

A Comparative Study on Uranium and ZrCo for the Storage of Tritium

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1. Introduction

Metal tritides are produced according to the reaction $M(s) + x/2Q_2(g) \leftrightarrow MQ_x(s)$ (Q = H, D, T) (1) Reaction (1) is exothermic and usually spontaneous at room temperature, particularly when the metal is in a powder form.

Safe handling, transport, and storage of tritium requires several conditions: very low equilibrium pressures over the tritide at room temperature, high dissociation pressure at moderate temperatures, existence of plateau regions in the loading/deloading isotherms, fast adsorption/desorption kinetics, no disproportionation, low reactivity of the metal/tritide system towards air and the major contaminants, low pyrophoricity, and low aging effects caused by the accumulated of He-3. [1]

Of the many getter materials, uranium and ZrCo have been the most extensively studied and widely used tritium getters because of their good properties as a material for a tritium storage. For this reason it is worth evaluating the properties of uranium and ZrCo.

2. The equilibrium pressures

The tritides should have a high dissociation pressure at moderate temperatures when used for a interim storage, to allow for a quantitative recovery of the incorporated gas with minimal permeation losses.

In the plateau region, the temperature dependency of the equilibrium pressure for a given metal/hydrogen composition can be described by the van't Hoff equation

$$\log P = -A/T + B, \quad (2)$$

in which A and B are empirical parameters.[2]

The temperature dependency of the equilibrium hydrogen pressure over ZrCoH_{0.8}, which is at about the

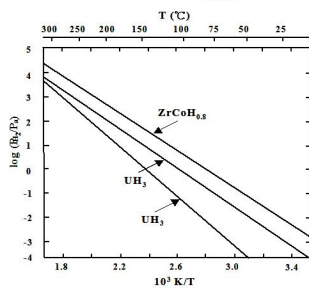


Figure 1. Temperature dependence of the equilibrium hydrogen pressure over ZrCoH_{0.8} and UH₃.

center of each sloping plateau, in the hydriding process is shown in Fig.1. The logarithmic pressure and the reciprocal temperature have a linear relationship. This result suggests that hydrogen can be recovered to a residual partial pressure of less than 10⁻⁴ Torr at room temperature and be released at 400°C at about 500 Torr.

The dissociation pressures of UH₃ are also shown in Fig. 1. The equilibrium hydrogen pressure of the ZrCo-H system is one or two orders of a magnitude higher than that of the U-H system in the temperature range from 130 to 300°C.

3. Hydrogen storage capacity and their volume expansion upon hydride formation

Storage of tritium in the form of hydrides is particularly attractive because of the achievable high hydrogen density. In fact, the hydrogen density of most metal hydrides is higher than that of liquid or solid hydrogen. It is apparent from a comparison that the volume expansion of the zirconium-cobalt hydride is about four times smaller than that of the uranium hydride. [1]

Table 1. Hydrogen storage capacity and their volume expansion upon hydride formation for uranium and ZrCo

System	N_H (10 ²² at/cm ³)	W. H (%) ^{a)}	ΔV (%) ^{b)}
H ₂ gas (298K, 200 bar)	1	100	
H ₂ liquid (20 K)	4.2	100	
H ₂ solid (4 K)	5.3	100	
ZrCoH ₃	7.6	1.97	20
UH ₃	8.2	1.25	75

a) Weight percent of hydrogen in the hydride.

b) Volume expansion on hydriding = $(V_{\text{hydride}} - V_{\text{metal}}) / V_{\text{metal}}$

4. Loading and deloading properties

Fig.2 shows the results of the loading and deloading experiments for uranium and ZrCo. [3] In the left of Fig.2 the relative getter loading (ratio of actual getter loading/maximum getter loading) at room temperature to a pressure less than 100 Pa is plotted.

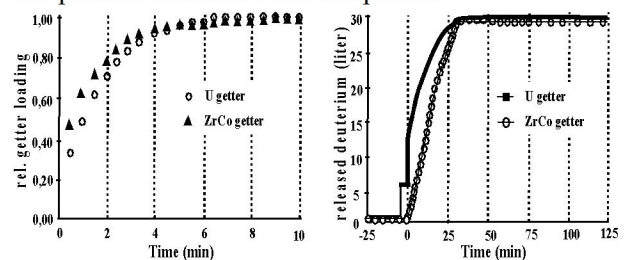


Figure 2. Left: Loading rate of U and ZrCo, Right: Desorption of deuterium at simultaneous heating and pumping (573-743K).

In this experiments the initial sorption rate of ZrCo is little higher than the sorption rate of uranium.

