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Short-term nitrogen trapping in liquid lithium by pure titanium

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Nitrogen in the liquid lithium target in IFMIF may enhance corrosion and erosion of the structural materials. Because nitrogen has a high solubility in lithium, hot trapping by getter materials is required. The function of pure titanium as a nitrogen absorber has been suggested and demonstrated by Hanford Engineering Development Laboratory and ENEA. However, there is a problem that nitrogen trapping is inhibited by TiN (titanium nitride) generated on the titanium surface. In this study, short-term nitrogen trapping effect was investigated to clarify the mechanism of initial TiN formation in lithium. The short-term (~27 hours) pot experiments with pure titanium plate were performed. As a result, the nitrogen concentration in lithium was reduced by pure titanium. However, the peak pattern of TiN was not observed with XRD in the titanium plate after an immersion experiment. By TEM observation of the titanium plate after the pot test with a high nitrogen concentration, it was shown that most nitrogen did not form TiN but diffused into the bulk of titanium plate. Therefore, efficient recovery may be possible in an early stage of the use of titanium as a hot trap, without being inhibited by formation of TiN.

Keywords: IFMIF, liquid lithium, nitrogen, pure titanium, hot trap

1. Introduction

Nuclear fusion reactors are under developement as the new power generation system which can produces large-scale energy with abundant resources.

To commercialize nuclear fusion energy by the D-T nuclear fusion reaction, blanket structural materials which are resistant to 14 MeV neutron load are required [1]. Development of the materials which can be used under this condition is one of the main subjects of nuclear fusion reactor engineering.

IFMIF (International Fusion Materials Irradiation Facility) is a facility which evaluates the property change of materials by 14 MeV neutron irradiation. It is under developement for the purpose of simulating nuclear fusion reactor environments [2,3]. IFMIF is the accelerator based neutron irradiation facility with a D-Li (Deuterium-Lithium) stripping reaction. The main systems of IFMIF consist of an accelerator system, a lithium target system, and a test cell system. An accelerator system consists of 2 sets of deuteron accelerators of 40 MeV and 125 mA [4-6].

Deuterons are injected to a flowing liquid lithium film of the target, generating neutrons for irradiation of test cell system. In the test cell system, control of irradiation conditions are performed. The neutron of 20 dpa/year is supplied by the lithium target system, and in order to remove the heat by deuteron beams with 10MW, it is necessary to flow the liquid lithium with a maximum flow velocity of 20 m/s. A target system consists of a target assembly, a lithium main loop, a lithium purification system, and a cooling system. The circulation of liquid lithium is induced by electromagnetic pumps. The lithium purification system consists of one cold trap and two hot traps, and reduces the nonmetallic impurities, which can lead to corrosion and erosion of structural materials[7].

Hydrogen isotopes, including the tritium generated by the D-Li reaction, carbon, nitrogen, and oxygen are the main nonmetallic impurities in liquid lithium. Keeping the level below 10 wt.ppm is required for carbon, nitrogen, and oxygen. For tritium, the reduction below 1 wt.ppm is required [8]. Since nitrogen impurities can prevent hydrogen isotope recovery, reducing the nitrogen level is strongly required for nitrogen. Since the solubility of nitrogen to lithium is high compared with oxygen or carbon, the hot trap by a chemical absorption reaction is required in addition to a cold trap. The materials which serve to recover substantially in the hot trap are called getter materials. Ti, Cr, V, V-Ti alloy and Fe-Ti alloy have been investigated in the past as getter materials for nitrogen. Fe-Ti alloy is the major interest in recent years [9-11]. Recently, a two-step recovery system using pure titanium as the material for the initial purification systems has been proposed [12]. Good performance of pure titanium has been suggested by Hanford Engineering Development Laboratory [13] and ENEA [14]. However, nitrogen recovery can be inhibited by TiN generated on the surface of titanium at an early stage. In this study, we are focusing on short-term nitrogen trapping effect to clarify the mechanism of an initial TiN formation. The short-term pot experiments with pure titanium plates were performed.

