

Wetting properties of liquid lithium on select fusion relevant surfaces



P. Fiflis*, A. Press, W. Xu, D. Andruczyk, D. Curreli, D.N. Ruzic

Center for Plasma Material Interactions, Department of Nuclear, Plasma and Radiological Engineering, University Illinois at Urbana-Champaign, Urbana, IL 61801, USA

HIGHLIGHTS

- Liquid lithium wets W, Mo, 316 SS, Ta, and TZM at sufficiently high temperatures.
- Wetting temperatures between 284 °C (TZM) and 353 °C (Ta) for untreated materials.
- Argon GDC and lithium evaporation treatments reduce wetting temperature.

ARTICLE INFO

Article history:

Received 21 November 2013
Received in revised form 29 January 2014
Accepted 21 March 2014
Available online 13 May 2014

Keywords:

Lithium
Plasma facing components
Wetting
Contact angle

ABSTRACT

Research into lithium as a plasma facing component material has illustrated its ability to engender low recycling operation at the plasma edge leading to higher energy confinement times. Introducing lithium into a practical fusion device would almost certainly require the lithium to be flowing to maintain a clean lithium surface for gettering. Several conceptual designs have been proposed, like the LiMIT concept of UIUC (Ruzic, 2011). Critical to the implementation of these devices is understanding the interactions of liquid lithium with various surfaces. For a device that relies on thermoelectric magnetohydrodynamic drive, such as the LiMIT concept, two of the critical interactions are the wetting of materials by lithium, which may be characterized by the contact angle between the lithium and the surface, and the relative thermopower between lithium and potential substrate materials.

Experiments have been performed into the contact angle of liquid lithium droplets with various surfaces, as well as methods to decrease the contact angle of lithium with a given surface. The contact angle, as well as its dependence on temperature was measured. For example, at 200 °C, tungsten registers a contact angle of 130°, whereas above its wetting temperature of 350 °C, the contact angle is less than 80°. Glow discharge cleaning of the target surface as well as evaporation of a thin layer of liquid lithium onto the surface prior to performing wetting measurements were both found to decrease the wetting temperature.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Increased attention has been focused on liquid lithium recently in order to increase energy confinement times [2,3]. Research into liquid metal divertor concepts has shown that they might provide a viable alternative to traditional solid divertors [1,4,5]. Solid divertors in magnetic confinement fusion devices suffer from limitations due to radiation damage, thermal stresses, and if sputtered into the fusion plasma can have adverse effects on power balance due to increased radiation losses [6,7]. Liquid metal divertors,

particularly those made of lithium address many of these concerns. A flowing lithium divertor would not erode or degrade as the constituent lithium would be constantly flowing through. Implantation of alpha particles and neutron damage to the lithium is also of negligible concern for the same reason. Several concepts to implement a flowing lithium divertor exist [1,4,8], however, it is crucial to the implementation of any of these that the interaction between the lithium and the surface that it flows on is well understood. One important measure of merit is the contact angle between a droplet of lithium and the surface in question. It is important to many of these concepts that the lithium wet the surface, such that the contact angle is less than 90°. The contact angle of a liquid on a surface is given mathematically by Young's equation [9]:

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos(\theta) \quad (1)$$

* Corresponding author at: 104 South Wright Street, Rm. 220, Urbana, IL 61801, USA. Tel.: +1 708 655 1432.

E-mail address: Fiflis1@illinois.edu (P. Fiflis).

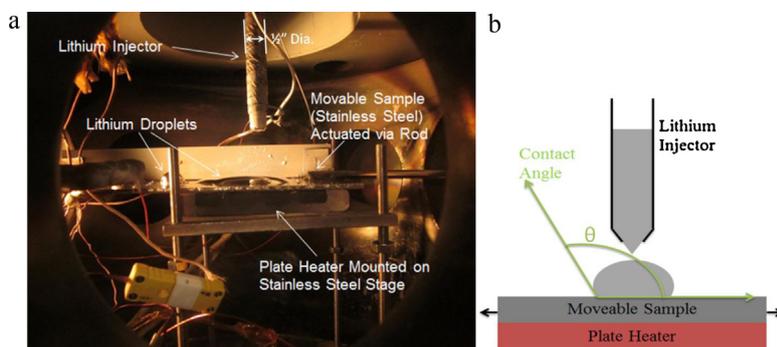


Fig. 1. Photo (left) and schematic (right) of experimental setup.

where θ is the contact angle, and the various γ are the solid–vacuum, solid–liquid, and liquid–vacuum interfacial energies.

