Wetting properties of liquid lithium on lithium compounds

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HIGHLIGHTS

- Contact angles of liquid lithium and Li_3N, Li_2O, Li_2CO_3 were measured.
- Liquid lithium wets lithium compounds at relatively low temperatures: Li_3N at 257 °C, Li_2O at 259 °C, Li_2CO_3 at 323 °C.
- Li wets Li_2O and Li_3N better than previously measured fusion-relevant materials (W, Mo, Ta, TZM, stainless steel).
- Li wets Li_2CO_3 better than most previously measured fusion-relevant materials (W, Mo, Ta).

ARTICLE INFO

ABSTRACT

Liquid metal plasma facing components (LMPFC) have shown a potential to supplant solid plasma facing components materials in the high heat flux regions of magnetic confinement fusion reactors due to the reduction or elimination of concerns over melting, wall damage, and erosion. To design a workable LMPFC, one must understand how liquid metal interacts with solid underlying structures. Wetting is an important factor in such interaction, several designs of LMPFC require liquid metal to wet the underlying solid structures. The wetting of lithium compounds (lithium nitride, oxide, and carbonate) by 200 °C liquid lithium at various surface temperature from 230 to 330 °C was studied by means of contact angle measurements. Wetting temperatures, defined as the temperature above which the contact angle is less than 90°, were measured. The wetting temperature was 257 °C for nitride, 259 °C for oxide, and 323 °C for carbonate. Surface tensions of solid lithium compounds were calculated from the contact angle measurements.

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1. Introduction

Liquid lithium is considered for use in plasma-facing components (PFC) of fusion devices for several reasons. Lithium has a low atomic number, a low melting point of only 179 °C, a high boiling point, and high surface tension. Liquid surfaces allow the avoidance of numerous problems that solid PFCs face due to intense heat loads observed in fusion installations. Lithium has also been shown to positively affect fusion plasmas, leading to a decrease in recycling and increase of the confinement time [1–5].

There are a number of PFC systems of different designs that use liquid lithium, such as capillary porous systems (CPS) [5–7] and liquid metal infused trench (LIMIT) systems [8,9]. Liquid lithium in these schemes is supported by a solid material, and wetting of the substrate by lithium is an important criterion required for many of the proposed designs to work. The CPS design is reliant on capillary forces to function and thus requires lithium to wet the CPS material. The LIMIT design relies on lithium flow in trenches, therefore lithium must wet the surfaces of channels. If lithium is used in upside-down or vertical elements, it must also wet their surfaces.

Lithium's ability to wet typical fusion-relevant materials, such as tungsten, molybdenum, TZM, stainless steel, and others has been studied. Lithium is very chemically active, and it reacts with all atmospheric gases and hydrogen, producing solid compounds with high melting temperatures [10–13]. It's impossible to guarantee that during operation, or in shutdown phase, when an installation is vented for maintenance purposes, such as to change diagnos-
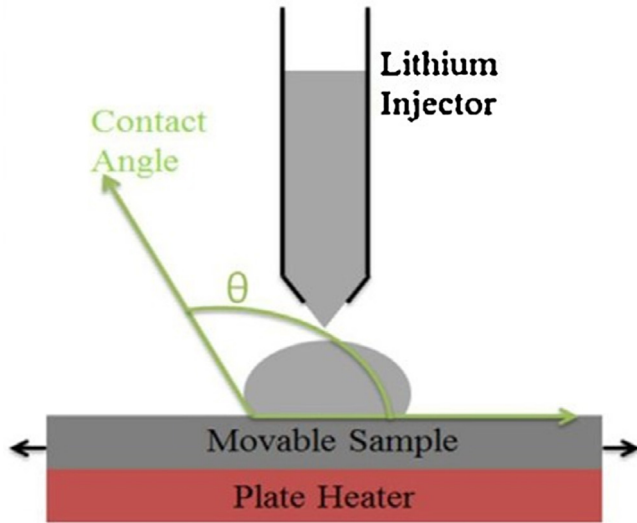
Fig. 1. Principal experimental scheme. Lithium droplets kept at a constant temperature are deposited onto a heated movable surface using mechanical lithium injector.
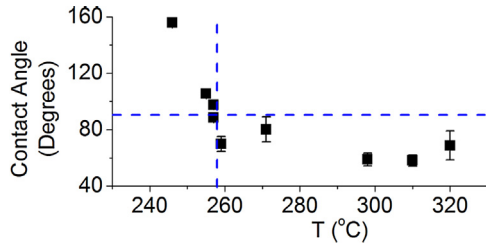

