Journal of Nuclear Materials 307–311 (2002) 1380–1385

journal of nuclear materials

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Control of the nitrogen concentration in liquid lithium by the hot trap method

Toshiharu Sakurai [a], Toshiaki Yoneoka [a], Satoru Tanaka [a,*], Akihiro Suzuki [b], Takeo Muroga [b]

[a] *Department of Quantum Engineering and Systems Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-Ku, Tokyo 113-8656, Japan*

[b] *National Institute for Fusion Science, Oroshi, Toki, Gifu 509-5292, Japan*

Abstract

The nitrogen concentration in liquid lithium was controlled by the hot-trap method. Titanium, vanadium and a V–Ti alloy were used as nitrogen gettering materials. Gettering experiments were conducted at 673, 773 and 823 K for 0.4–2.8 Ms. After immersion, the nitrogen concentration increased in titanium and V–Ti were tested at 823 K. Especially the nitrogen gettering effect by the V–10at.%Ti alloy was found to be large. Nitrogen was considered to exist mainly as solid solution in the V–10at.%Ti alloy. The decrease of the nitrogen concentration in liquid lithium by the V–Ti gettering was also confirmed.

1. Introduction

The compatibility of various materials with liquid lithium is affected by non-metallic impurities like nitrogen in liquid lithium. If the nitrogen concentration in liquid lithium is high, the chromium component in stainless steel reacts with nitrogen and lithium, and the steel may be embrittled [1]. Furthermore, a precipitate of lithium nitride may erode tubing materials. Therefore, the purpose of the present study is to control the nitrogen concentration in liquid lithium by the hot-trap method. Hot trapping is performed by materials for gettering nitrogen, which are immersed in liquid lithium. Metals, which are easily forming nitrides and have a high compatibility with lithium, are considered as gettering materials [2]. Gettering metals used in the present study were titanium, vanadium and an alloy of these two metals. Fig. 1 shows that titanium nitride has a high thermodynamic stability compared with lithium nitride (Li_3N). Vanadium nitride is also stable in liquid lithium when the nitrogen concentration in lithium is above 10^{-4} mass%. This figure shows that the affinity of titanium to nitrogen is higher than that of vanadium. However, the diffusion coefficient of nitrogen in vanadium is considered to be larger by three orders of magnitude than that in titanium at 800 K [3,4], because the crystal structure of vanadium is bcc and that of titanium is hcp. Therefore, vanadium was considered to be a candidate for the gettering materials even though the affinity for nitrogen is not so high. The alloy of titanium and vanadium is considered to have these merits of a high affinity for nitrogen by titanium and large nitrogen diffusivity of vanadium at the same time. From these considerations, a V–Ti alloy was also chosen as one of the nitrogen gettering materials.

2. Experimental

The purity of titanium and vanadium was higher than 99.9%. Two types of alloys (V–5at.%Ti and V–10at.%Ti) were made from the same metals by a plasma jet-melting furnace. The shape of the nitrogen gettering

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[*] Corresponding author. Tel.: +81-3 5841 6970; fax: +81-3 5841 8625.

E-mail address: s-tanaka@q.t.u-tokyo.ac.jp (S. Tanaka).

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PII: S0022-3115(02)01125-X

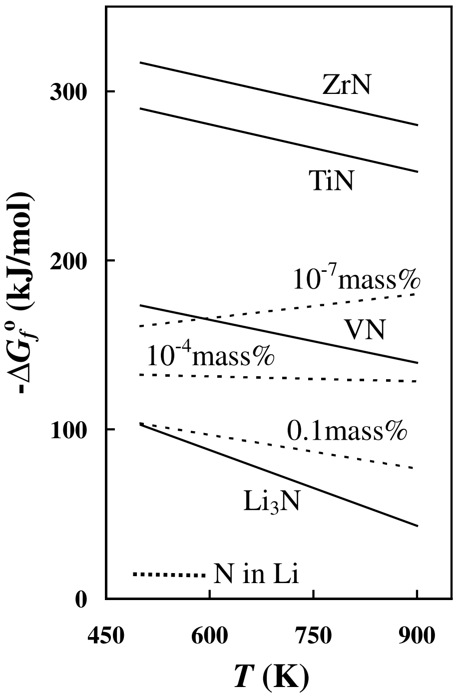

Fig. 1. Thermodynamics stability of nitrides.

metals was a plate. The size of the titanium and vanadium plates was $1 \times 10 \times 50$ mm^3 and that of the alloys $0.6 \times 10 \times 40$ mm^3. The mass of lithium was 12 or 25 g. The purity was higher than 99.9%. The concentration of the nitrogen impurity in the as-received lithium was about 10^{-2} or 5×10^{-3} mass%. In one experiment, in order to increase the nitrogen concentration in lithium, the Sieverts' method was used. The nitrogen concentration was increased to about 3.7×10^{-2} mass% by this method.

