

論 文

Zr<sub>9</sub>Ni<sub>11</sub>合金を充填したトリチウム  
貯蔵容器の性能試験

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Feasibility Tests of Tritium Container Packed  
with Zr<sub>9</sub>Ni<sub>11</sub> Alloy

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**Abstract**

Reliable techniques for storage, supply and recovery of tritium gas are indispensable to ensure safe handling of large amounts of tritium. From this viewpoint, we made a tritium container packed with Zr<sub>9</sub>Ni<sub>11</sub> alloy (1.5 g) in order to examine its feasibility by using deuterium gas as an alternative of tritium. This container was made of 316 stainless steel with double containment concept and equipped with a handmade ohmic heater. This heater was able to elevate the temperature of the container up to 500°C with small power of 65 W. The as-received Zr<sub>9</sub>Ni<sub>11</sub> alloy used consisted of a mixture of intermetallic compounds such as ZrNi, Zr<sub>9</sub>Ni<sub>11</sub> and Zr<sub>7</sub>Ni<sub>10</sub>. It was easily activated with vacuum heating at 400°C for 1 hr. It was revealed that the container is applicable to supply tritium gas of about 1 atm at 350°C and to recover it with considerably high absorption rate at room temperature. Apparent absorption rate, however, has significantly been affected by desorption of the deuterium ad/absorbed on/in the inner tube of the container.

**1. Introduction**

Safe handling techniques of tritium will have to be established before D-T burning

experiments in large-scale devices such as ITER, DEMO and so on. Metallic uranium has been widely used as a reversible tritium getter in a variety of tritium handling systems including laboratory scale devices and is a potential candidate for the D-T burning devices. However, the uranium getter is not necessarily advantageous from the viewpoints such as its high dissociation pressure, complicated activation processes, flammability against air exposure and so on<sup>1)</sup>. Accordingly, it is required to search for more feasible getter materials than uranium for the safe handling of tritium gas.

We have reported<sup>2)</sup> that an intermetallic compound,  $Zr_9Ni_{11}$ , in Zr-Ni alloys shows some advantageous features in comparison with uranium getter. In the present paper, we will describe the results of feasibility tests of a tritium container packed with  $Zr_9Ni_{11}$  alloy.

## 2. Experimental

Figure 1 shows a cross-sectional view of the tritium container fabricated in the present study. The container was mainly constructed of 316 stainless steel (SS316), following double containment concept to minimize tritium release to the environment. This stainless steel, SS316, is one of austenitic stainless steels showing low permeability to tritium<sup>3)</sup>. An inner tube, which was connected to a vacuum system via two metal bellows valves, was 9.53 mm in outer diameter and 1.25 mm in thickness. The outer surface of the inner tube was electroplated with gold to prevent corrosion of the SS316 surface and permeation of tritium at elevated temperatures. The  $Zr_9Ni_{11}$  alloy used in the present study was purchased from Japan Metals and Chemicals Co. The alloy had been prepared with argon arc melting method and pulverized with exposing it to hydrogen of 10 atm at 200°C. Subsequently, the absorbed hydrogen had been evacuated at 800°C. The powder of  $Zr_9Ni_{11}$  alloy was examined with a conventional X-ray diffractometer. It was revealed that the alloy powder consisted of  $ZrNi$ ,  $Zr_9Ni_{11}$ ,  $Zr_7Ni_{10}$  and Zr.

On account of the small diameter of the inner tube, the alloy powder was screened