In the right of Fig.2, it shows the recoverability of the deuterium absorbed in uranium and ZrCo hydride powders. For the unloading procedure the getter bed was heated from 573 K to 743 K then (time = zero) the pumping system was started. From the comparison it appears that hydrogen is liberated somewhat slower from uranium than from ZrCo during the initial heating stage.

6. Disproportionation

A disproportionation does not occur in uranium. However in the case of an intermetallic compound ZrCo, it occurs under high temperature and hydrogen pressure. [4] While ZrCo compound reacts with hydrogen to form $ZrCoH_{(0-3)}$ below 400°C, the disproportionation reaction, $2ZrCo + H_2 \rightarrow ZrH_2 + ZrCo_2$ occurs above 400°C under hydrogen pressure higher than the equilibrium decomposition pressure of $ZrCoH_{(0-3)}$. Thus ZrCo become lost the storage capacity of hydrogen. But The disproportionated ZrCo can be recovered into the starting ZrCo by a vacuum treatment at or above 500°C, recovering the hydriding capacity of ZrCo.

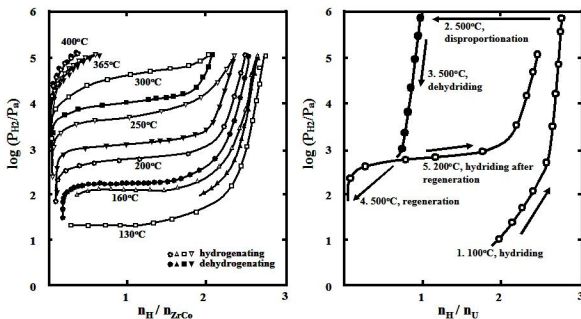


Figure 3. Left: Pressure-composition isotherms of the ZrCo-H₂ system, Right: Examples of the apparent isotherm for the ZrCo experienced disproportionation.

7. Pyrophoricity

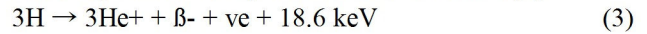
It is well known that uranium has been activated by cycles of hydriding and dehydriding is extremely pyrophoric when exposed to air or other oxidizers. Therefore it is necessary for utmost care to avoid a contact of uranium powder with the atmosphere.

ZrCo as well as its hydride show a more moderate reactivity toward air, oxygen and water than uranium. $ZrCoH_3$ inert to air, moisture, and dilute mineral acids (Padurets et al). Neither ZrCo nor $ZrCoH_{2.8}$ ignite at room temperature, but $ZrCoH_{2.8}$ reacts with air at 300°C (Nagasaki et al). But very finely divided ZrCo powder reacts with oxygen (Irvine et al). And exposure of

$ZrCoH_x$ to air at room temperature results in $O/ZrCo < 0.01$ without spontaneous ignition (Penzhorn et al). [1]

8. Aging

When pure metals or intermetallic compounds are used for the high density storage of tritium, aging effects caused by the accumulation of He-3 generated in the host lattice by tritium decay need to be considered. [1]



1. Uranium

UTx had less than a 2% He-3 release rate during 280 days. After several hundred days, the rate of the He-3 release increased rapidly. After 1000 days, the He-3 release rate was the same as that of the generation rate.

2. ZrCo

During 18 months, the He-3 release rate was less than 3%. After 2 years, the He-3 release rate increased to 25% from about 0.15 of the He-3/ZrCo ratio. At 600°C, less than 15% of the He-3 was released. Therefore U and ZrCo were almost the same for the He-3 release rate.

9. Conclusions

Considerations of the results from the literature allow for the following conclusions:

- Uranium has some advantages for a tritium storage: (i) very low equilibrium pressure at room temperature, (ii) rapid recovery, rapid supply, (iii) used most extensively. The main drawbacks of uranium are seen as (i) the nuclear material: radioactivity of uranium, (ii) dispersion or damage to valves and other components due to a fine uranium powder (iii) a large volume expansion upon a hydride formation (iv) a high pyrophoricity of U powder in air.

- ZrCo has some advantages for a tritium storage: (i) non-nuclear character, (ii) comparatively low pyrophoricity, (iii) a small volume expansion upon hydride formation tritium supply at relatively low. The main drawbacks of ZrCo are seen as (i) a slightly higher hydrogen dissociation pressure of the ZrCo hydride at room temperature, (ii) the stringent conditions needed to quantitatively recover the gettered tritium.

Therefore selection of uranium and ZrCo for a tritium storage is dependent on the purpose of usage and an operating condition.

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