A Preliminary Study on the Production of Tritium from Neutron-irradiated Lithium-aluminum Alloy

Masakazu Tanase, the late Koichi Yamaguchi and Kichizo Tanaka*

Radioisotope Center, Japan Atomic Energy Research Institute
Tokai-mura, Naka-gun, Ibaraki Pref. 319-11
*Tokai Research Establishment, Japan Atomic Energy Research Institute
Tokai-mura, Naka-gun, Ibaraki Pref. 319-11
Received June 5, 1982

The release of crude tritium gas from neutron-irradiated LiAl alloy, and the following purification and the trapping of the gas have been preliminary studied to obtain information necessary for the development of tritium technology.

The percentages of the fractions of H2(T) and H2O(T) occupying about 99% among gaseous species(T) released were largely influenced by pre-irradiation treatment of the alloy and especially by heating temperature of the irradiated alloy. In the isothermal heating at 850°C, about 95% of tritium was released as H2(T). For obtaining all of tritium as H2(T), the fraction of H2O(T) was successfully converted to H2(T) with U turnings at 800°C. Hydrogen (T) could be effectively trapped in a pulverized U getter at room temperature.

Key Words: tritium production, lithium-aluminum alloy, neutron irradiation, chemical purification, tritium trapping, uranium turnings, uranium powder

1. Introduction

Research and development for the production of tritium(T) with neutron-irradiated 6LiAI alloy have been started in the author’s laboratory to establish the technology of production and handling of T of large scale as required in the development of a controlled thermonuclear reactor.

Some basic phenomena concerning the formation or the release of T in the neutron-irradiated 6LiAI alloy have been studied by Owen, et al.2 7 and for example the production of T from the alloy already has been put into practice at Marcoule17. However, only little information concerning the effect of pre-irradiation treatment of the alloy on the release behavior of T species during post-irradiation heating, and of the following processes of chemical purification and trapping of the T species, has been issued so far.

The present work has aimed at fulfilling the lack of the above information necessary for the T production. First, in order to obtain T as H2(T) as much as possible, the effect of pre-irradiation treatment of the alloy and the temperature effect of the irradiated alloy were preliminarily examined in relation to the relative yield of T species extracted from the alloy. Since the extracted T gas was mostly composed of H2(T) and H2O(T) with a small amount of CH4(T), it had to be purified chemically to HE(T) before further treatment such as isotopic enrichment. Therefore, conversion of H2O(T) and CH4(T) to H2(T) on U turnings has been examined as a function of temperature of the turnings. Finally, trapping of H2(T) purified with pulverized U has been tried after reactivity of the U turnings with H2 and equilibrium pressure of H2(T) over U hydride(T) were studied. Although conversion and trapping of hydrogen with U were well known in principle, practical conditions of operation had to be known in detail to be applied to a test production apparatus8 for T at a 3.7 TBq (100 Ci) level.
2. Experimental and Results

2.1 Release of tritium from neutron-irradiated LiAl alloy

2.1.1 Procedure and apparatus

An Al alloy containing 1.1 weight percent of Li of natural isotopic composition was manufactured by Mitsubishi Atomic Power Industries Co. The alloy was rolled into 0.87 mm thick, which was cut into pieces weighing 20 to 50 mg. Before irradiation, some pieces of the alloy were heated for 1 h at a predetermined temperature between 100 and 500°C in air, He (>99.999% in purity) or H₂ (>99.99999% in purity). The surface of some other alloy samples were sandpapered in the He atmosphere. Among these treatments, heating in air is carried out to examine the influence of oxygen in the alloy. The alloy pieces both untreated and pretreated, were enclosed in quartz tubes under vacuum and irradiated for 20 min in JRR-2 or -4 in a neutron flux of about $5 \times 10^{18}$ cm$^{-2}$s$^{-1}$. After cooling for 1 to 2 weeks, each one of the sample pieces was placed in the reaction tube of an apparatus shown in Fig. 1. The apparatus consisted of the reaction tube, 3 water-bubblers (23 ml) and 2 CuO (Analytical Grade, Kishida Chemical Co.) columns. The first column was heated at 400°C and the second one at 800°C. Among T species released from the alloy on heating, H₂O(T) was accumulated in the first bubbler, H₂(T) in the second one and CH₄(T) in the third one. The sample was heated isothermally or isochronally at temperatures below 850°C in the He gas stream with the flow rate of 20 ml/min$^{-1}$. In order to determine the relative yields of T species, 0.1 ml of water in each bubbler was pipetted with adequate intervals and the T radioactivity was measured for 20 min with a liquid scintillation counter (Beckman LS-100). After all procedures were completed, T remained in the alloy was estimated also by liquid scintillation counting after dissolving the alloy with 10 ml of 4 mol/l NaOH at 90°C under the O₂ stream of 20 ml/min$^{-1}$. A mixture of toluene containing 4 g-l$^{-1}$ of 2,5-diphenyloxazole and ethanol (8:2.5) was used as a liquid scintillation cocktail. Prior to the measurement, the counting efficiency of the counter was determined by using a standard solution of T-labeled $n$-hexadecane (Radiochemical Center, Amersham).