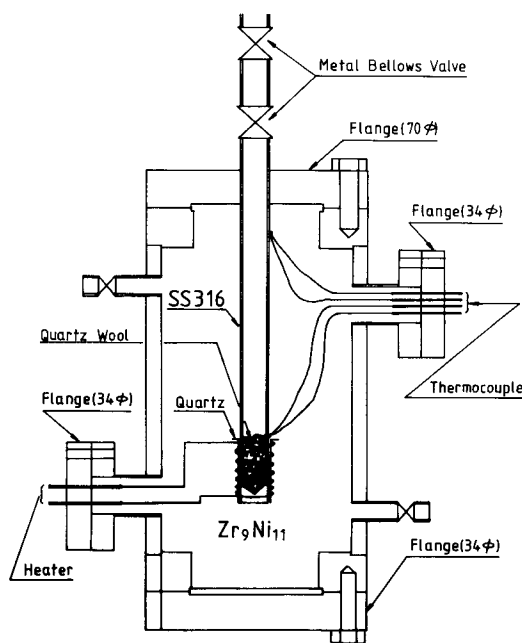


Fig. 1. A cross-sectional view of a tritium container constructed of SS316.

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by using mesh sieves. The size and weight of the powder used were over 60 mesh (0.25 mm) and 1.5 g, respectively. A small handmade ohmic heater, which was insulated from the inner tube by using quartz glass tubes, was installed in the tritium container for activation of the powder and for temperature control during the measurements of dissociation pressure. The temperature was measured at two different points of the outer surface of the inner tube with two thermocouples spot-welded.

Figure 2 shows a schematic diagram of the experimental apparatus used. This is essentially an ultra-high vacuum system equipped with three kinds of pumps : sputter ion pump, turbomolecular pump and oil-sealed rotary pump. The residual pressure of the system was usually below  $3 \times 10^{-9}$  Torr (1 Torr = 133 Pa). Two precise capacitance manometers (MKS Baratron : model 390 HA with 1 or 1000 Torr head) were used to measure the dissociation pressure of  $Zr_9Ni_{11}$  deuteride at various temperatures and for other pressure measurements. Feasibility tests of the tritium container were carried

out by using deuterium gas as an alternative of tritium, because 20 Ci/day is the maximum amount of tritium permitted to use in our facilities. This amount is equivalent to about 8 cm<sup>3</sup> (STP)/day. With

use of a quadrupole mass spectrometer, the purity of the deuterium gas was confirmed to be over 97% : main impurities were hydrogen and carbon monoxide.

Dissociation pressures of deuterides having various stoichiometric compositions were measured with a closed system. Namely, after a given amount of deuterium gas was absorbed at room temperature, the valve No.10 was closed. Subsequently, the temperature of the sample was raised stepwise from room temperature and the dissociation

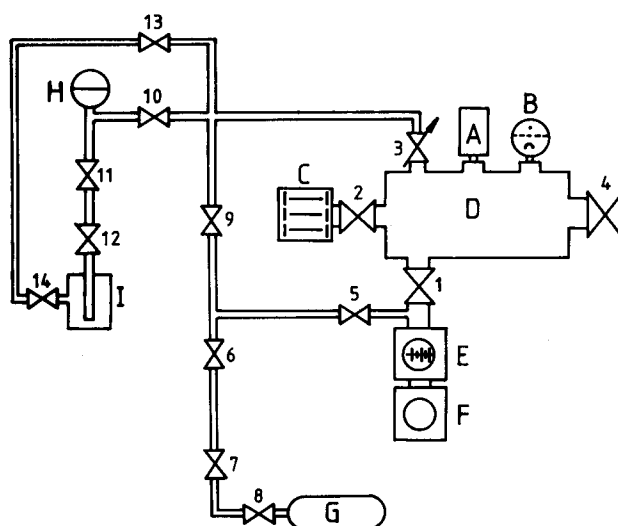


Fig. 2. Block diagram of the vacuum system connected with the tritium container : A, quadrupole mass spectrometer ; B, ionization gauge ; C, sputter ion pump ; D, vacuum chamber ; E, turbomolecular pump ; F, rotary pump ; G, D<sub>2</sub> cylinder ; H, capacitance manometers (1 and 1000 Torr heads) ; I, tritium container. All of numbers in the figure describe the metal bellows valve.

pressure was measured at each temperature. After a series of measurements, a given amount of deuterium gas was added at room temperature and the dissociation pressure was again measured through similar processes.

