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Measurement of hydrogen absorption in flowing liquid lithium in the flowing lithium retention experiment (FLIRE)

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Abstract

Flowing metal plasma facing components (PFCs) have the ability to withstand the extreme conditions of future tokamaks. The FLIRE facility at the University of Illinois measures the retention properties, both for helium (ash pumping) and hydrogen (recycling regime, tritium inventory), of candidate liquid PFCs, such as lithium. Results of hydrogen absorption measurements in flowing liquid lithium are presented. Absorption experiments with a flowing lithium stream passing through a low-pressure neutral deuterium gas show 0.1–0.2% D concentration retained long-term in the sample. A similar experiment with a high deuterium pressure of approximately 1 Torr shows the same long-term deuterium retention. These values indicate that the deuterium absorption rate is limited by the dissociation rate of the molecular deuterium gas on the Li surface.
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1. Introduction

The use of flowing liquid metals for plasma facing components (PFCs) would allow fusion reactor designs which produce a higher heat flux to the divertor, faster recovery after an off-normal event such as a disruption, and give a higher thermodynamic efficiency. The disadvantages of a flowing liquid PFC include its interaction with the edge plasma. If too much fuel is absorbed, replenishing the plasma at a fast enough rate may be impossible. Some authors have suggested that all implanted hydrogen stays within the lithium [1]; making the liquid PFC a no recycling surface, which would result suppression of the temperature pedestal between the plasma core and the edge of the device [2]. While this would enable much hotter edge plasma and therefore a smaller major radius for the same total fusion power, rapid recovery of tritium fuel would be necessary. The issue of hydrogen transport by flowing liquid PFCs is vitally important for fusion reactor design due to its impact on fuel recycling, operating regime [3], tritium trapping and subsequent tritium recovery. Extensive studies have been conducted for most of the typical solid PFC materials, such as carbon, beryllium and tungsten [4], but very little data exists for liquid PFC materials such as lithium, tin or FLIBE.

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The solubility of hydrogen in lithium may lead to the formation of a hydrogen solution in lithium or formation of a hydride phase. The flowing liquid retention experiment (FLIRE) [5] allows the exposure of flowing liquid lithium to both neutral hydrogen/deuterium gas as well as a hydrogen/deuterium ion beam to study the absorption of hydrogen in the flow.

Before studying the absorption with ion beam implantation, the uptake of hydrogen from the background deuterium gas must be studied. To do this in FLIRE, a stream of molten lithium is flowed down ramps in the presence of a low-pressure deuterium gas. Fig. 1(a) shows a diagram of the upper chamber in FLIRE where the flowing stream is exposed, and Fig. 1(b) shows a diagram of the ramps in the upper chamber. At the bottom of the ramps, the flow(s) drains through a small (1 cm × 0.3 cm rectangular) orifice into a separate lower chamber, creating a vacuum seal that isolates gas in the upper chamber from the lower chamber.

Some of the deuterium promptly diffuses out of the stream in the lower chamber, where its partial pressure can be measured with a magnetic sector residual gas analyzer (MS-RGA) that is very sensitive to low-mass species. Long-term trapping of deuterium also occurs and is particularly relevant to tritium inventory control. The long-term hydrogen concentration in the lithium equilibrates for a given temperature and gas-phase hydrogen partial pressure.

The method used to determine the amount of long-term trapped hydrogen is thermal desorption spectroscopy (TDS). This method consists of heating the liquid lithium sample in a linear fashion while maintaining vacuum on top of the liquid and measuring the partial pressure of deuterium as the sample is heated. The neutral-gas exposure experiments discussed here investigate to what degree neutral deuterium molecular gas is absorbed by the flowing lithium stream.