![Fig. 1 Apparatus for examining release of tritiateP species from neutron-irradiated LiAl alloy.](image)

![Fig. 2 Release of tritiated species from unpre-treated LiAl alloy.](image)
2.1.2 Release of T from neutron-irradiated LiAl alloy

(1) Effect of pretreatment before irradiation

Figure 2 shows typical release curves for the T species in question, obtained by heating an untreated alloy sample. Temperature was raised stepwise from 100°C to 800°C with the 100°C interval after being kept for 30 min at each temperature. Before this experiment, the amount of T in the atmosphere of the quartz ampoule was confirmed to be negligibly small. The relative yields of \( \text{H}_2(T) \), \( \text{H}_2\text{O}(T) \) and \( \text{CH}_4(T) \), saturated above 600°C, were 0.64, 0.35, and 0.01, respectively. Figure 2 also shows that the release of \( \text{H}_2(T) \) was preceded by the \( \text{H}_2\text{O}(T) \).

Figure 3 shows the relative yields of each species of T released from the samples pretreated in different atmospheres as a function of pretreatment temperature. The yields were determined from the amount of each of T species recovered after the completion of the process described above. For the alloy pretreated in air, the \( \text{H}_2\text{O}(T) \) fraction tended to increase slowly with the temperature increase in contrast to the decrease of the \( \text{H}_2(T) \) fraction. Microscopically observation of the alloy samples pretreated in air revealed that the surfaces of the samples were covered with thin layer different from the interior of the alloy and its thickness increased with the temperature increase of pretreatment. Furthermore, an analysis of the oxygen content, O/Al, with an Auger spectrometer (ANELVA Corp., EMAS-2) confirmed that the surface layer contained much more quantity of oxygen than the interior of the material. However, pretreatment in He did not show any remarkable differences from the results of the untreated samples. Sandpapering of the alloy surface did not affect the relative yields of T species, either. The O/Al of the surface of the alloy heated in He or sandpapered was approximately equal to that of the interior. From these results, it might be concluded that the formation of \( \text{H}_2\text{O}(T) \) depended on the oxygen content of the alloy surface.

On the other hand, although the samples were pretreated in the \( \text{H}_2 \) atmosphere with the purpose of decreasing the \( \text{H}_2\text{O}(T) \) fraction, the pretreatment did not show any significant improvement.

(2) Effect of heating temperature

The release of T species from untreated, irradiated samples was studied also by isothermal heating ranging from 520°C to 850°C for 5 h. As shown in Fig. 4, the fraction of \( \text{H}_2\text{O}(T) \) remarkably decreased with increasing temperature in contrast to the increase of the \( \text{H}_2(T) \) fraction, which amounted to about 95% at 850°C. These results might show that a combi-
nation of H(T) and OH(T) on the alloy surface would be rather difficult at higher temperatures. In order to recover T as H₂(T), the process should be carried out at a high temperature although the formation of H₂O(T) and CH₄(T) species could not be completely prevented in the practical process.