All loading operations of specimens into the stainless steel pot were carried out inside the glove box filled with high-purity argon gas. Lithium lump, nitrogen gettering materials, the molybdenum crucible with the inner size of 48 mm in diameter and 49 mm in height, the furnace for melting lithium, and the stainless steel pot were prepared in the glove box. In the molybdenum crucible within the furnace, lithium was melted at about 500 K, then gettering materials were immersed into the liquid lithium. The molybdenum crucible with gettering materials was loaded into the stainless steel pot. A lid made of vanadium or tantalum was put on the crucible. This lid was considered to be effective to prevent impurities from entering the crucible. During the test, high-purity argon gas was used to flow through the pot at the rate of 5 ml/min. This experimental apparatus is shown in Fig. 2. The experimental temperatures were 673, 773 and 823 K and the immersion periods were 0.4 Ms (5 days), 2.5 Ms (29 days) and 2.8 Ms (33 days), respectively. These parameters are shown in Table 1.

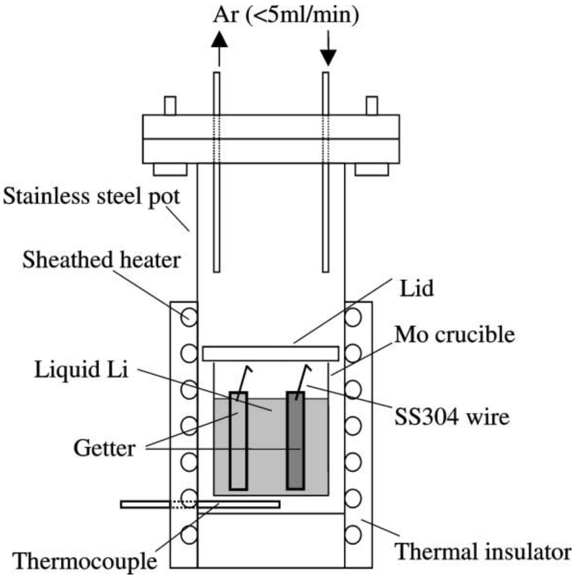

Fig. 2. Experimental apparatus.

Table 1
Experimental parameters

Temp. (K)	Time (Ms)	Getter	N in Li ($\times 10^{-4}$ mass%)
673	2.5	Ti & V	100
773	2.5	Ti & V	100
823	2.8	Ti & V	100
823	2.8	V–5at.%Ti	50
823	2.8	V–10at.%Ti	50
823	0.4	V–10at.%Ti	370

After the corrosion test, gettering materials were taken out from the liquid lithium in the glove box filled with argon gas. Lithium, adhered on the gettering material, was removed by reaction with methanol and water. After that, measurements of impurity concentrations and XRD (CuKα line) were performed on the gettering materials. The impurity concentration in the gettering materials was measured by a nitrogen/oxygen analyzer made by LECO Corporation. The result measured by this analyzer was the averaged value including the surface and the bulk of the specimen. The nitrogen concentration in liquid lithium was measured by the ammonia method, in which the nitrogen in lithium was converted to ammonia by the hydrogenation reaction with nascent hydrogen formed by reaction of lithium with water. The amount of the ammonia was measured by an ammonia sensor [5].

3. Results

3.1. Nitrogen concentration change and XRD analysis

3.1.1. Change of the nitrogen concentration and the mass in the gettering materials

The nitrogen concentration in gettering materials, that were immersed in liquid lithium during 2.5–2.8 Ms, were measured by a nitrogen/oxygen analyzer. Measured results are shown in Table 2. The nitrogen concentration in the titanium and vanadium plates tested at 673 and 773 K was found to be somewhat increased. The nitrogen concentration in titanium and the V–5at.%Ti and V–10at.%Ti alloys tested at 823 K was found to be increased. In spite of the lower initial nitrogen concentration in liquid lithium in the case of V–10at.%Ti alloy than that in the case of titanium, the increase of the nitrogen concentration in V–10at.%Ti alloy was larger than that in titanium.