### 3. Results and discussion

#### 3. 1. Heating ability

Table 1 shows the electric power needed to heat the inner tube up to a given temperature. In this test, the outer tube had been evacuated in advance. The table shows that even a little electric power was sufficient to heat the inner tube up to 500°C. In addition, the temperature of the outer tube went up to only about 100°C even though the inner tube was heated up to 500°C. This suggests that no special cooling device is necessary for this tritium container.

#### 3. 2. Activation processes

Figure 3 represents the variation of absorption rates of deuterium gas with the temperatures of vacuum heating of the loaded alloy powder to examine activation. The vacuum heating was performed for 1 hour at temperatures of 300, 400 and 500°C. Those procedures will be denoted as "processing" below. After each vacuum heating, the alloy powder was cooled to room temperature. The alloy powder was exposed to deuterium gas of 9 Torr and the pressure decrease was measured with the capacitance manometer. In the case that the absorption rate obeys the first-order kinetics with respect to deuterium pressure (i.e.,  $dP/dt = -kP$ , where  $P$  is the deuterium pressure at a time,

Table 1. Temperatures of the double shielded container and electric power supplied.

Temp. of Container (°C)	Temps. of Flange Surf. (°C)		Electric Power Supplied to the Container (W)
	Upper	Lower	
200	—	—	11
250	—	45	16
300	42	50	25
350	—	—	34
400	52	68	45
450	—	—	55
500	74	104	65

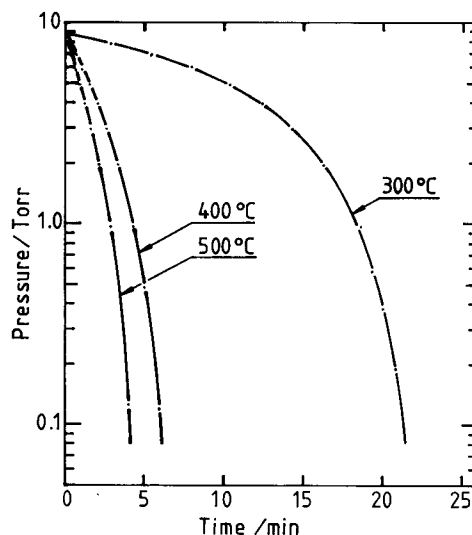


Fig. 3. Effect of evacuation temperature on activation of the as-received alloy.

k the rate constant of absorption), the variation of the deuterium pressure should be described by a simple exponential function<sup>4)</sup>. No linear relation, however, was observed at any processing temperature except for the initial stage of absorption. In addition, the absorption was accelerated with time and/or absorption.

Such behavior is attributed to generation of heat owing to the adsorption of deuterium. Supposing the adsorption of deuterium molecules takes place initially at certain active sites, a given amount of heat is generated and liberated around the active sites. This causes local heating of the respective parts of crystallites because of the low thermal conductivity of the packed alloy powder, accelerating the absorption rate. This is an advantageous point for fast absorption. However, appropriate counterplans against the local heating would be important for the design of a tritium container since the residual pressure of tritium is basically determined by the temperature of those parts.

Figure 3 also shows that the absorption rate increases with the processing temperature. On the basis of these observations, we adopted the evacuation at 400°C for 1 hr as the standard activation process of the as-received  $Zr_9Ni_{11}$  alloy. In general, the absorption rate reduces owing to the adsorption of contaminants such as  $H_2O$ ,  $CO$  and  $CO_2$ . Therefore, it will be necessary to re-activate of the alloy powder to regain the absorption rate. In this case, the standard activation process could be employed for the re-activation.

With respect to the processing at 400°C, the alloy powder released considerable amounts of gaseous products such as  $H_2O$  and  $CO$  as well as  $H_2$ , whereas the gas release decreased substantially above 400°C. This is very similar to the observations for  $Zr_2Ni$  by Ichimura et al<sup>5)</sup>. According to Ichimura, in addition, zirconium is in oxidized states on the as-received surface of  $Zr_2Ni$ , whereas it gradually changes to metallic state with heating above 400°C. It appears plausible to expect similar phenomena for  $Zr_9Ni_{11}$ .