Fig. 2. Contact angles of 200 °C lithium drop on lithium nitride. Blue dashed line indicates wetting point temperature. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
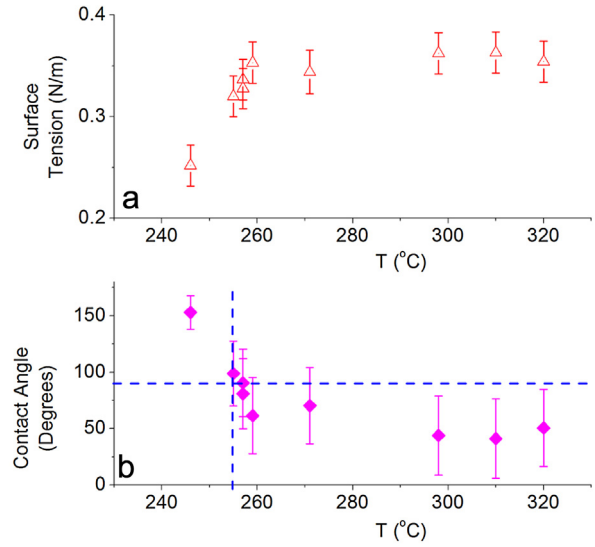

Fig. 3. Temperature dependences calculated from experimental contact angle measurements (Fig. 1): (a) surface tension of lithium nitride at different temperatures, (b) contact angles of lithium on lithium nitride assuming that the temperature of lithium and lithium nitride are the same; blue dashed line indicates wetting temperature for this case. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
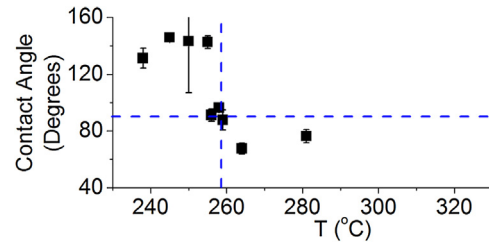

Fig. 4. Contact angles of 200 °C lithium drop on lithium oxide. Blue dashed line indicates wetting temperature. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

tics, lithium won't come in contact with atmospheric air. It's also possible that it'll form compounds with residual gas components. Therefore, it is important to know how lithium wets the surfaces of solid lithium compounds.

In this work, wetting of solid lithium compounds formed during interaction with primary atmospheric gases (lithium nitride, lithium oxide and lithium carbonate) by liquid lithium was studied, and wetting temperatures were determined. The dependence of the surface tension of lithium nitride, oxide and carbonate on temperature was also calculated. Contact angles and wetting temperatures were estimated for the case that the temperature of the lithium and the substrate are equal.

2. Basics

Wetting of flat solid surfaces is described by Young's equation

$$\gamma_S = \gamma_{SL} + \gamma_L \cos\theta \tag{1}$$

where γ_S, γ_L, are surface tensions (energies) of the solid being wetted and the wetting liquid respectively, γ_{SL} is the surface tension at the interface between the solid and the liquid, and θ is the contact angle. Liquid is considered to wet the solid surface if $\theta < 90°$. It can be shown [14,15] that γ_{SL} is a function of γ_S, γ_L, and can be empirically described as

$$\gamma_{SL} = \gamma_S + \gamma_L - 2\sqrt{\gamma_S\gamma_L}e^{-\beta(\gamma_S-\gamma_L)^2} \tag{2}$$

where $\beta = 123.4\left(m/N\right)^2$ is an empirical constant. When combined with Young's Eq. (1), it results in the equation

$$\cos\theta = -1 + 2\sqrt{\frac{\gamma_S}{\gamma_L}}e^{-\beta(\gamma_S-\gamma_L)^2} \tag{3}$$

that can be used to obtain γ_S if values of γ_L and θ are known.