2. Experimental setup

To properly investigate the wetting properties of liquid lithium, it is important that the lithium surface be as clean as possible. Due to the highly reactive nature of lithium with many atmospheric species, the tests were conducted in vacuum to minimize the oxidation rate. Tests were performed quickly at a base pressure of 3e–6 Torr. Lithium droplets were injected via a lithium injector onto the material to be tested. The lithium injector consisted of a reservoir, tube and nozzle. To inject lithium, lithium is placed in the reservoir, the chamber is pumped to vacuum, the injector is heated past the melting point of the lithium and a pressure of Argon is applied to the backside of the lithium reservoir, forcing it down the tube and out the nozzle. The material to be investigated is placed on a moveable stainless steel stage, actuated by a stainless steel rod welded to the stage which passes through an Ultra-Torr vacuum feedthrough. The temperature of the stage is variable and can be adjusted via a plate heater situated below the stage. A photo and schematic of the experimental setup can be seen in Fig. 1. The procedure utilized was to place a drop, record images of the droplet, and heat the sample while taking still frames at various temperatures. Though the oxidation rate is suppressed by the vacuum, it is still significant at the temperatures investigated. To combat this, at set intervals, the stage was moved and a new droplet was placed to ensure that the surface of the lithium would be fresh. A diagram of this process is shown in Fig. 2. The still frames were then analyzed to determine the contact angle. This was done via a MATLAB program which employed MATLAB's image processing toolbox. The various contact angles measured are reported here. For the purpose of this paper, lithium was defined to wet if the contact angle was less than 90°, and to not wet if the contact angle was greater than 90°, with critical wetting defined to occur at 90°.

3. Results and discussion

The first material analyzed was 316 stainless steel. Several runs of the experiment were performed on bare stainless steel to ascertain the wetting temperature, i.e. the temperature above which lithium will wet stainless steel and below which it will not. The results of these tests are shown in Fig. 3. It can be seen in this figure that the different runs agree well, except in the region around the wetting temperature. It is hypothesized that this is due to the oxidation of the lithium. Once the surface of the droplet oxidizes to a certain extent, the contact angle does no longer changes with temperature, as though the contact angle were 'locked in' at specific temperature due to oxidation. This ensures that wetting occurs almost exclusively when a new droplet is placed on the sample. The variety in the measured wetting temperatures is due to a droplet being placed, the contact angle 'locking in', and wetting not occurring until the next droplet is placed. In order to zero in on the wetting temperature, the final run placed many droplets on the stainless steel plate in a narrow temperature range. The wetting temperature was taken as the lowest temperature at which a crossover between wetting and non-wetting was seen. Transitions appearing to occur at higher temperatures were due to "locking in" of the contact angle by oxidation. This resulted in a measured wetting temperature of 315 ± 1 °C.

Several different methods were then implemented in an attempt to reduce the wetting temperature of lithium on stainless steel. The first of these was the application of a layer of diamond like carbon to the surface of the stainless steel. It was thought that since Li intercalates into C [10], that application of such a layer would decrease the wetting temperature. It was found, however, that this is not actually the case, as can be seen in Fig. 4. For the temperatures visited, the lithium did not wet the DLC coated stainless steel. Rather, the lithium completely eroded the DLC layer and the eroded carbon helped form an impurity layer on the surface of the lithium.