### 3. 3. Dissociation pressure

Figure 4 shows the temperature dependence of the dissociation pressure over  $Zr_9Ni_{11}D_x$ , where x is the value determined at room temperature. As seen in the figure, the logarithm of the dissociation pressure varied linearly with the reciprocal temperature in a relatively low temperature region (below about 150°C) for all values of x examined. Above this temperature region, the dissociation pressure deviated downward from the respective straight lines: the higher the temperature was, the larger the deviation. It is considered that the deviation is due to the large variation of deuterium concentration

in a series of measurements. In the case of  $Zr_9Ni_{11}D_{3.49}$ , however, the dissociation pressure reached about 500 Torr at 350°C. In this case, the initial absorption amount of deuterium in  $Zr_9Ni_{11}D_{3.49}$  was  $3.03 \times 10^4$  Torr·cm<sup>3</sup> (STP) at room temperature, which is equivalent to about 100 Ci of tritium gas. On the other hand, the released amount was  $1.87 \times 10^4$  Torr·cm<sup>3</sup> (STP) at 350°C. Namely, the ratio of them attained to 0.62. This indicates that most of the initially loaded tritium can be supplied to gas phase at 350°C.

Table 2 is a summary of thermodynamic data evaluated from the linear part of the lines shown in Fig. 4. The thermodynamic data were evaluated by applying the equation,  $d(\ln K_p)/d(1/T) = \Delta H^\circ/R$ , where  $K_p$  is the equilibrium constant,  $T$  the absolute

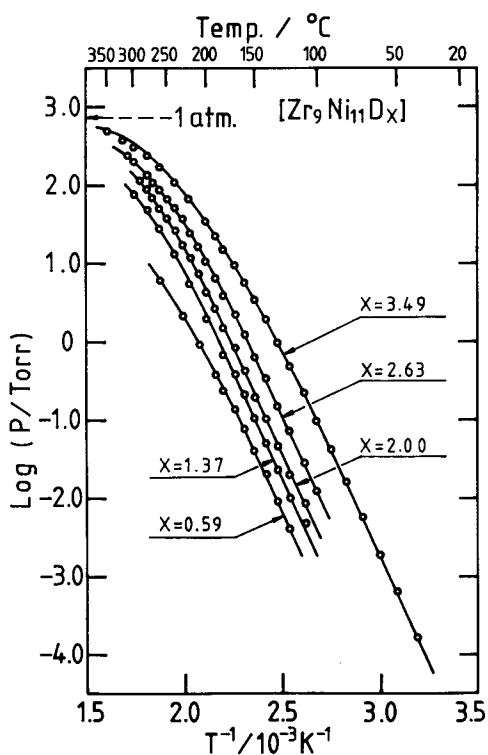


Fig. 4. Temperature dependence of the dissociation of the as-received alloy.

Table 2. Summary of thermodynamic data for deuterides having various stoichiometric compositions.

Composition of Deuteride	Amount of Absorption ( $\times 10^{20}$ atoms)	$-\Delta H^\circ$ (kcal/mol)*	$-\Delta S^\circ$ (cal/mol·K)*
$Zr_9Ni_{11}D_{0.59}$	3.61	24.9	39.3
$Zr_9Ni_{11}D_{1.37}$	8.45	25.7	43.0
$Zr_9Ni_{11}D_{2.00}$	12.3	25.8	44.7
$Zr_9Ni_{11}D_{2.63}$	16.2	25.1	45.4
$Zr_9Ni_{11}D_{3.49}$	21.4	25.2	49.6

\*) "mol" in parentheses means unit molar deuterium.

temperature,  $R$  the gas constant and  $\Delta H^\circ$  the standard enthalpy change. The standard enthalpy change was about  $-25$  kcal/mol( $D_2$ ) irrespective to the stoichiometric compositions of deuterium and agreed well with the results obtained from our previous work<sup>2)</sup>. On the other hand, the standard entropy change( $\Delta S^\circ$ ) increased with the deuterium concentration. The absolute entropy of deuterium gas is  $34.6$  cal/mol( $D_2$ )  $\cdot$  K. The observed values were apparently larger than this.