In the gettering material immersed at 823 K for 2.8 Ms, the mass of vanadium was not changed, and that of titanium and the V–5at.%Ti and V–10at.%Ti alloys was increased as shown in Table 3. The results of the nitrogen/oxygen analyzer showed that the nitrogen concentrations in the titanium and the V–Ti alloy getters were increased in this experiment, and the oxygen concentrations in these materials were not changed after immersion. From the XRD results, impurities were not found on the surface of these samples. Therefore, the mass increase of titanium and the V–Ti alloy tested at 823 K was considered to be due to the uptake of nitrogen from liquid lithium.

The increase of the nitrogen concentration in the V–10at.%Ti alloy, which was calculated from the mass change, was larger than that measured by the nitrogen/oxygen analyzer. The increase of the averaged nitrogen concentration in the V–10at.%Ti alloy was 2×10^{-2} mass% by the nitrogen/oxygen analyzer. On the other hand, it was 5×10^{-2} mass% from the mass change, assuming that the mass increase was due to the uptake of nitrogen. In the other samples, results of the nitrogen/oxygen analyzer almost agreed with those evaluated from the mass change. In the analysis by the nitrogen/oxygen analyzer, part of the sample was analyzed. The overall sample was used in the mass measurement. In addition, in the process of the specimen preparation for the nitrogen/oxygen analyzer, a part of the specimen surface was presumably ground. Therefore, the reliability of results of the mass measurement was considered to be larger than that of the nitrogen/oxygen determinator.

Table 3
Mass change of the gettering materials. Measurement error: 0.02 mg

Getter	Tested at 673 K (mg)	Tested at 773 K (mg)	Tested at 823 K (mg)
V	− 0.79	+ 0.02	+ 0.04
Ti	+ 0.03	+ 0.03	+ 0.39
V–5at.%Ti alloy	–	–	+ 0.22
V–10at.%Ti alloy	–	–	+ 0.60

3.1.2. XRD results

On the surface of the titanium plate tested at 823 K for 2.8 Ms, titanium nitrides (TiN and Ti_2N) were found to be formed as shown in Fig. 3(b). Moreover, several XRD peaks of titanium were found to be widened to a lower angle side. This shows that the lattice spacing of titanium became larger, because nitrogen was dispersed in titanium by diffusion and formed a solid solution with titanium. It should be noted that an expansion was not found in all lattice directions but in some specific ones. When the surface of this titanium plate was polished by 2 μm in depth, these peaks of the titanium nitride and the broadening of the peaks disappeared as shown in Fig. 3(c).

On the surface of the V–10at.%Ti alloy that was immersed at 823 K for 2.8 Ms, a VN–TiN (nitride of titanium and vanadium) layer was found to be formed as shown in Fig. 4(b). In addition, extremely broad peaks of the V–Ti–N solid solution were also confirmed, just in the case of titanium. Fig. 4(c) shows, when the surface of this alloy was polished by 4 μm in depth, peaks of the VN–TiN layer disappeared and only the nitrogen solid solution was confirmed. When the surface was polished by 8 μm Fig. 4(d), shifted and broadened peaks disappeared almost and these peaks backed to sharp ones as shown in Fig. 4(a).

Table 2
Nitrogen concentration in the gettering materials

Getter	As-received ($\times 10^{-4}$ mass%)	Tested at 673 K ($\times 10^{-4}$ mass%)	Tested at 773 K ($\times 10^{-4}$ mass%)	Tested at 823 K ($\times 10^{-4}$ mass%)
V	113 ± 8	123 ± 8	133 ± 2	104 ± 34
Ti	57 ± 1	65 ± 4	103 ± 10	191 ± 4
V–5at.%Ti alloy	15 ± 10	–	–	160 ± 20
V–10at.%Ti alloy	30 ± 1	–	–	252 ± 5