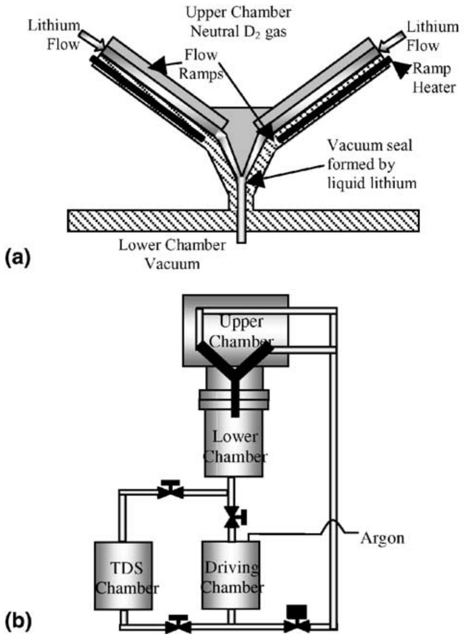

Fig. 1. (a) Diagram of FLIRE systems. (b) Diagram of upper chamber internal ramps.

2. Flire and TDS experimental setup

Before reaching the TDS chamber, approximately 400 g of lithium flows through the upper chamber, where it is exposed to deuterium gas at a specified pressure. Two neutral-gas exposure runs are discussed: (1) at 7.5×10^{-5} Torr at an average speed of 44 cm/s for a duration of 30 s and (2) at 1 Torr and an average speed of 22 cm/s for a duration of 60 s. Molecular-deuterium partial pressures in a tokamak edge are typically between 10^{-4}–10^{-5} Torr, which is similar to the low-end pressure of the experiments discussed here. However, the absorption mechanisms of deuterium atoms and ions (primary constituents of divertor plasma) is different than that of molecular deuterium gas, and measuring the absorption of deuterium atoms and ions in FLIRE will require a plasma ion source that is intense enough to cause a measurable difference in the absorbed deuterium. In the lower chamber, the prompt release of the absorbed deuterium is measured by the MS-RGA. The upper chamber flow path and the lower chamber are maintained at a temperature of 230 °C.

After measuring the prompt release in the lower chamber for 5 min, the lithium is transferred to the TDS chamber which is maintained at 250 °C. A Balzers TPH-062 turbomolecular pump with a pumping speed of 50 l/s maintains vacuum in the TDS chamber. The MS-RGA is shared between the TDS chamber and the lower chamber; gate valves on either side of the MS-RGA allow its dual use for both chambers. A 4-kW Thermcraft cylindrical clamp furnace, controlled by a fuzzy logic PID controller and a solid-state relay, heats the TDS chamber. Thermocouples monitor the temperature at different points of the chamber during the experiment. The temperature program used for the TDS studies in FLIRE is a linear ramp of 2 °C/min, starting at 250 °C and finishing at 600 °C. The batch soaks at 600 °C for one hour after the temperature ramp to remove as much hydrogen as possible. After the soaking time is over, heating is stopped, and the lithium cools to 250 °C.

3. Hydrogen data analysis

Analyzing the raw partial pressure data from the TDS experiment requires a careful analysis of the lith-