Both γ_S and γ_L depend on the temperature. For a given liquid temperature, wetting is possible above a certain temperature of the solid surface, called the wetting temperature. Dependence of the surface tension of liquid lithium on the temperature is described in several literature sources (e.g. [16,17]), though there is no good agreement between them. In this work we use the following equation from Ref. [17].

$$\gamma_L\left[\frac{N}{m}\right] = 0.43898 - 1.844 \cdot 10^{-5}T\,[K] - 1.3220 \cdot 10^{-7}T^2$$
$$+ 3.744 \cdot 10^{-11}T^3 \tag{4}$$

3. Experimental

Experiments were performed using the MCATS installation as in Ref. [18]. The experimental scheme is shown in Fig. 1. As Li is chemically active, vacuum conditions were improved, and residual gas pressure was reduced to 4×10^{-5} Pa. The gas-backed lithium
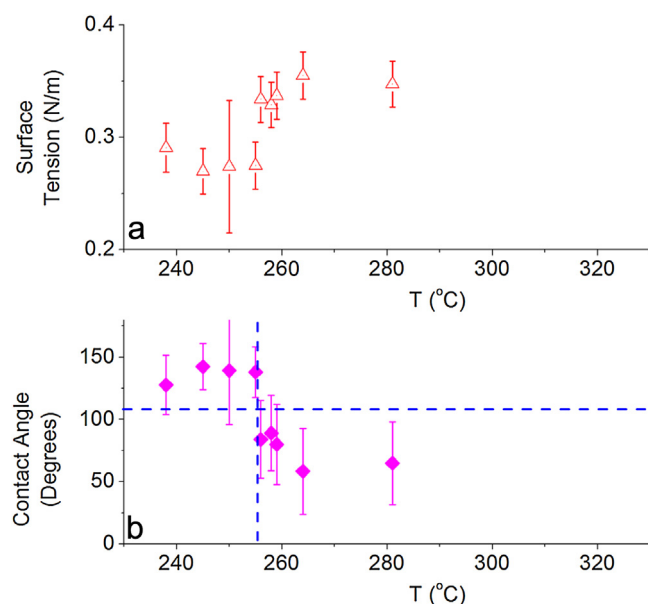
Fig. 5. Calculated data based on the experimental contact angle measurements of lithium on lithium oxide: (a) surface tension of lithium oxide at different temperatures, (b) contact angles of lithium on lithium oxide assuming that the temperature of lithium and lithium oxide are the same; blue dashed line indicates wetting temperature for this case. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
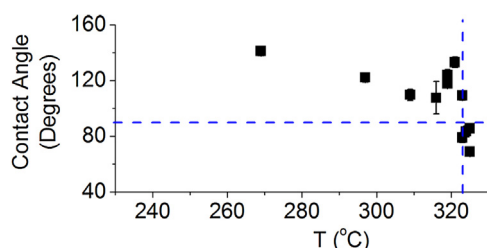

Fig. 6. Contact angles of 200 °C lithium drop on lithium carbonate. Blue dashed line indicates wetting point. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

injector was replaced with a mechanical one, utilizing a ceramic plunger, which gives more precise control over the droplet size.

Lithium compounds, on which droplets were deposited, were produced in the following way. First, lithium was evaporated on a movable stainless steel plate (movable sample shown in Fig. 1) about 10 cm wide, which had previously been cleaned in water, acetone and alcohol. The total thickness of evaporated lithium layer was about 10 μm. After the Li coating was created, reactive gases were introduced – either pure nitrogen for production of nitride or pure oxygen for production of oxide – to pressures of about 10^4 Pa. The purity of both nitrogen and oxygen was (99.999%). The lithium coating was left to react with the gases at room temperature for several hours, and then it was gradually heated to about 200 °C to finish the reaction if it had not yet concluded To produce lithium carbonate, the coating was exposed to atmospheric air at room temperature overnight.

The compositions of compounds produced were analyzed by XPS using control samples produced in similar conditions.