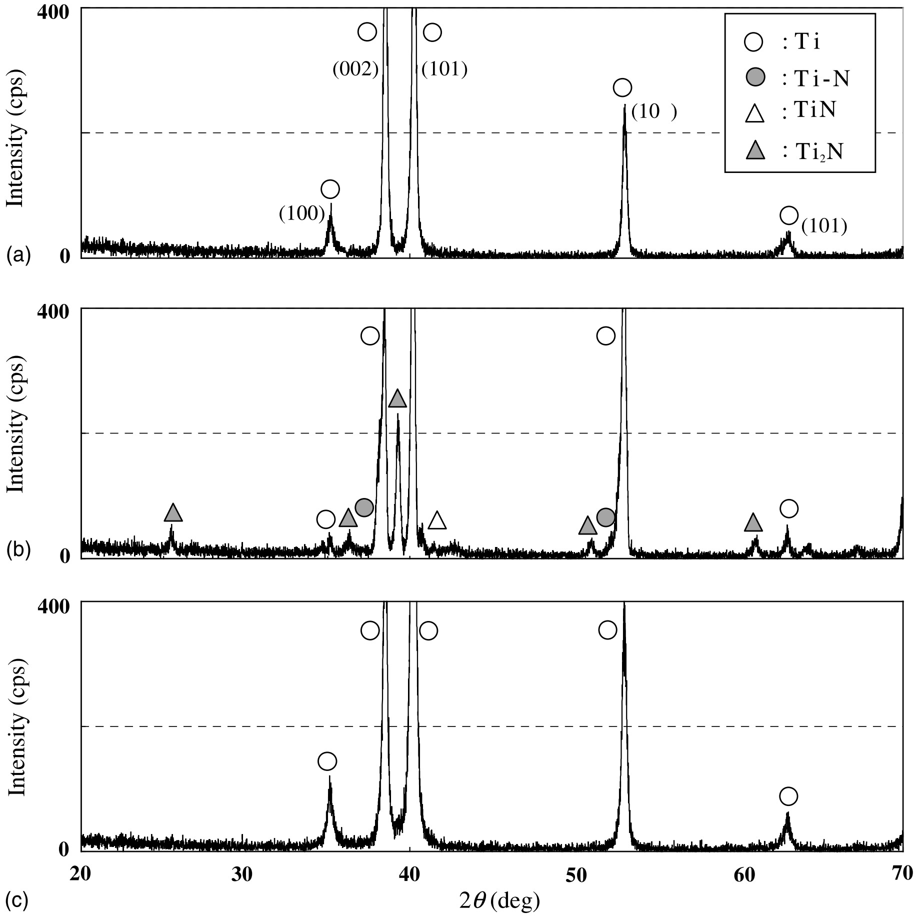

Fig. 3. XRD results of titanium plate, (a) as-received, (b) after immersion at 823 K, for 2.8 Ms, (c) after polished by 2 mm. Ti–N: nitrogen solid solution in titanium.

3.2. Decrease of nitrogen concentration in liquid lithium

In order to examine the nitrogen gettering rate of the V–10at.%Ti alloy, the following experiment was conducted. At the beginning, the nitrogen concentration in liquid lithium was increased to about 3.7×10^{-2} mass% by the Sieverts' method. The change of the nitrogen concentration in liquid lithium by gettering was measured by the ammonia method. Three V–10at.%Ti alloy plates ($0.6 \times 10 \times 40$ mm^3) were immersed in liquid lithium. The immersion temperature was 823 K and the total experimental period was 0.4 Ms. Using the square root of the immersion time of the V–Ti alloy, experiment results are shown in Fig. 5. The nitrogen concentration in liquid lithium was found to be decreased to about 2.2×10^{-2} mass% during 0.4 Ms. In this figure, the nitrogen concentration showed a linear relationship with the square root of time. From this, a diffusions process of nitrogen in the alloy was considered to be related with the nitrogen gettering.