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2. Experiment

2.1 Getter materials immersion experiment in a pot

In this study, the immersion experiment was performed with liquid lithium in the pot made of a stainless steel, using 0.2 mm thick pure titanium plates as the getter material. A portion of lithium and a titanium plate were taken out with a scheduled time interval, and a chemical analysis was performed. For the immersion, temperature was set at 500 °C and 600 °C and the duration was set for 1 hour ~ 27 hours. Handling of lithium and the immersion experiment were carried out in a glove box with high purity argon atmosphere. A schematic figure of the apparatus is shown in Figure 1.

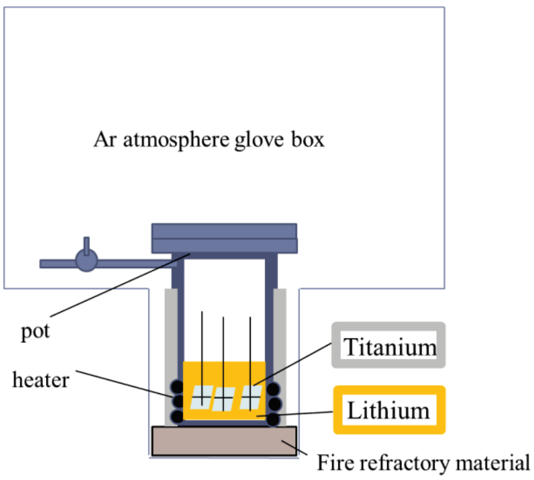

Fig.1 The experimental conceptual figure

The Sieverts' method was used for the adjustment of the initial nitrogen concentration in lithium. This is a method for measuring the amount of gas absorption by contacting the molten metal with known amount of gas.

In a pot made of a stainless steel, 50 gram molten lithium was installed, and five titanium plates (20mm x 20mm x 0.2mm) were immersed. The immersion experiment was started at 500 °C. When 27 hours had passed after starting the immersion, sampling of lithium and a titanium plate was performed.

2.2 Nitrogen concentration measurement in lithium

Nitrogen concentration in lithium was measured by the ammonia conversion method, which is schematically explained in Fig. 2. Lithium sample was sealed in a reaction vessel in a glove box with argon atmosphere. The reaction vessel in a mantle heater was connected to a Liebig condenser and a gas inlet system. A flow of high purity argon gas removed the air remaining in the gas line, and about 80ml of pure water was added to the pot to react with lithium. Equation (1) expresses the reaction.

$$Li + H_2O \rightarrow LiOH + H \quad (1)$$

The hydrogen generated produces ammonia by reacting with nitrogen in lithium by Equation (2).

$$N + 3H \rightarrow NH_3 \quad (2)$$

In a trap of recovered water connected to the gas line (about 0.01mol/l hydrochloric acid), ammonia molecules reacted to form ammonium ions by Equation (3).

$$NH_3 + H^+ \rightarrow NH_4^+ \quad (3)$$

Ammonia concentration in the recovered water was measured, and the concentration of nitrogen in lithium was calculated.

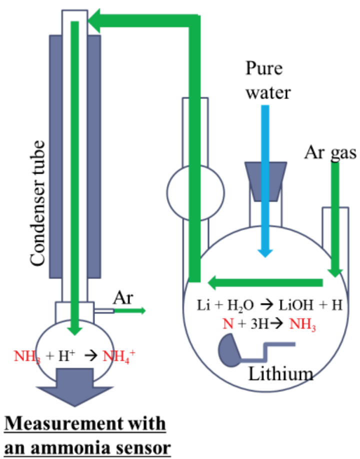

Fig.2 The ammonia conversion method

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We assumed that all nitrogen in lithium converted to ammonia. Thus, it is possible to evaluate the change of the concentration of nitrogen in liquid lithium during the immersion experiment.