The movable sample and its coating were heated using a contact ceramic heater, and its temperature was monitored using a K-type thermocouple. The surface temperature was controlled in the interval from 200 to 350 °C, and the droplet temperature was about 200 °C in all experiments at the time when it was dropped from the injector. The mean diameter of the drop was about 1 cm. After
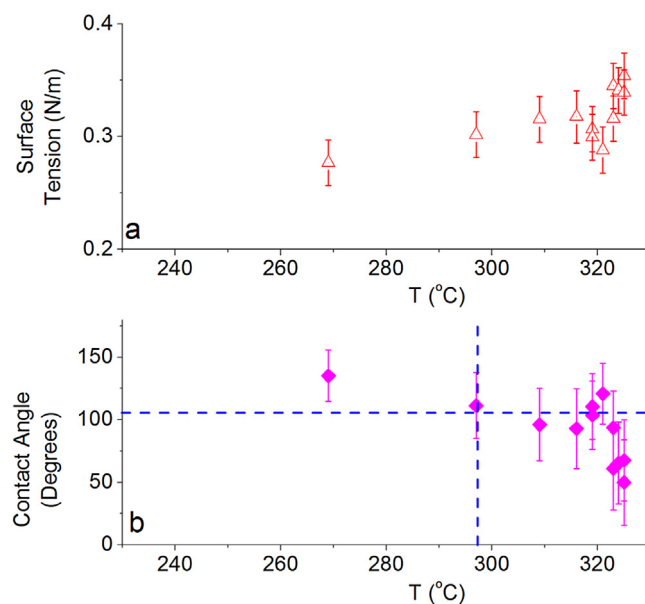

Fig. 7. Calculated data based on the experimental contact angle measurements of lithium on lithium carbonate: (a) surface tension of lithium carbonate at different temperatures, (b) contact angles of lithium on lithium carbonate assuming that the temperature of lithium and lithium carbonate are the same; blue dashed line indicates wetting temperature for this case. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

each droplet was deposited, the surface was moved to a side, the temperature changed, and a new droplet was deposited to observe wetting at a different surface temperature.

Each droplet was photographed from several angles immediately after the landing to minimize the effects introduced by the droplet heating up from the contact with the hotter surface. The photos were analyzed using the Dropshape plugin for the ImageJ software package [19]. Error margins were calculated based on the scatter of observed contact angle at different photos with 95% confidence.

4. Results

4.1. Lithium nitride

The chemical reaction that likely took place during nitriding was $6Li + N_2 = 2Li_3N$. Its rate was non-linear: no changes in the Li film were visually observed during the first hour, but then it changed color from metallic to dark red within the span of several minutes. Finally, the obtained compound was dark red in color, indicative of a nitride. Due to technical problems it wasn't possible to obtain XPS data for this compound, so no direct verification that the produced compound was Li_3N is available. However, because the only compound that can be reasonably expected to appear in Li reaction with dry N2 and has dark red color is Li_3N, it's reasonable to assume that the produced compound was, in fact, Li_3N.

The contact angles of the Li drop (200 °C) on the lithium nitride surface at different surface temperatures are shown in Fig. 2. It was noted that the contact angle didn't change significantly with time, despite the presumed change in droplet's temperature. The same locking effect was observed in the previous work [18], and is attributed to fresh liquid lithium oxidation or hydroxylation. The wetting temperature is estimated to be (257 ± 1) °C.

Based on the contact angle measurements, and the liquid lithium's surface tension at 200 °C calculated by Formula (4), the temperature dependence of the surface tension of lithium nitride
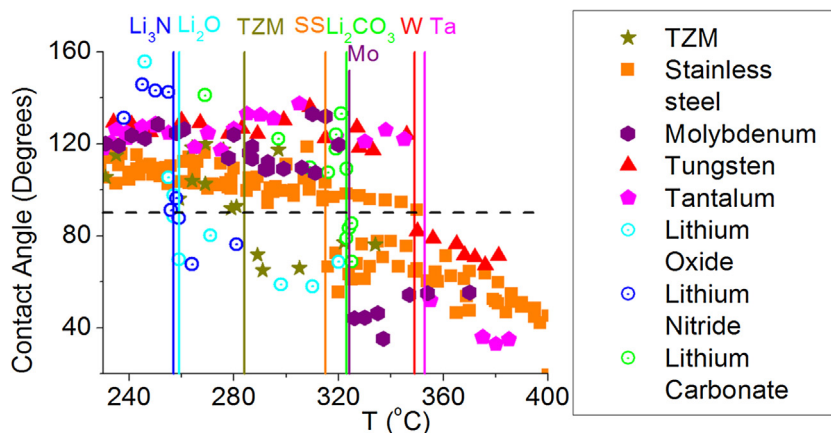
Fig. 8. Experimentally measured contact angles of lithium on various materials: tungsten, stainless steel, tantalum, TZM, molybdenum, lithium oxide, lithium nitride, and lithium carbonate.

was estimated from Eq. (3) (Fig. 3a). Surface tension increased from 0.25 N/m at 240 °C up to about 0.36 N/m at 320 °C.