In our previous work on the heat of deuteride formation of  $Zr_9Ni_{11}$  alloy<sup>2)</sup>, the standard entropy change was close to the absolute entropy of deuterium gas. In this experiment, the as-received  $Zr_9Ni_{11}$  alloy used was in a form of plate and consisted mostly of  $Zr_9Ni_{11}$  intermetallic compound, which was confirmed with the X-ray diffractometer. The alloy was pulverized under milder conditions than the present sample, exposing it to deuterium below 1 atm at room temperature before measurements of the dissociation pressure. The primary difference between the previous and the present works lies in the fact that the sample consisted mostly of a metallic compound,  $Zr_9Ni_{11}$  in the former, whereas it was a mixture of metallic compounds in the latter. The dissociation pressure observed in the present study should be a function of the number and type of coexisting metallic compounds, and deuterium concentration in each compound and/or respective deuterides. The temperature dependence of the dissociation pressure should be related to those factors. Namely, it is likely that the coexistence of intermetallic compounds plays an important role for large apparent standard entropy changes observed in the present study.

### 3. 4. Absorption rate

Effects of stoichiometric deuterium concentration in the alloy on an absorption rate were examined. Figure 5 shows the change in the absorption rate of deuterium gas at room temperature with the deuterium concentration in the alloy. The deuterium pressure was set low enough to keep the deuterium concentration almost constant during the absorption measurements. Namely, the amount of deuterium gas added to deuteride at a given stoichiometric deuterium concentration was  $63$  Torr  $\cdot$  cm<sup>3</sup> in each run,

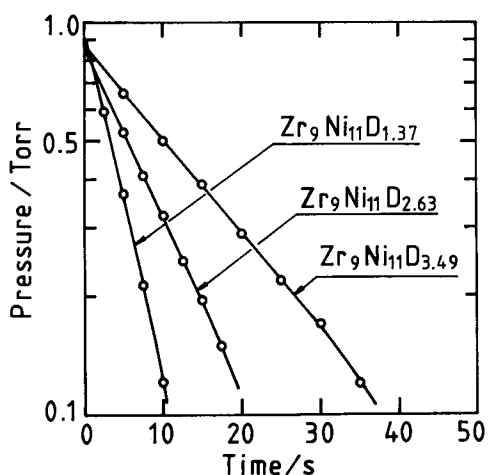


Fig. 5. Effect of deuterium concentration on absorption rate of deuterium gas.

which increases the deuterium composition only 0.004. It is seen in this figure that the pressure decreased exponentially with time, irrespective to the initial deuterium concentration. As mentioned above, this indicates that the absorption rates of deuterium obeys the first-order kinetics with respect to deuterium pressure. Therefore, slopes of the lines in the figure correspond to the rate constants of the absorption. It is clear from this figure that the absorption rate constant is influenced by the initial deuterium concentration: one can see about four times difference in the rate constants in Fig. 5. This appears due to variation of the number of adsorption sites or activation energy of adsorption of deuterium molecules with deuterium concentration. Anyhow, in the practical use, such effect must be considered to determine the appropriate working range of the alloy for tritium handling.

We also examined the absorption process under near practical conditions. Namely, after closing the valve Na10 and opening two valves of Na11 and 12, most of the deuterium absorbed as  $Zr_9Ni_{11}D_{3.49}$  was first released to gas phase with heating it up to  $350^\circ\text{C}$ , where the gas pressure went up to 488 Torr. Subsequently, the container was allowed to cool with switching off the power supply. The pressure decrease is shown in Fig. 6. The gas pressure initially ran parallel

with temperature decrease. The absorption rate, however, gradually decreased in spite of the further decrease of temperature. Supposing the equilibrium is established quite readily at each temperature, the deuterium pressure is expected to decrease as a dashed line shown in this figure. It is seen that the observed pressure deviates further from the dashed line with time. Three mechanisms appear to be plausible for this phenomenon:

( 1 ) the temperature difference between the wall and the alloy powder, ( 2 ) the change in the material properties and ( 3 ) wall effects.