2.3 Titanium plate analysis after immersion

In this study, we use XRD (X-ray diffraction) for analyzing the experimental products. In this study, we analyzed the samples before and after ion sputtering for digging the sample to check the depth distribution of nitrides. In addition, by using Cu-Kα x-ray, we performed XRD analysis with the parallel beam method in θ-2θ measurement. We also obtained the depth profile by PHI5000 VersaProbe XPS (X-ray Photoelectron Spectroscopy) with Ar sputtered etching of the surface of the titanium plate. Depth profiles of N-1s and Ti-2p spectra were measured and the atomic ratio of elements was then calculated by comparing the areas of these peaks. Furthermore, we performed the cross-sectional observation of the titanium plates after immersion using TEM (Transmission Electron Microscope) to obtain the distribution of nitrides in the titanium plate.

3. Results & Discussions

3.1 Time dependence of nitrogen concentration in lithium

The change of the nitrogen concentration in lithium with the immersion time was obtained. In addition, a blank experiment was performed without using the getter material. The results are shown in Figure 3

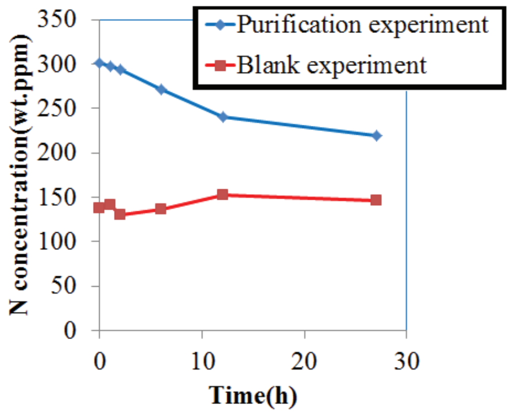

Fig.3 Changes of nitrogen concentration in lithium

In the blank experiment, the variation of nitrogen concentration was 22wt.ppm. Therefore, the decrease of the nitrogen concentration in the immersion test with the getter is statistically significant.

3.2 *Observation nitrogen in titanium*

We performed XRD analysis for the untreated titanium plate after immersion and after digging to 1.8 μm from the surface. Since the sizes of these samples were different, the intensities were so different. The results normalized are shown in Figure 4 with the analytical data of unimmersed titanium and the JCPDS data of the powder X-ray diffraction of TiN.

Results normalized to confirm the presence of the TiN has been shown. No XRD peak pattern of TiN was observed for all cases examined. We performed XPS analysis for the nitrogen depth profile of the titanium plate of the immersion experiment for 27 hours. Experimental result and the simulation obtained with the nitrogen diffusion limit model are shown in Figure 5. We determined that the boundary condition of N/Ti (nitrogen / titanium) in the simulation was 0.47 obtained by XPS analysis on the surface of the immersed titanium. Hanford showed that the diffusion coefficient (cm^2/s) of nitrogen in α-Titanium a given by Equation (4) [13].

$$D = 1.2 \times 10^{-2} \exp - \left(\frac{45252 \pm 2250}{RT} \right) \tag{4}$$

R = universal gas constant (1.987cal/mol)
T = absolute temperature

The results show that the N/Ti ratio decrease with time, showing diffusion-induced. The results show that the N/Ti (nitrogen / titanium) ratio on the surface is about 0.5 and the invasion of nitrogen in titanium by hot trapping is in accordance with the diffusion of nitrogen in titanium.

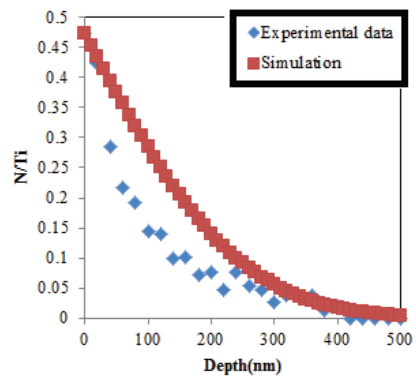

Fig.5 XPS analysis of the titanium plate comparing with a simulation.