The next treatment experimented with was an Ar glow discharge cleaning. An 80 mA, 250 V discharge at approximately 200 mTorr was applied to the sample before injecting droplets of

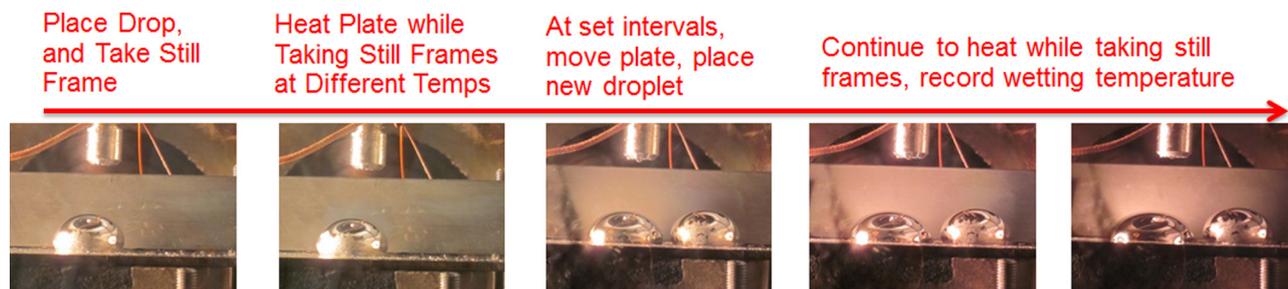


Fig. 2. Experimental procedure.

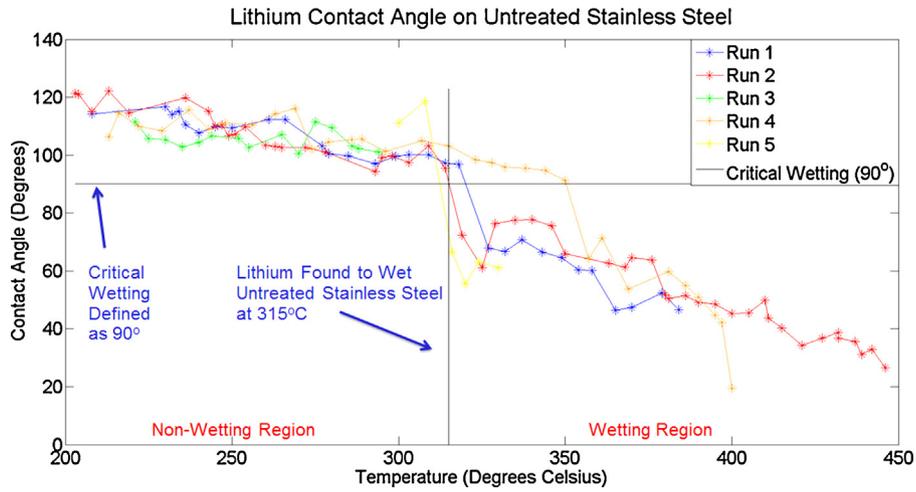


Fig. 3. Contact angle of lithium on untreated stainless steel.

lithium. The flux of Ar^+ ions for this discharge was $2.5 \times 10^{19} \text{ m}^{-2} \text{ s}^{-1}$. This corresponds to a sputtering rate of approximately 8 nm/min using a sputtering yield of approximately .1 atoms/ion obtained from a run of the TRIDYN [11] code to simulate sputtering yields of 250 eV Ar^+ oxidized stainless steel. One experiment employed Ar cleaning for 15 min which resulted in a reduction of the wetting temperature by $7 \pm 2^\circ\text{C}$, and the second experiment cleaned for 30 min and resulted in a reduction of the wetting temperature by $18 \pm 2^\circ\text{C}$. Saturation of this effect, for stainless steel, occurred in less than 30 min, as cleaning for longer periods of time resulted in no further reduction of the contact angle. Saturation after 30 min would imply removal of 250 nm of material from the surface, which is roughly on the order of the surface roughness which is approximately a few microns as determined from the grit of the sandpaper used. The results are tabulated in Fig. 5. After storing the sample at a pressure of a few mTorr of air for a week, the effect of argon plasma cleaning on the wetting temperature began to subside. These results are indicative of the presence of chemical compounds (e.g. oxides) on the surface of the stainless steel.