2.2 Chemical purification of crude T gas by U turnings

Conversion of H₂O and CH₄ to H₂ was tested in relation to the heating temperature of U turnings. The apparatus used in this work was shown in Fig. 5. Argon (40 ml) with H₂O saturated by bubbling through a water bubbler at room temperature or 1.1 ml (STP) of CH₄ (>99.9% in purity) was introduced by the Ar flow of 20 ml·min⁻¹ into a column packed with about 10 g of U turnings (Mitsubishi Atomic Power Industries Co., dipped in HNO₃ (1:3), washed with H₂O and acetone). The column was connected to a gaschromatograph (Gasukuro Kogyo Co., KOR-1), and heated at a predetermined temperature between 100°C and 800°C. The gaschromatographic column of 3 mm in inner diameter and of 3 m long was filled with active carbon (80~100 mesh, Gasukuro Kogyo Co.) which can separate H₂ and CH₄ mutually at 50°C (the carbon had been reactivated beforehand by heating it at 220°C in the Ar flow for 7 h). The conversion factor of H₂O to H₂ at each temperature was determined by assuming the peak area of H₂ obtained at 800°C as 100%. The peak area was obtained by a thermal conductivity detector of this gaschromatograph. The conversion factor of CH₄ to H₂ was estimated from the ratio of peak areas between H₂ and CH₄.

Conversion of tritiated water to H₂(T) was also tested, using H₂O(T) of 31 MBq·ml⁻¹ (0.85 mCi·ml⁻¹, Radiochemical Center, Amersham). An aliquot of H₂O(T), 10 μl, was taken to a sampler which was connected to the column filled with 10 g of U turnings (Fig. 6).
water(T) was evaporated by heating under the He flow of 20 ml·min⁻¹ and led into the heated column. Unreduced H₂O(T) was collected in a trap cooled with dry-ice-acetone mixture, while resulting H₂(T) was oxidized by a CuO column heated at 400°C so as to be trapped in the water bubbler. The conversion factor of H₂O(T) to H₂(T) was expressed by the percentage of T collected in the water bubbler against the sum of the T activities found in the cold trap and in the water bubbler.

The results obtained are shown in Fig. 7. The conversion factor for H₂O and H₂O(T) increased with temperatures of U turnings. It exceeded 95% above 600°C, whereas conversion of CH₄ was not completed even at 800°C. In the case of H₂O(T), however, the total recovery of H₂O(T) trapped both in the cold trap and in the water bubbler was 70 to 90% of the original samples except in the experiment with U heated at 800°C. Most of unrecovered H₂O(T) was found trapped in the U turnings.

2-3 Trapping of H₂(T) with U
2-3-1 Reactivity of U turning with H₂ and preparation of U powder
As a getter material for the purified H₂(T), U, which has been widely used¹⁰,¹¹, was chosen. The reactivity of U turnings against H₂ used as a starting material was examined first in relation to the surface treatment of the turnings. The experimental apparatus is illustrated in Fig. 8. One gram portion of the turnings was treated in 2 different ways; (1) dipping in HNO₃(1:1), washing with water and acetone, and drying in the He atmosphere, (2) drying in air after the treatment with HNO₃ and washing. The turnings were placed in a reaction tube B (77 ml) in Fig. 8 and brought into contact with about 13330 Pa (100 Torr) of H₂ (>99.99999% in purity, Nihon Sanso Co.) which is planned to be the handling tritium level in the production runs. Temperature of the reaction tube was raised from room temperature to 550°C at a rate of 2.2°C·min⁻¹, and the H₂ pressure was measured by an Hg manometer or an MKS Capacitance Manometer (range, 1.333 to 0.1333 Pa (10⁻² to 10⁻³ Torr), accuracy ±0.08%) to follow the progress of the reaction of U with H₂. The change of the H₂ pressure is shown in Fig. 9 for treated U turnings and untreated turnings as well. No significant
differences were observed among the curves. Uranium began to absorb H₂ as temperature was raised above 200°C, but the absorption rate was exceeded by the desorption rate above 300°C.

Since the U turnings did not completely trap H₂ in the reaction tube as shown by the residual pressure at 250°C in Fig. 9, another U getter was then tested. One gram of U turnings treated in the way ① was fully hydrogenated at 250°C by adding 13330 Pa (100 Torr) of H₂ repetitively and dehydrogenated by heating the resulting U hydride at 500°C. The composition of U hydride thus obtained was estimated to be UH₉₂₄. Powder U prepared by this procedure was found to react with H₂ even at room temperature.

