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Evolution of thermodynamics in Pd-H(D) system by tritium aging

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HIGHLIGHTS

- Thermodynamics in Pd-H(D) system were measured after tritium storage.
- Entropy changes maintain a linear relationship with helium content in Pd.
- Enthalpy changes keep constant with helium content in Pd.

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ABSTRACT

Experiments on investigating the thermodynamics properties of palladium hydride after aging as palladium tritide with different storage periods upto 6.5 years have been performed. By analyzing the experimental results, it is found that during the formation and the decomposition of palladium hydride the entropy changes maintain a linear relationship with the helium content in solid, whereas the enthalpy changes keep constant. The sum of interstitial sites in the host palladium matrix is expected to be affected by helium, resulting in the modification on the entropy changes.

1. Introduction

As an essential element, tritium is used for the future thermonuclear energy production. Due to its radioactivity and high mobility, metal hydride is commonly used for tritium processing and storage. In recent years, an increasing level of research has been concentrated on the properties of palladium tritide due to its low equilibrium pressure, high absorption capacity, retention of decay ^{3}He, as well as its poison resistance [1–12].

Tritium decay introduces aging effects in palladium hydride, which are caused by the host structural changes due to the deposition and migration of ^{3}He atoms accumulated in lattices. Generally, these changes induced by aging are observed to result in lower plateau pressures, a decrease of absorption rate in the palladium tritium system, a shift of α phase zone, etc. However, the reports on the modifications of thermodynamic properties caused by tritium aging in Pd-H and Pd-D systems are still rare and not systematically. In addition, some experimental phenomena are still not well explained. For instance, how the helium accumulation affects the entropy changes in aged palladium tritide.

In this work, the enthalpy and entropy changes in Pd-H and Pd-D systems were experimentally investigated after tritium aging for 1.65, 3.5 and 6.5 years, respectively. By comparing with the thermodynamic properties of fresh palladium protide and deuteride, the observed tritium aging phenomenon was explained based on the occupying state and distribution of helium in the solid phase.

2. Experimental

Palladium used in this research was provided by Northwest Institute for Non-ferrous Metal Research of China, which consisted of the aggregate of palladium micro-particles, with their particle size ranging from 100 to 200 nm. The detailed information of the palladium samples such as specific area, purity was reported elsewhere [7,11].

Three tritium-aging samples were prepared by placing these palladium powders into stainless steel sample holders equipped

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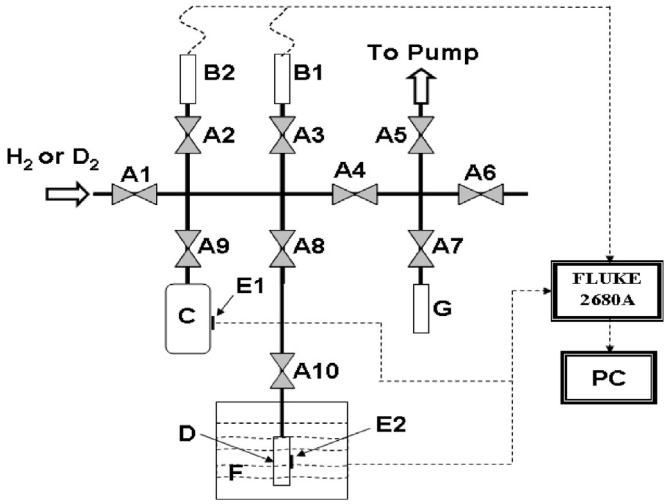

Fig. 1. Experimental system of the pressure-composition isotherm measurements. A1 ~A10 — valves; B1 — 25 bar manometer; B2 — 0.25 bar manometer; C — standard pressure vessel; D — palladium bed; E1~E2 — Pt100; F — thermostat; G — vacuum gauge.

with valves. Before tritium loading, each sample was activated in three absorption/desorption cycles by deuterium at 280 °C. Subsequently, pure tritium (the purity of tritium was >98% and impurities determined by high resolution mass spectrometry only consisted of deuterium) was introduced into sample holders at room temperature. The palladium samples were initially tritiated up to β phase (T/Pd = 0.65), which were evaluated by the PVT method. These samples had been stored for 1.65, 3.5 and 6.5 years at room temperature, respectively. Thus, the content of helium in palladium due to tritium decay can be estimated by using the beta decay rate, i.e. the ratios between He and Pd were calculated to be 0.058, 0.115 and 0.198. Before analyzing the properties of Pd-H and Pd-D systems, tritium was desorbed from the aged palladium at 280 °C, at which temperature the majority of helium (~97%) was found to remain in palladium [11,13,14], and the T/Pd (the ratio between the residual tritium and the Pd atoms) in aged samples was evident to be too small to influence further thermodynamcis characterization [4,7].