4. Discussion

The nitrogen gettering effect of the V–10at.%Ti alloy was found to be larger than that of vanadium and titanium. As described before, the V–10at.%Ti alloy incorporated nitrogen up to about 8 μm in depth from the surface. From the XRD peak area in Fig. 4(b) and the X-ray penetration depth, the thickness of the VN–TiN layer was roughly estimated to be 0.1 μm [6]. The formation of this VN–TiN layer corresponded to the averaged nitrogen concentration increase in the overall alloy of about 7×10^{-3} mass%. On the other hand, the result of the mass change showed that the total increase of the nitrogen concentration in this alloy was about 5×10^{-2} mass%. Therefore the remaining nitrogen, which corresponds to the averaged concentration of 4.3×10^{-2} mass%, was considered to exist as a V–Ti–N solid solution in this alloy. Contrary to this result, titanium incorporated nitrogen up to 2 μm depth from the surface. From the XRD peak area in Fig. 3(b), the

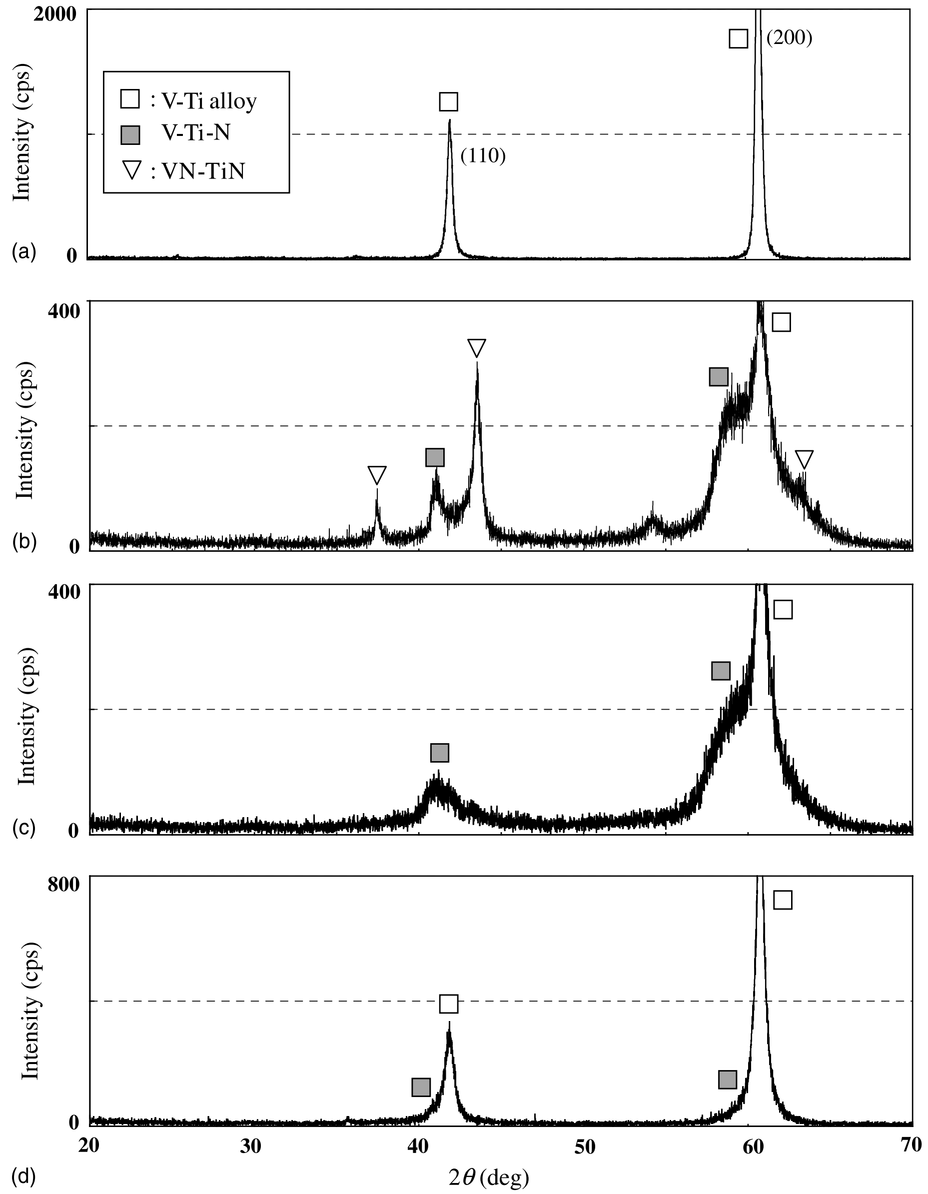

Fig. 4. XRD results of the V–10at.%Ti alloy, (a) as-received (annealing at 823 K, for 1.5 Ms), (b) after immersion at 823 K, for 2.8 Ms, (c) after polished by 4 mm, (d) after polished by 8 mm. V–Ti–N: nitrogen solid solution in the alloy, VN–TiN: nitride of titanium and vanadium.