The final treatment option explored was coating the surface with a thin layer of evaporated lithium before injecting the lithium droplet. Early attempts at this failed because the evaporated lithium oxidized before the injector heated up over the course of approximately 30 min. It was learned by this that lithium does not wet lithium oxide, however, this did not aid the attempt to reduce the wetting temperature. This issue was solved by heating the

injector and sample before evaporating lithium onto the sample. The results of lithium evaporation is detailed in Fig. 6. As can be seen in the figure, evaporation of a layer of lithium cause the lithium to wet over the entirety of the range of temperatures investigated, yielding an effective wetting temperature at its melting point. The evaporated layer was $2.5 \pm 0.5 \mu\text{m}$ in thickness as calibrated via profilometry.

The final test performed on stainless steel was a cooldown test. All of the previous tests had been conducted by placing droplets and heating the sample. The reverse test was tried to determine whether a single droplet of lithium would unwet the surface, i.e. to transition from wetting the surface to not wetting merely by cooling the sample. A single droplet was placed on the stainless steel at 380°C , and allowed to cool. The contact angle did not change while the drop cooled down, and the drop remained wet even as the sample passed below the wetting temperature. The placement of a new droplet at 272°C that did not wet the surface ensured that the stainless steel had definitely transitioned from the wetting region to the non-wetting region. The results of this test are summarized in Fig. 7.

Tungsten, molybdenum, TZM (99.4% Mo, .5% Ti, .08% Zr), and tantalum were investigated alongside stainless steel. For each, the wetting properties of the untreated case as well as the effect of Argon plasma cleaning and lithium evaporation are detailed here. For untreated molybdenum, the wetting temperature was $324 \pm 1^\circ\text{C}$. Argon plasma cleaning reached saturation after 90 min

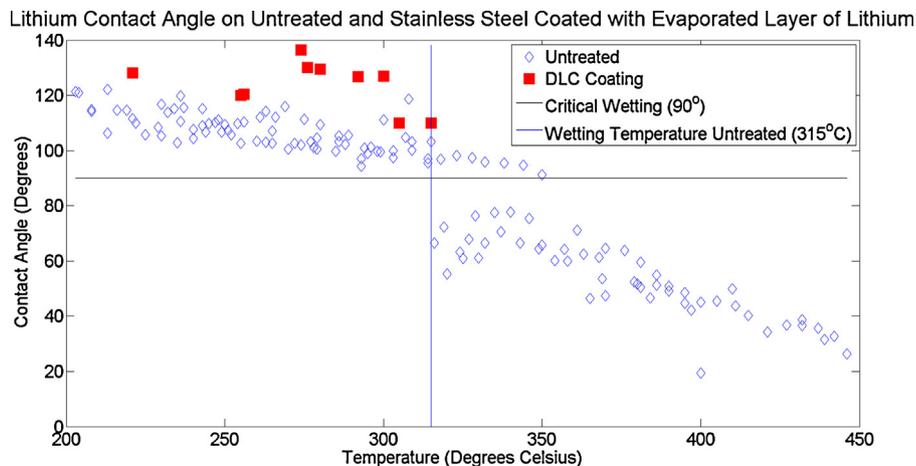


Fig. 4. Deposition of thin layer of diamond like carbon on stainless steel. No observable decrease in wetting temperature.

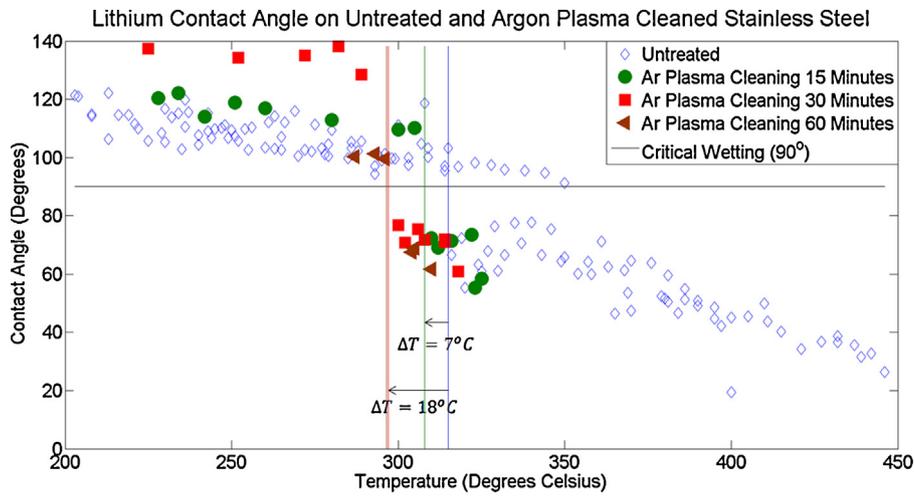


Fig. 5. Argon plasma cleaning of stainless steel resulted in a reduction of the wetting temperature by 18 °C after 30 min of glow discharge cleaning.