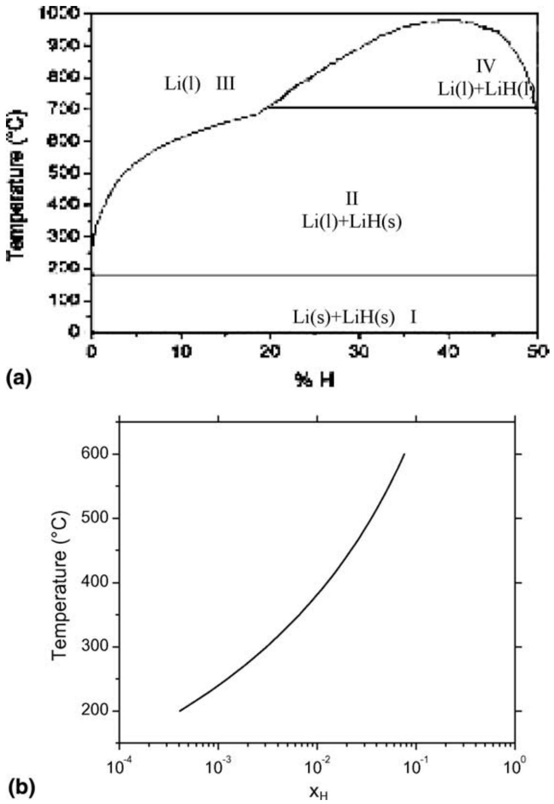

Fig. 2. (a) The lithium–hydrogen phase diagram (from [7]). (b) The low-concentration end of the Li–LiH phase diagram.

ium/hydrogen phase diagram shown in Fig. 2. Several important regions can be identified in Fig. 2(a) (from [7]). Region I is bounded by a line at approximately 180 °C (eutectic temperature): the lithium phase changes from solid to liquid. In Region II, solid-phase lithium hydride coexists with liquid lithium. A critical concentration (~19%) can be identified, below which a transition is made to Region III, comprised of the liquid lithium phase only. Since the deuterium concentration expected in FLIRE is very low, detailed information about the miscibility gap for low hydrogen concentrations is desired. Between 200 and 600 °C, the miscibility gap curve is well approximated by the following expression [6], plotted in Fig. 2(b):

$$\ln(x_{\mathrm{LiH}}) = 3.679 - \frac{5472}{T}. \tag{1}$$

The fractions of hydrogen and lithium hydride are related by

$$x_{\mathrm{H}} = \frac{x_{\mathrm{LiH}}}{1 + x_{\mathrm{LiH}}}. \tag{2}$$

At low pressures (and hence low concentrations), the lithium–hydrogen equilibrium can be described adequately by Sievert's law [8]:

$$n_{\mathrm{s}} = K_{\mathrm{s}} P^{1/2}. \tag{3}$$

The following expression can been used to calculate solubility of hydrogen isotopes in lithium [9]:

$$K_{\mathrm{s}} = 1.2 \times 10^{-5} \exp\left(\frac{44\,400}{RT}\right), \tag{4}$$

K_s has units of at%/Pa$^{1/2}$, T is in K and R in J/mol K. The expression above is a fit to data for temperatures between 723 and 923 K (450–650 °C). During exposure in FLIRE, the lithium temperature is typically 230 °C. However, the extrapolation of Eq. (4) should allow a good estimate for the concentration at the surface during exposure assuming that Sievert's law still holds.

In the case of FLIRE, the operating temperature is typically between 230 and 300 °C. This means that the minimum concentration required to form the hydride phase is between 0.1% and 0.3%. Hence, the pressure required to precipitate would be between 7×10^{-8} and 4×10^{-6} Torr. The ion source in FLIRE requires a neutral gas pressure on the order of 10^{-5} Torr to produce the ion beam. This means that the backfilling pressure in the chamber will induce hydride formation in the lithium flow if equilibrium is reached, since it is above the pressure threshold required to enter the two phase region.

4. Results

The first experiment in the TDS chamber was performed on unexposed lithium to verify its purity. TDS pressure traces for the different species are shown in Fig. 3(a). Fig. 3(b) shows background traces taken a day before with an empty chamber. A strong hydrogen signal is observed in both cases at temperatures over 400 °C. This is caused by desorbtion from steel [6] and other colder surfaces where Li condensed from previous experiments. Further supporting evidence for this is that there is no increase in the lithium signal, despite a much higher vapor pressure at elevated temperatures (~100 mTorr at 600 °C [7,10]).

In the second experiment, the absorption of deuterium by flowing lithium was measured by flowing lithium through the upper chamber with a background gas pressure of 7.5×10^{-5} Torr. At the moment of transferring Li (5 min into the scan), from the lower chamber (at 230 °C) to the TDS chamber (at 250 °C), a weak release of hydrogen and deuterium appears, as shown in Fig. 4. This indicates that very small amounts of deuterium were trapped during the exposure and released when the temperature was raised in a step-wise manner.