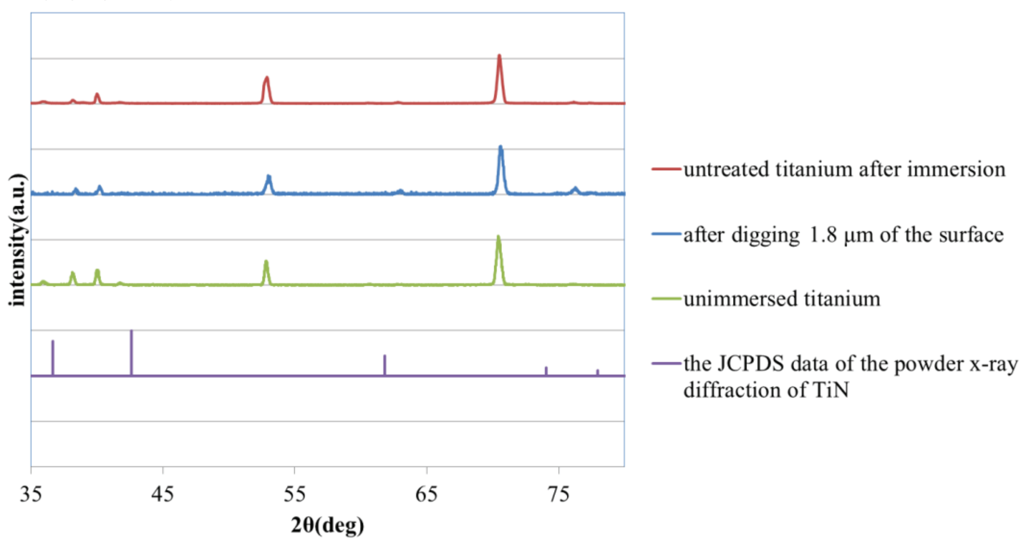

Fig.4 XRD analysis of the titanium plates

3.3 Experiment in high nitrogen concentration.

In order to check the existence of nitrogen in titanium, the immersion experiment of the titanium plate was performed in the conditions that the immersion time was 27 hours, the temperature was 600°C and the initial nitrogen concentration was high, followed by TEM observation of the titanium plate. The result is shown in Figure 6.

According to the dark-field image, some titanium nitride microcrystallites exist near the surface. In the corresponding bright-field image, the nitrogen invading from the surface are seen as the dark portions. Thus, most nitrogen does not serve as TiN crystal formation and the formatiom of TiN takes place in limited crystal grains. It is concluded that most of the nitrogen recovered is dissolved in titanium in solution.

4. Conclusions

In this study, short-term immersion experiments in liquid lithium was performed using pure titanium plates. The result showed effective nitrogen recovery by titanium. At the early stage of the immersion, the trapped nitrogen diffused into the bulk of titanium without forming surface TiN films. Most of the nitrogen recovered was dissolved in the titanium as a solution. Therefore, at the early stage, the hot trapping with pure titanium was not inhibited by TiN formation. Therefore the possibility of efficient recovery is expected using pure titanium.

5. References

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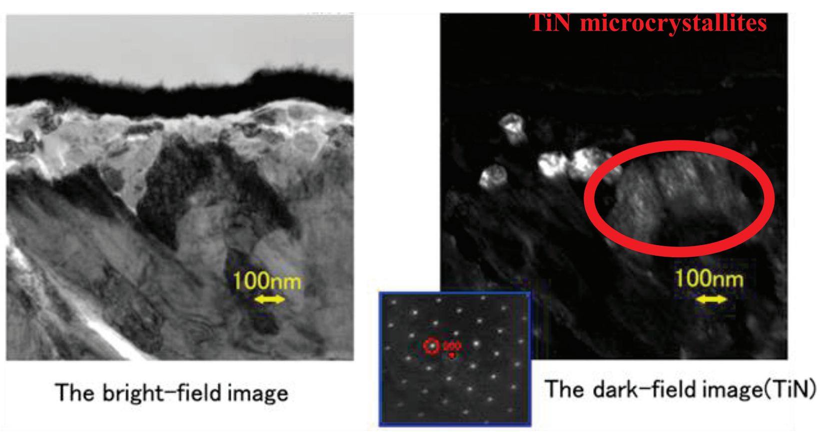

Fig.6 TEM observation of the titanium plate