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The evolution of helium from aged Zr tritides: A thermal helium desorption spectrometry study

G.J. Cheng [a, b], G. Huang [a, b], M. Chen [b], X.S. Zhou [b], J.H. Liu [b], S.M. Peng [b], W. Ding [b], H.F. Wang [b], L.Q. Shi [a, *]

[a] Applied Ion Beam Physics Laboratory, Institute of Modern Physics, Fudan University, Shanghai 200433, PR China
[b] Institute of Nuclear Physics and Chemistry, China Academy of Engineering Physics, Mian Yang 621900, China

HIGHLIGHTS

- At least five forms of He in aged Zr-tritide in whole life period were distinguished.
- The crucial transition points for each form of He in aged Zr-tritide were revealed.
- The primary factors influencing He retention for tritium storage materials were obtained.

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ABSTRACT

The evolution of He from Zr-tritides was investigated for aging times up to about 6.5 years using analytical thermal helium desorption spectrometry (THDS). Zr films were deposited onto Mo substrates and then converted into Zr-tritides ($ZrT_{1.70\sim1.95}$) inside a tritiding apparatus loaded with pure tritium gas. During aging, there are at least five forms of He in Zr-tritides, and more than 99% of He atoms are in the form of He bubbles. The isolated He bubbles in lattices begin to link with each other when the He/Zr atom ratio reaches about 0.21, and are connected to grain boundaries or dislocation networks at He concentration of He/Zr ≈ 0.26. An interconnected system of channels decorated by bubbles evolves from the network dislocations, dislocation loops and internal boundaries. These He filled networks are formed completely when the He/Zr atom ratio is about 0.38. Once the He/Zr reached about 0.45, the networks of He bubble penetrate to the film surface and He begins an "accelerated release". This critical ratio of He to Zr for He accelerated release is much greater than that found previously for Ti-tritides (0.23–0.30). The difference of He retention in Zr-tritides and Ti-tritides was also discussed in this paper.

1. Introduction

Tritium (T), an isotope of hydrogen (H), is one of essential elements for future thermo-nuclear energy production [1]. However, the radioactive nature of tritium imposes many conditions on its handling and storage. It has been recognized that the best way to store tritium is in the form of a tritide, and the metals such as Pd, Ti, Zr, Er, U and the intermetallic alloys such as $LaNi_5$, ZrCo, etc., are commonly used for this purpose [2]. One important problem for nuclear application is the generation and accumulation of He by tritium decay in metals [3]. This accumulation of He atoms can result in a swelling of the lattice because of the formation of He bubbles. During the early aging process, He atoms are mainly trapped in the lattice and form He clusters and bubbles. When they reached a critical value (R_c) of He concentration, He atoms will release from the material at a rate equal to or even higher than the generation rate. This phenomenon is known as the "accelerated release stage" [4], and it is very detrimental to the applications involving tritium [5], such as tritium storage bed, the release of the He from the tritides will lead to security problems. Moreover, retained He before accelerated release, can significantly degrades the mechanical properties of the material and cause void swelling, low temperature intergranular embrittlement, surface roughening and blistering of the components, etc. Therefore, it is a great interest to understand how these bubbles form, grow, and interact, both theoretically and experimentally, along with their effects on a metal matrix's electrical, magnetic, mechanical, and structural properties [6].

* Corresponding author.
E-mail address: lqshi@fudan.edu.cn (L.Q. Shi).

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As shown in recent studies [6–10], each He atom, formed by tritium decay, occupies a tetrahedral (T) or octahedral (O) interstitial site during the first few days following tritium introduction into the metal. He has a strong tendency to precipitate into clusters by a 'self-trapping' mechanism and accumulate to form bubbles. According to the dislocation loop-punching mechanism and the dislocation dipole expansion mechanism, He bubbles grow in multiple stages [10]. As the bubbles grow up to a certain of size, a transition from stress-assisted block loop punching growth to inter-bubble fracture, and then the accelerated He release was observed. The previous study on the behavior of He in aged Ti-tritides [6] has indicated that there was four states of He at least in various stages: mobile He atoms, He bubbles in lattice, bubbles in the grain boundaries or network of dislocations, and at later stages He bubbles near or linked with the film surface. The concentration of mobile He atoms remains constant at less than 0.01% after nucleation, and more than 90% of He atoms remain in the form of He bubbles for the atom ratio of He/Ti < 0.14. The networks of bubbles threaded together at grain boundaries are formed for He/Ti atom ratios up to 0.18. According to the existing research results, the value of R_c for Ti-tritides was 0.23–0.30 [10–12].