After unsealing the sample holder in a glove box, 12.0 g aged palladium powder was reloaded into a new stainless steel bed, the inner size of which was Φ12.0 mm × 78.0 mm, the wall thickness was 2.5 mm. After a leak detection by helium mass spectrometry (the leak rate $<1.0 \times 10^{-9}$ Pa·m^3/s), the aged palladium bed was connected to the experimental system. Then, the sample was activated by using high purity hydrogen (the impurities <10 ppm) under 0.4 MPa at 250 °C in order to remove the surface oxidization, impurities such as N_2, CO_2 etc, which can be absorbed on the surface of Pd during the process of reloading. The fresh palladium sample was also prepared in the same conditions.

The experimental system consisted of vacuum pump, protium

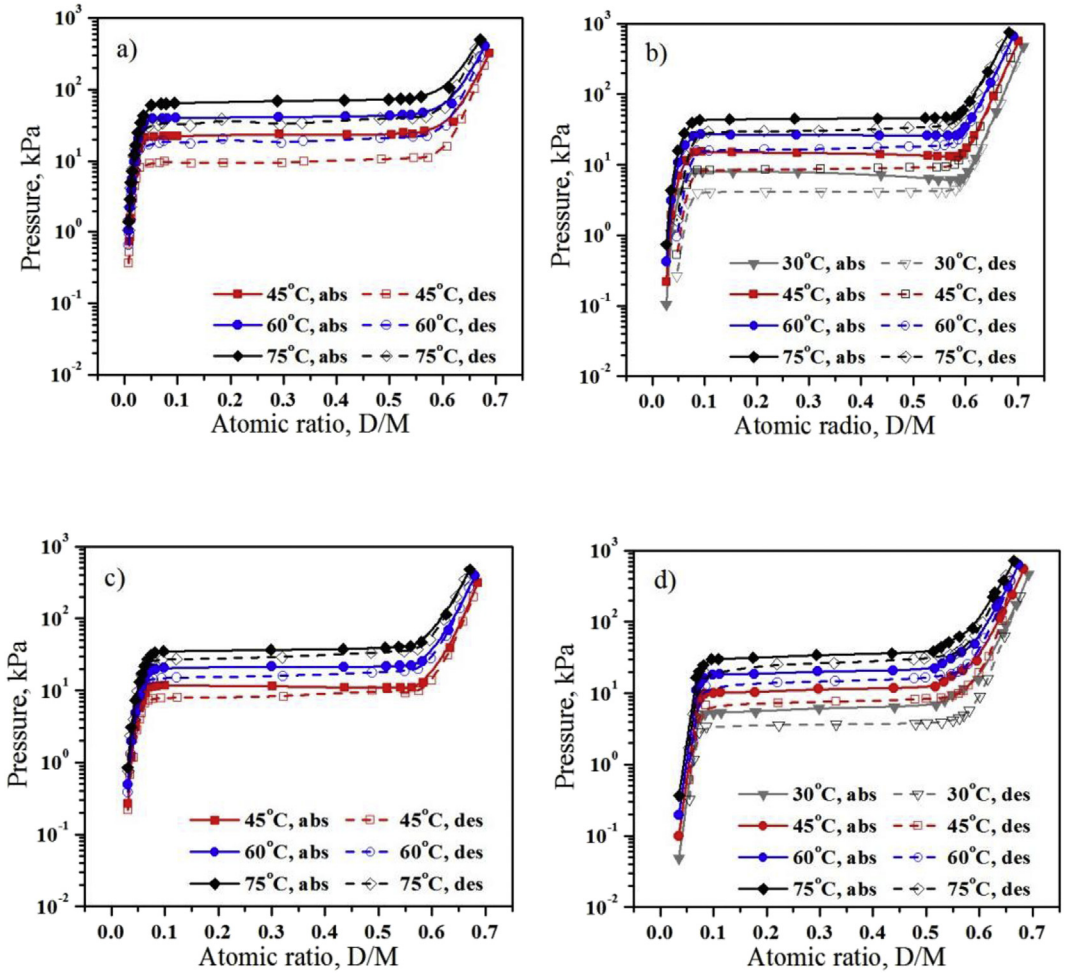

Fig. 2. Absorption isotherms (solid line) and desorption isotherms (dash line) of unaged and aged Pd-D system: a) 0 a; b) 1.6 a; c) 3.5 a; d) 6.5 a.