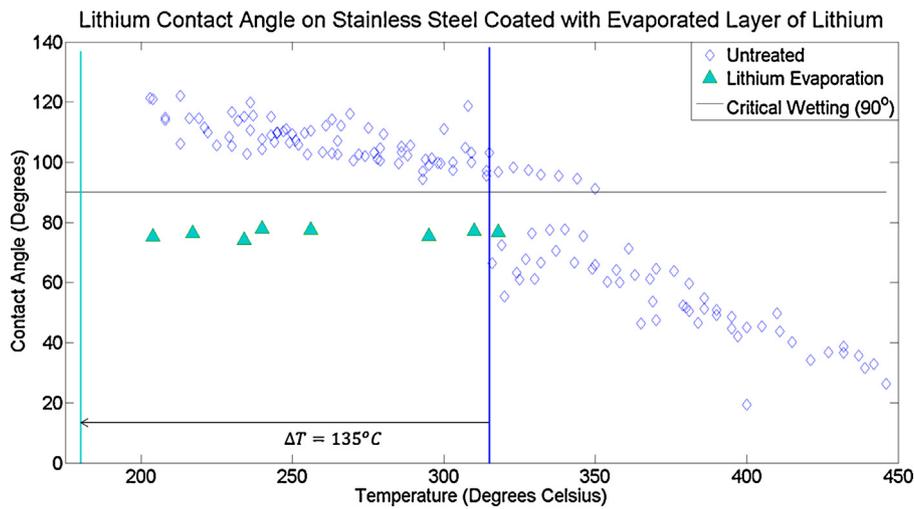


Fig. 6. Evaporation of a thin layer of lithium yields the greatest reduction in wetting temperature, reducing it to the melting point of lithium.

resulting in a reduction of 81 ± 2 °C in the wetting temperature. Fig. 8 details these results. The wetting temperature of TZM was found to be 284 ± 1 °C. After argon plasma cleaning, a reduction of contact angle saturating at 41 ± 2 °C after 90 min of cleaning was

observed. Fig. 9 shows the corresponding data and wetting temperatures for TZM. For tungsten, both regular and dendritic tungsten were experimented on, however, there was no appreciable difference between the two; the wetting temperature for each was

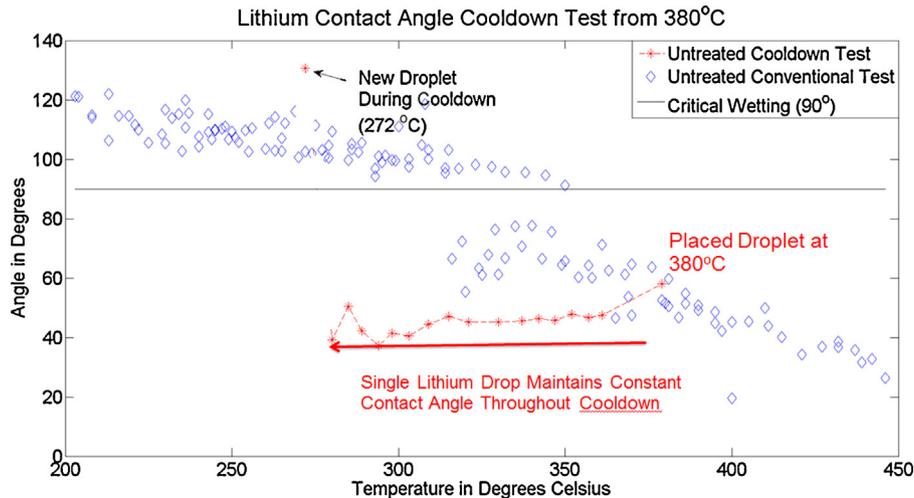


Fig. 7. Cooldown test of lithium on stainless steel.