Then, using the Eqs. (3) and (4) again, contact angles were estimated for the case where the temperatures of liquid lithium and lithium nitride are the same; these results are shown in Fig. 3b. The contact angles in Fig. 3 follow about the same temperature dependence as those in Fig. 2 but are systematically slightly lower, as wetting by hotter liquid lithium must be better. The estimated wetting temperature in this situation was 255 °C.

4.2. Lithium oxide

Lithium oxide was produced presumably due to the reaction $2Li + O_2 = Li_2O$. No color change was observed during slow heating of the sample to 240 °C when it was kept in oxygen. Also, no melting was observed, indicating that the product is a solid compound with a relatively high melting point. Additionally, no signs of combustion were observed, either visually or from abnormal temperature increase. The test samples were studied by XPS indicating that oxide Li_2O was produced.

The contact angles of a lithium drop (200 °C) on the surface of lithium oxide kept at various temperatures are shown in Fig. 4. The wetting temperature for lithium oxide was (259 ± 1) °C, almost the same as that for lithium nitride.

The surface tension of lithium oxide at different temperatures is shown in Fig. 5a and b demonstrates the contact angles recalculated for the case where the temperature of the liquid lithium drop is the same as that of the lithium nitride substrate. The wetting temperature in this case is about 256 °C. One must mention that the surface tension and contact angles of lithium oxide are close to those of lithium nitride.

4.3. Lithium carbonate

Lithium carbonate was a final product of a multi-reaction chain between lithium and atmospheric gases, including water vapor. Lithium reacted with O_2, N_2, and H_2O, forming Li_2O, Li_3N and LiOH respectively. Then Li_2O and Li_3N further reacted with water vapor forming LiOH. Finally LiOH reacted with CO_2, forming Li_2CO_3. After twelve hours in air, noticeable dark spots on the surface were still visible, indicating that the reaction had not been completely finished yet, and the film still contained nitrides and oxides besides carbonate. XPS measurements performed on the areas where the reaction had already been finished verified formation of carbonate.

The contact angles of 200 °C liquid lithium on a lithium carbonate surface at different surface temperatures are shown in Fig. 6. The

wetting temperature is (323 ± 1) °C, which is remarkably higher than for nitrides and oxides. The estimated surface tension of carbonate (Fig. 7a) was less than that for nitrides and oxides. Wetting temperature estimated for thermal equilibrium between the Li drop and Li_2CO_3 surface (Fig. 7b) was about 300 °C.

4.4. Comparison with fusion relevant materials

Obtained contact angles were compared to those known for several fusion-relevant materials [18], such as stainless steel, TZM, molybdenum, and tungsten (Fig. 8). It was observed that the wetting temperature of Li_3N and Li_2O is less than those for metals mentioned, while the wetting temperature of Li_2CO_3 is in the middle of the range of values fir these metals. Out of all metals analyzed, only argon-plasma cleaned molybdenum and TZM have lower wetting points than lithium oxide and nitride.

5. Conclusions

Wetting of lithium compounds by liquid lithium was studied at various temperatures. If a Li drop was kept at 200 °C, and the temperature of the substrate increased, the wetting temperatures of Li_3N, Li_2O, and Li_2CO_3 were found to be (257 ± 1) °C, (259 ± 1) °C, and (323 ± 1) °C, respectively.

Surface tensions of Li_3N, Li_2O, and Li_2CO_3 were determined at various temperatures from the contact angle measurements. Using the data obtained, contact angles were calculated for the case where the temperatures of the lithium drop and the substrates are equal.

It was observed that lithium wets solid Li_3N and Li_2O compounds at generally lower temperatures than it wets fusion-relevant metals, while the wetting temperature of Li_2CO_3 is in the middle of values typical for these metals. Out of all metals analyzed, only stainless steel, and argon-plasma cleaned molybdenum and TZM have lower wetting points than Li_2CO_3. This indicates that presence of some lithium compound contaminants on the surfaces of liquid lithium PFCs should not significantly hinder lithium ability to wet them and may even promote wetting.

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