, and the hydrogen desorption profiles changed with the He content in the material [6]. A lower temperature hydrogen state which was generated at ~470 K was found in these tritides at the 'free-release' stage [6]. The release of helium became significant after a longer period of aging, and the ^{3}He desorption near room temperature has also been reported [6].

The evolution of helium in titanium tritides has been investigated using various experimental approaches and theoretical analysis [30–39]. In a recent experimental study using X-ray diffraction analysis, crystal lattices and properties of the titanium tritide films were found to be affected by generation and accumulation of helium in the film [30]. In addition, generation and evolution of the helium bubbles inside the titanium tritides during their decays were studied using a transmission electron microscope [31], and various bubble morphologies at different temperatures were observed due to the differences in the availability of thermal vacancies during helium clustering [32]. Below ~600 K, helium atoms diffuse interstitially in the lattice and form interstitial clusters, whereas at a higher temperature above ~600 K, diffusion and clustering of the helium were significantly affected by the increased vacancy concentration in the matrix [32]. Thermal desorption technique was also applied to investigate the ^{3}He evolution behavior inside titanium tritide powders during its aging until the atomic ratio of $^3He_{gen}$/Ti reached ~0.81 [33]. Depending on the amount of He generated during the decay process of the tritium, thermal desorption spectra for the ^{3}He between room temperature and 1773 K showed one to five peaks, corresponding to different states of helium in the titanium tritide lattice [33].

Long-term storage of the tritium in a metallic tritide films is critical for nuclear applications, such as neutron generators [7,40–43]. The aging behavior of the tritide film is influenced by the properties of substrate, because the crystal orientation (texture) of tritide film could be determined by the substrate, and geometry of the substrate will limit the expansion of grains [25,38]. Various types of tritide films (i.e., those of titanium, scandium, erbium) have been used as main substrates for the nuclear applications, and their aging behavior have been studied [40–43]. Previous research on aging effects of the tritium in the Ti thin films revealed that the thermal desorption of He showed only two peaks [44], which is considerably different from five peaks obtained by Vedeneev et al. [33] using the titanium tritide powders. The various stages of the tritium desorption as a function of aging duration and the nucleation of helium bubble at an 'early-release' stage of titanium tritide have not been clearly understood. It is of great scientific interest to clarify the desorption mechanisms of the vacuum deposited titanium tritide films, and compare its behavior with those of titanium tritide powders and other tritide films.

However, systematic studies of aging behavior of metal tritides are difficult because the rate of helium accumulation is quite small and a detailed study to map the whole life of the metal tritides requires several years of experimental work. In this paper, the behavior of helium evolution in the titanium tritide films and the aging effect on tritium desorption states in a four year period have been systematically investigated using a thermal desorption method, together with analysis from X-ray diffraction (XRD). Formation, growth and evolution of the ^{3}He bubbles inside the titanium tritide films have been investigated during both the initial aging stage and the accelerated release stage.

Experimental

Titanium films of ~4 μm thick were deposited onto molybdenum plate (1 mm thick) using a standard electron-beam evaporator using pure titanium as the evaporation source. Substrate temperature during evaporation was 450 °C and the deposition rate was 10 nm/s. The deposited titanium films were placed inside a tritiding apparatus, which was then loaded with high-purity tritium gas to produce a tritide with stoichiometry close to $TiT_{1.5-1.8}$. According to the Ti–H phase diagram, at room temperature, the δ phase (i.e., titanium hydride with a CaF_2 structure which contains four titanium atoms forming an fcc lattice, with the tritium atoms occupying the tetrahedral sites) is stable with a H/Ti ratio between 1.5 and 2, especially with stoichiometric defects of ~25% vacancy of tetrahedral site in a fcc lattice. The stoichiometric defects may enhance trapping of helium atoms by acting as initial nuclei for helium. Morphology and crystallinity of the