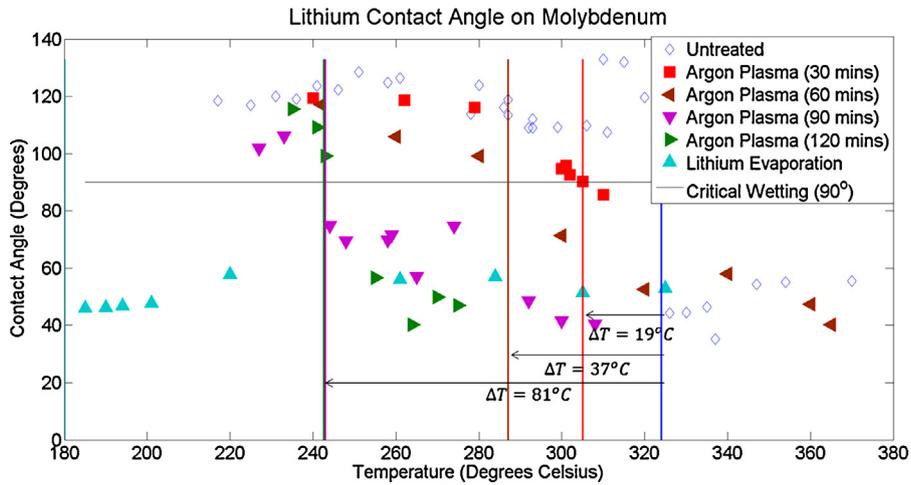


Fig. 8. Lithium contact angle on molybdenum, showing reduction in wetting temperature via glow discharge cleaning and lithium evaporation.

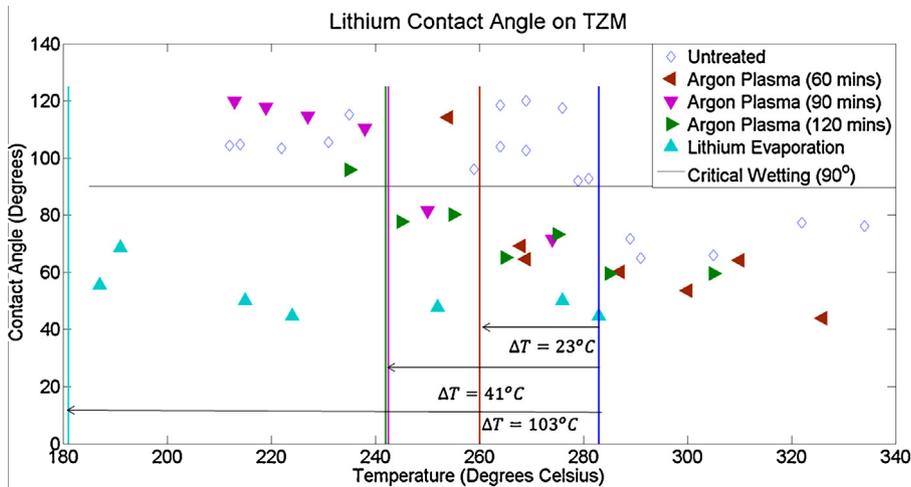


Fig. 9. Lithium contact angle on TZM. Saturation of wetting temperature after glow discharge cleaning occurs at same temperature as molybdenum (Expected as TZM is 99.4% Mo).