nitrogen in titanium was considered to exist mainly as titanium nitride. The reason for this difference in the gettering effect was considered to be due to the diffusivity of nitrogen. As mentioned before, the nitrogen gettering was considered to be related to the diffusion of nitrogen in the gettering materials. The diffusion coefficient of nitrogen in titanium at 823 K is about 10^{-18} m^2/s [3], and that in vanadium is about 10^{-15} m^2/s [4]. In the case of titanium, nitrogen that was incorporated from liquid lithium scarcely diffused to the inside of the sample and the titanium nitride was considered to be formed at the surface. The diffusivity of nitrogen in the V–10at.%Ti alloy is considered to be in the same order as in pure vanadium and to be larger than that in titanium. Therefore the nitrogen at the surface of the alloy was considered to diffuse mainly to the inside and to form the solid solution.

At the second point, the difference between the gettering effect of the V–Ti alloy and that of vanadium will be discussed, considering the existence of nitrogen in the

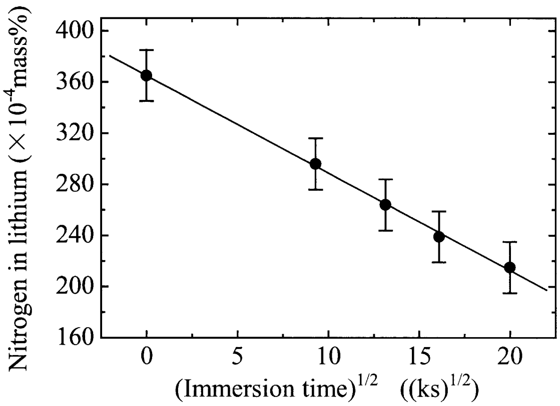

Fig. 5. Change of nitrogen concentration in lithium.

V–Ti alloy. Fig. 1 shows that titanium nitride is more stable than vanadium nitride. Titanium is also more attractive for nitrogen gettering than vanadium. In the case of the V–10at.%Ti alloy, the nitrogen concentration in the alloy was increased by about 5×10^{-2} mass%. However, from results of the nitrogen/oxygen analyzer and the mass change, the nitrogen concentration in the vanadium plates was found to be scarcely changed after the immersion at 823 K compared with the as-received sample. Therefore titanium that is a component of the V–Ti alloy was considered to play an important role in the nitrogen gettering. As mentioned before, the increase of the averaged nitrogen concentration in the V–10at.%Ti alloy by the formation of the V–Ti–N solid solution was evaluated to be 4.3×10^{-2} mass%. Fig. 4(d) shows that the penetration depth of nitrogen in the alloy was about 8 μm. If nitrogen, which corresponds to the averaged nitrogen concentration of 4.3×10^{-2} mass%, was uniformly distributed up to 8 μm in depth, the averaged nitrogen concentration in the solid solution would be about 1.6 mass%. This value is considered to exceed 0.7–0.8 mass% that is the solubility limit of nitrogen in vanadium at 823 K [7]. Titanium atoms in the alloy were considered to be dispersed randomly, because the XRD peaks except those of the V–Ti alloy were not confirmed on the surface of the as-received specimen. As described before, the V–Ti–N solid solution and the VN–TiN layer were confirmed on the surface and the inside of the alloy after immersion. Therefore nitrogen atoms in the solid solution were considered not to form titanium nitride but to be trapped near titanium atoms, because of the high affinity for nitrogen by titanium. This nitrogen trapping effect by titanium atoms in the alloy is considered as a reason for the high nitrogen concentration in the solid solution.

5. Conclusions

The nitrogen concentration in liquid lithium was controlled by the method of hot trapping at 673–823 K for 0.4–2.8 Ms. From these experiments, the following conclusions were derived:

- Titanium and V–Ti alloys were effective for controlling the nitrogen concentration in liquid lithium.
- Especially the V–10at.%Ti alloy has a large nitrogen gettering effect, compared with other gettering materials.
- Nitrogen atoms in the V–10at.%Ti alloy formed mainly the solid solution.

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