Zr is an attractive material for storage of tritium, due to its high hydrogen capacity, low equilibrium pressure and acceptable He retention rate. The R_c is around 0.38–0.53 for Zr-tritides [13,14], much greater than for Ti-tritides, and the reason for which is still unclear. To understand the evolution behavior of He in aged Zr-tritides, the static thermal desorption method [6] was used. We then determine the different trapping states and the proportion and dissociation energy of He in the Zr-tritides for various stages. The behavior of He evolution over the whole lifetime combined with results for static storage experiments is discussed. Furthermore, the primary influence factors of He retention in some representative tritium storage materials, such as Zr-tirtides and Ti-tritides is discussed too.

2. Experiments

The sample preparation has been previously described [13,15,16]. Zr films were deposited onto molybdenum substrates by electric resistance evaporation technique in vacuum, and then the deposited Zr films were heated in tritium atmosphere at temperature of ~673 K to make the tritium to be absorbed in the zirconium. The initial tritium content in the sample was firstly determined through the equations of state [6].

$$A = \frac{2f(P_2 - P_1)VM}{RTW} \quad (1)$$

where A is the atomic ratio of T/Zr, f is the abundance of tritium, P_1 and P_2 are the initial and final tritium pressure, V is the volume of tritiding chamber, M is the molar mass of zirconium, W is the weight of zirconium, T is the absolute temperature of tritium gas, and R is the gas constant. The calculated tritium content in the samples is also checked by the proton backscattering analysis under 2MeV proton beam with scattering angle of 165°at the NEC 9SDH-2 tandem accelerator in the Institute of Modern Physics of Fudan University. The samples were stored in a vacuum vessel at room temperature before the desorption measurement. The initial T/Zr ratio and final He/Zr ratio of samples are listed in Table 1. The final He/Zr ratio was given based on the equation.

$$C_{He} = C_{T,0}\{1 - \exp(-\lambda t)\} \quad (2)$$

where λ is decay constant of tritium and $C_{T,0}$ is the initial tritium concentration.

Table 1
The initial ratio of T/Zr and final He/Zr of samples.

Sample	Initial ratio of T/Zr		Aging time (days)	He/Zr
	Calculated	Measured		
1#	1.90	1.87	76	0.022
2#	1.83	1.82	191	0.053
3#	1.86	1.82	330	0.092
4#	1.90	1.85	460	0.13
5#	1.95	1.93	596	0.17
6#	1.70	1.70	770	0.19
7#	1.84	1.81	789	0.21
8#	1.84	1.80	910	0.24
9#	1.72	1.71	1070	0.26
10#	1.89	1.88	1165	0.31
11#	1.90	1.88	1280	0.34
12#	1.83	1.79	1515	0.38
13#	1.87	1.85	1790	0.45
14#	1.78	1.76	2400	0.55

The static mode of thermal He desorption technique and principle of THDS measurement was fully described in ref. [6]. THDS technique is based on the determination of helium release rate from sample during heating in a known profile with time (usually linear), and the samples were heated in a vacuum (initially $< 5 \times 10^{-6}$ Pa) up to 1773K at a rate of 1 Ks^{-1}. The helium released from samples is detected with a Quadrupole Mass Spectrometer (QMS)through a quantitative valve. In order to avoid the interference of tritium and obtain a high vacuum as well, ZrVFe getter was located between the samples and QMS.

3. Results and discussion

3.1. Thermal desorption behavior of He

Fig. 1 presents the static THDS of Zr-tritides for He/Zr atom ratios from 0.022 to 0.55. The THDS of all samples during whole lifetime can be divided into five zones by its prominent feature, called as zone I, II, III, IV and V, which reflects five He basic trapping states respectively. With increasing He concentration, the temperature range for each zone shifts toward to lower temperatures except for zone I. He release in zone I keeps a low and relatively constant speed for younger samples (He/Zr ≤ 0.19)over a broad temperature range up ~1200K to 1500K. Zone II appears at the highest release

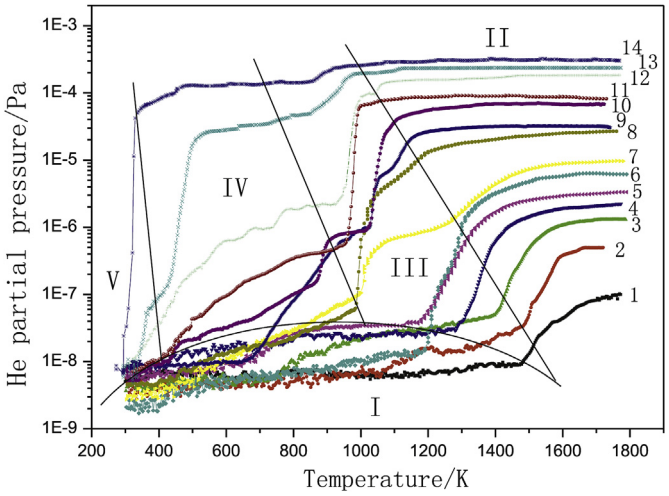

Fig. 1. The static THDS of aged Zr tritide samples at different He concentration. The numbers on the plots are the sample numbers shown in Table 1.