349 ± 1 °C. Argon plasma cleaning was employed on the tungsten, resulting in a reduction of the wetting temperature by 41 ± 2 °C, saturating in 120 min of cleaning. The results of these two tests are shown in Fig. 10. Below the wetting temperature, the contact

angle of lithium on tungsten is greater than that of stainless steel, strongly not wetting. Tantalum proved the most difficult to wet. Wetting of untreated tantalum was not observed until temperatures in excess of 353 ± 1 °C. Argon plasma cleaning did little to

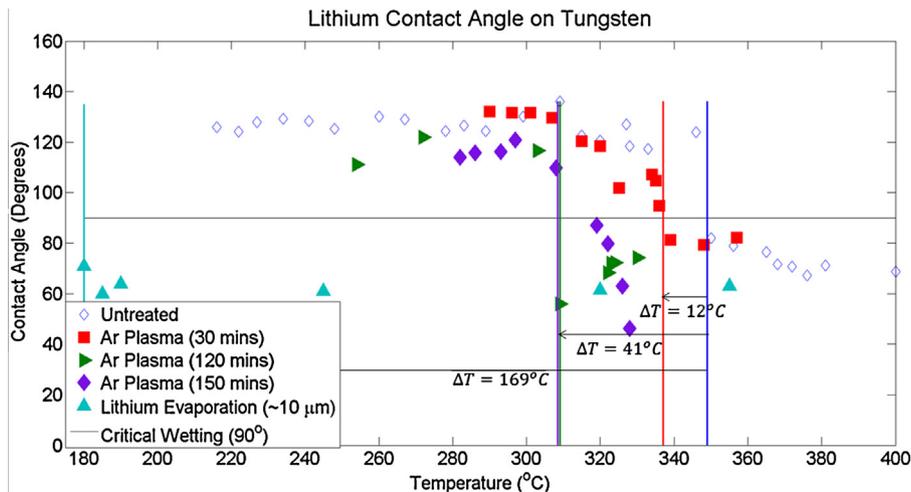


Fig. 10. Lithium contact angle on untreated tungsten vs various treatments.

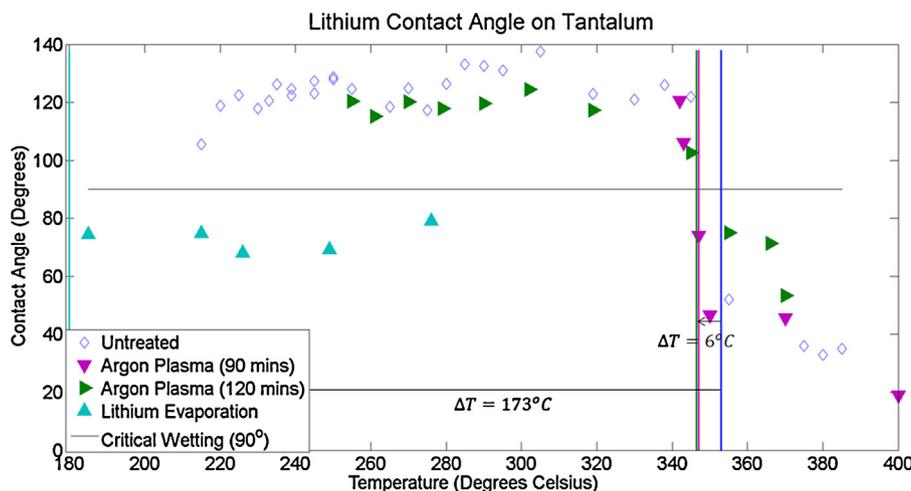


Fig. 11. Lithium contact angle on untreated tantalum vs various treatments.

Table 1
Summary of wetting temperatures.

Wetting temperatures of lithium on various surfaces	Untreated	Argon plasma cleaning	Lithium coating
Stainless steel	315 °C	297 °C	180 °C
Molybdenum	324 °C	243 °C	180 °C
Tantalum	353 °C	347 °C	180 °C
TZM	284 °C	243 °C	180 °C
Tungsten	349 °C	337 °C	180 °C

decrease the wetting temperature, unlike the effect observed on the other materials. Argon plasma cleaning resulted in a reduction of the contact angle by 6 ± 2 °C saturating after 90 min of argon plasma cleaning, the data for which can be seen in Fig. 11. However, lithium evaporation did prove to radically decrease the wetting temperature. Much like for stainless steel, evaporation of a clean layer of 2–3 μm of lithium effectively reduced the wetting temperature to the melting point of lithium. Tungsten, molybdenum, TZM, and tantalum also were wetted after lithium evaporation, which is also displayed in each of the respective figures (Table 1).