2.3.2 Synthesis of U hydride as a source of H₂(T)

Prior to the trapping of H₂(T) by this powder, another U hydride(T) was synthesized for obtaining an H₂(T) generator. About 5 g of U powder was completely hydrogenated with H₂ (T) containing 19 GBq (500 mCi) of T. A Ti target (IAEA) was used as the T source. It was heated at 510°C in the reaction tube B to generate T₂ which was diluted with H₂ from a cylinder. The chemical form of the gas released from the synthesized U hydride(T) was confirmed to be H₂(T) by the radiogaschromatography. The equilibrium pressure of H₂(T) over U hydride(T) was measured at various temperatures (Fig. 10). From the results, the following equation was deduced;

\[ \log_{10} P(Pa) = - \frac{4.30 \times 10^3}{T} + 10.90, \]

where \( P \) is the pressure of H₂ presented in Pascal and \( T \) temperature in Kelvin. The values of \( \Delta H_{f,298}^0 \) and \( \Delta S_{f}^0 \) evaluated from the equation were \(-123 \text{ kJ} \cdot \text{mol}^{-1} \) (\(-29.4 \text{ kcal} \cdot \text{mol}^{-1}\)) and \(-169 \text{ J} \cdot \text{T}^{-1} \cdot \text{mol}^{-1} \) (\(-40.4 \text{ cal} \cdot \text{T}^{-1} \cdot \text{mol}^{-1}\)), respectively. These values were consistent with those described in several literatures\(^{13-14}\). This equation allows to obtain a desired amount of H₂(T) easily by heating U hydride(T) at an adequate temperature.

2.3.3 Trapping of H₂(T) with U powder

Finally, the trapping and release of H₂(T) with the U powder prepared by the hydrogenation-dehydrogenation process from 1 g of U turnings were tested using H₂(T) released by heating U hydride(T) at 350°C. The powder was brought into contact with H₂(T) at 13330 Pa (100 Torr) in the reaction tube B, whose temperature was kept at room temperature or at 150°C. As shown by the drop in the reading of the vacuum gauge indicating the H₂(T) pressure in the system, over 98% of H₂(T) was easily trapped in the U getter within a few minutes (Fig. 11). The T radioactivity meas-
measurement with the ionization chamber (Ohkura Electric Co.) also gave a consistent result. Then, almost all of trapped H₂(T) could be released in the reaction tube B by heating the U getter at about 500°C.

3. Conclusion

The relative yield of H₂(T) or H₂O(T) species released from the neutron-irradiated alloy on heating was affected by the treatment of the alloy before irradiation and by the heating temperature of the neutron-irradiated alloy. The pretreatment of heating the alloy in air or the H₂ atmosphere increased the fraction of the H₂O(T) species, but the pretreatment in He and sandpapering did not show any significant effect. In the isothermal heating of the untreated alloy, increase of the temperature remarkably increased the amount of the H₂(T) species which reached to about 95% at 850°C.

In the chemical purification of the extracted T gas, the H₂O(T) species was converted to H₂ (T) with U turnings with a factor of more than 95% by passing through the U turnings heated above 600°C, but CH₄ was not fully decomposed even at 800°C.

Hydrogen(T) was confirmed to be successfully trapped at room temperature and released at 500°C with pulverized U.

On the basis of these studies, a facility consisting of a vacuum furnace, a U purifier, and U getter was constructed for test production of T at a level of 3.7 TBq (100 Ci), and has been well operated⁷.

Acknowledgement

The authors wish to express their thanks to Dr. T. Furuta for his analysis of alloys by Auger spectroscopy.

The authors also thank Messrs. K. Takano and H. Kamioki for their kind assistance in this work.

References

3) R.H. Wiswall and E. Wirsing: BNL-19766 (1975)
要 旨

中性子照射した LiAl 合金からのトリチウム製造に関する予備研究

棚瀬正和，故山口康市，田中吉左右*

319-11 茨城県那珂郡東海村 日本原子力研究所アイソトープ事業部
319-11 茨城県那珂郡東海村 日本原子力研究所東海研究所

LiAl 合金の中性子照射によるトリチウム製造技術の開発を目標として，まず予備的に照射済み合金からのトリチウム放出と，そのトリチウムの化学的精製や捕集について実験を行った。

合金から放出したトリチウムの気体状化学種の約99%を占める H₂(T) と H₂O(T) 成分の割合は，合金の前処理と，その加熱温度の影響を強く受ける。このうち，850°C での等温加熱でトリチウム成分の約95%は H₂(T) として放出された。すべてのトリチウムを H₂(T) として回収するために，H₂O(T) は 800°C の金属ウラン粉末で効果的に H₂(T) に変換された。H₂(T) は金属ウラン粉末により室温下でも捕集されることを確認した。