As for the first mechanism, the measured temperature appears to be evidently lower than that of the alloy because heat is evolved in the inner tube owing to the absorption of deuterium. To examine this effect, the valve Na12 shown in Fig. 2 was temporarily closed for about 10 minutes during the measurements. This is shown as "CLOSE" along with arrow in Fig. 6. A pressure rise was observed after closing the valve, indicating

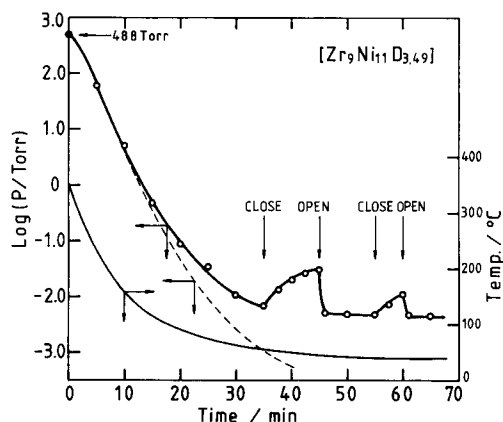


Fig. 6. Deuterium absorption behavior during the cooling of tritium container.



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the desorption of deuterium from the surface of stainless steel tubes. Opening the valve (indicated "OPEN" in the figure) caused sudden pressure decrease. The pressure, however, did not attain to a level expected as shown by the dashed line, although the temperature decreased further. This behavior was reproducible as seen in the figure. In addition, the pressure did not decrease further even after sufficient cooling time and was kept almost constant at about  $4.5 \times 10^{-3}$  Torr. These observations indicate that the pressure difference between the observed and expected is not due to the temperature difference between the outer surface of the inner tube and alloy.

To examine the second mechanism, namely the possibility of changes in material characteristics affecting the dissociation pressure, a part of tubes was evacuated overnight rigorously by closing the valve №12. Subsequently, the pressure was again measured by opening the valve. It was observed that pressure was at the level expected from the dashed line. This indicates that substantial characteristics concerning with the dissociation pressure did not change in adsorption processes. Namely, it appears that the third mechanism would play an important role for the pressure difference. It is seen that the pressure difference is mostly due to the desorption of deuterium from the inner surface of the tubes.

Similar phenomena would be also expected to occur in tritium handling systems. Namely, tritium storage materials can not fully display their ability under such conditions. Consequently, it is of importance to development materials inactive to tritium adsorption and/or absorption. Matsuyama et al. have reported<sup>6)</sup> that the adsorption as well as desorption of tritium on/from SS304 can be reduced to below 1/100 by preparing surface passivation layers; for example, ceramic coating with such as boron nitride and electrochemical passivation.

## 4. Conclusions

A tritium container packed with powdered  $Zr_9Ni_{11}$  alloy was fabricated from 316 stainless steel. Its feasibility was examined by using deuterium gas as an alternative of tritium. The conclusions obtained were as follows:

- (1) A compact heater incorporated into the container was sufficient to heat up the alloy powder to temperatures above 500°C. This was enough to activate the alloy powder and liberate deuterium gas at 1 atmospheric pressure.
- (2) The as-received  $Zr_9Ni_{11}$  alloy could be activated by the evacuation at 400°C for 1 hr. These conditions would be also applicable to reactivation of  $Zr_9Ni_{11}$ -tritide.
- (3) It was possible to supply deuterium gas near 1 atm at about 350°C and to absorb

most of it at room temperature, although the as-received alloy was a mixture of intermetallic compounds such as  $ZrNi$ ,  $Zr_9Ni_{11}$  and  $Zr_7Ni_{10}$ ,

- (4) The apparent absorption rate was affected by the stoichiometric deuterium concentration in the alloy and the desorption of deuterium from the inner surface of constructing materials. Especially, the latter effect will impair functions of reversible tritium getters.

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