At 230 °C, the equilibrium concentration is 0.1%. At 250 °C it is 0.2%. The fact that D was observed upon raising the temperature implies that the fraction of LiH in the sample was greater than 0.1% and less than

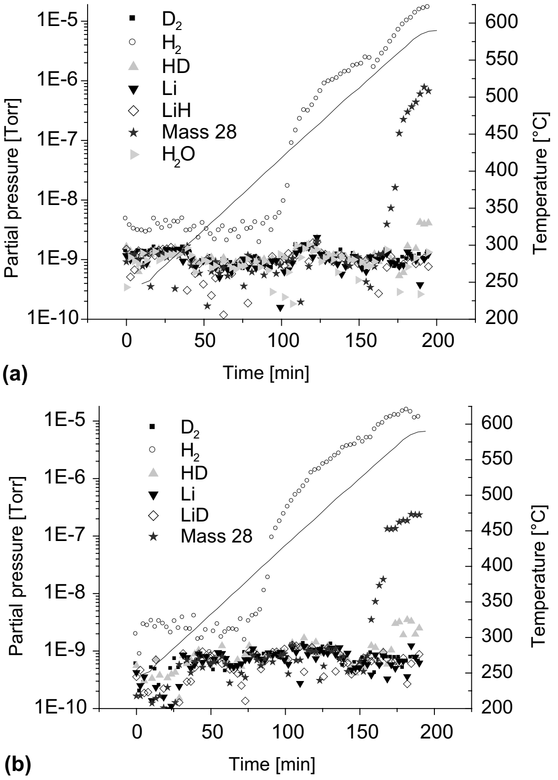

Fig. 3. (a) TDS spectrum with lithium in TDS chamber but no exposure to deuterium. (b) TDS spectrum with no lithium in chamber.

0.2% prior to the temperature step. The uncertainty associated with this range is due primarily to the step change in temperature from 230 °C to 250 °C, and better matching of these temperatures could further refine this range. This deuterium concentration is close to the deuterium concentration expected from exposure to ~10^{-6} Torr of deuterium, as calculated above; however, the actual background gas pressure was 7.5×10^{-5} Torr. This implies that the deuterium absorption rate may be too slow for the surface concentration to equilibrate within the residence time of the lithium in the upper chamber. However, this absorption rate is still much greater than the injection rate provided by FLIRE's ion gun (~10^{12} ions/s). Hence, a more intense ion-implantation source is needed to measure retention of atomic/implanted deuterium. Future experiments will address this by using a higher-intensity plasma ion source.

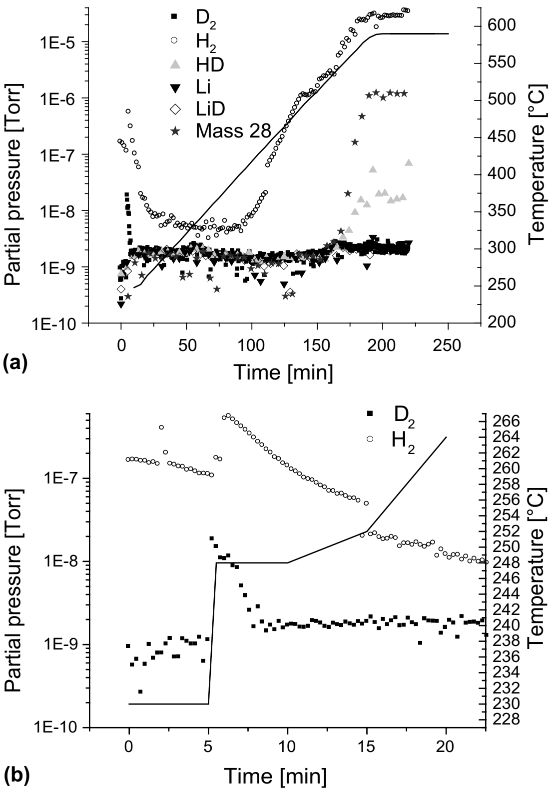

Fig. 4. (a) TDS spectrum of lithium exposed to neutral deuterium gas without deuterium beam. (b) Close-up of TDS spectrum of lithium exposed to neutral deuterium gas only (no beam).