From this it can be seen that, without cleaning, TZM has the lowest wetting temperature. However, after glow discharge cleaning of the surface, both TZM and molybdenum have the same wetting temperature, which is to be expected due to the 99.4% concentration of molybdenum in TZM. Also, while TZM and molybdenum saw strong reductions in the wetting temperature after glow discharge cleaning, the other materials saw a much more modest reduction in wetting temperature, with tantalum only seeing a 6 ± 2 °C reduction in the wetting temperature. Also, as expected lithium evaporation was an excellent technique to reduce the wetting temperature, so long as lithium droplets could be deposited soon after coating. With too long of an interlude, a layer of lithium oxide formed, preventing wetting of the droplets. The knowledge that lithium does not wet lithium oxide has prompted a series of experiments investigating the possibility of lithium containment with a coating of lithium oxide whose preliminary results indicate that lithium oxide can function as a good seal for lithium.

4. Conclusion

To properly implement flowing lithium divertor concepts, it will be important to understand the wetting properties of lithium on the constituent materials of the divertor concept. Manipulation of these wetting properties, specifically the ability to decrease the wetting temperature of lithium on different materials may prove crucial to successful implementation of a flowing lithium divertor. Both plasma cleaning via an argon glow and pre-coating the surface with a layer of evaporated lithium proved very effective in reducing the wetting temperature of lithium on these surfaces. Since lithium does not un-wet a surface once wet, the best course of action may be to temporarily raise the temperature of the surface, evaporated a layer of lithium, introduce the lithium to be flowed, and reduce the temperature of the device. Also, in general, the best candidate from the perspective of wettability for a liquid lithium wall component for a fusion device is either molybdenum or TZM after glow discharge cleaning.

References

- [1] D.N. Ruzic, W. Xu, D. Andruczyk, M.A. Jaworski, Lithium-metal infused trenches (LiMIT) for heat removal in fusion devices, *J. Nucl. Fusion* 51 (2011).
- [2] R. Majeski, S. Jardin, R. Kaita, T. Gray, P. Marfuta, J. Spaleta, et al., Recent liquid lithium limiter experiments in CDX-U, *J. Nucl. Fusion* 45 (2005).
- [3] D.K. Mansfield, H.W. Kugel, R. Maingi, M.G. Bell, R. Bell, R. Kaita, et al., Transition to ELM-Free improved H-Mode by lithium deposition on NSTX graphite divertor surfaces, *J. Nucl. Mater.* 390–391 (2009) 746–767.
- [4] L. Zakharov, Magnetic propulsion of intense lithium streams in a tokamak magnetic field, *Phys. Rev. Lett.* 90 (2003) 045001.
- [5] Z. Sun, J.S. Hu, G.Z. Zuo, J. Ren, J.G. Li, L.E. Zakharov, et al., Development and experiments with liquid lithium limiters on HT-7, *J. Nucl. Mater.* 438 (2013) S899–S904.
- [6] M.J. Baldwin, R.P. Doerner, Formation of helium induced nanostructure “fuzz” on various tungsten grades, *J. Nucl. Mater.* 404 (2010) 165–173.
- [7] R.E. Nygren, D.F. Cowgill, M.A. Ulrickson, B.E. Nelson, P.J. Fogarty, T.D. Rognlien, et al., Design integration of liquid surface divertors, *Fusion Eng. Des.* 72 (2004) 223–244.
- [8] W. Xu, D. Curreli, D. Andruczyk, T. Mui, R. Switts, D.N. Ruzic, Heat transfer of TEMHD driven lithium flow in stainless steel trenches, *J. Nucl. Mater.* 438 (2013) S422–S425.
- [9] J.C. Berg, *An Introduction to Interfaces and Colloids: The Bridge to Nanoscience*, World Scientific, 2010.
- [10] R. Yazami, Y. Reynier, Thermodynamics and crystal structure anomalies in lithium-intercalated graphite, *J. Power Sources* 153 (2006) 312–318.
- [11] W. Moller, W. Eckstein, TRIDYN – a TRIM simulation code including dynamic composition changes, *Nucl. Instrum. Methods Phys. Res. Sec. B: Beam Interact. Mater. Atoms* 2 (1984) 814–818.