Quantifying the release is difficult due to the presence of both hydrogen and deuterium in the sample. However, a wetted wall tower model [11], which assumes a saturated hydrogen concentration at the liquid surface (50% atomic fraction of hydrogen) and diffusion into the bulk, indicates that an average deuterium concentration of ~3% is expected for typical FLIRE conditions. Clearly, the model overestimates the amount trapped, which is not surprising since it assumes all H in the gas is in the form of atomic H and not molecular H_2. Comparing the predicted 3% concentration to the measured 0.1–0.2% concentration, we see that the degree of surface dissociation of H is at most 0.03–0.06, assuming a linear relation between surface dissociation and absorption.

To verify this conclusion, the residual lithium in the TDS chamber was cleaned, reinstalled and baked out up to 600 °C, and the dry-run measurement was repeated. Following this experiment, the lithium charge was transferred to the TDS chamber after exposure to approximately 1 Torr of deuterium. The purpose of this experiment was to examine the influence of deuterium pressure in the upper chamber on the deuterium concentration in the lithium. Hence, the same lithium charge was also exposed to 1 Torr of deuterium in the upper chamber before being transferred (after prompt release) to the TDS chamber. Despite several orders of magnitude higher pressure, the deuterium pressure trace still exhibited a peak between 230 and 250 °C, hence the absorbed deuterium concentration was still between 0.1% and 0.2%.

The results from these TDS experiments demonstrate that the TDS system in FLIRE is capable of obtaining deuterium absorption measurements in flowing lithium. The release of deuterium seems to be very sensitive to impurities present in the chamber, hence a very clean environment is necessary to perform the experiment. The presence of residual hydrogen in the vacuum system is especially harmful to the analysis, since it contributes to the hydrogen content along with the deuterium to the establishment of an equilibrium state. Compared to the amount of deuterium that can be implanted by the existing ion gun, deuterium absorption directly from the background gas dominates. A higher-ion flux is needed to examine the effects of plasma-implanted deuterium. Plans for a plasma source to interact with the flowing lithium are in progress.

5. Conclusions

The absorption of deuterium in a flowing lithium stream was measured in FLIRE for deuterium gas pressures of 7.5×10^{-5} Torr and 1 Torr using TDS with temperatures between 250 °C and 600 °C. Both of these experiments resulted in a deuterium concentration of ~0.1–0.2%, indicating that the absorption rate is limited by surface dissociation of the molecular deuterium.

No lithium vapor was observed, indicating that lithium vapor condenses on cooler surfaces between the lithium charge and the RGA. This condensed layer causes some absorption and re-release of impurities during the TDS run, but desorption from remote condensed surfaces occurs at sufficiently high temperatures in the TDS tank itself to avoid interference with the measurement of low concentrations of deuterium.

Experimental results were compared to a wetted wall tower theoretical model. The model assumed that the surface concentration of absorbed deuterium was saturated at 50%, but over-predicted the average concentration by more than an order of magnitude (3% as opposed to 0.2%). This shows that the surface of the flowing liquid is not quickly saturated with deuterium, relative to the exposure times in FLIRE (~0.5 s), which further indicates that dissociation of the molecular deuterium limits its absorption rate. Measurement of absorption and retention of atomic/ionic deuterium will require a more intense ion source than FLIRE's existing ion gun; a plasma ion source is being built to carry out these measurements.

Acknowledgments

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