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Section 2. Surface physics of materials under particle bombardment

Plasma–surface interactions on liquids

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Abstract

Liquid plasma-facing surfaces have been suggested as an option for advanced fusion devices, particularly in regions where solid materials may not survive over long operating periods. Because liquid surfaces can be replenished, they offer the possibility of tolerating intense particle bombardment and of recovering from off-normal events. As a preliminary step in understanding the nature of plasma–surface interactions on liquids, we consider some of the surface processes occurring in liquids undergoing irradiation by energetic particles. These include (1) sputtering, (2) segregation of liquid component species and impurities, (3) evaporation, and (4) trapping and release of incident particles. Aspects of these processes are examined for a few candidate liquids of various types: pure metals (Li), metallic alloys (Sn–Li), and compound insulators (Li_2BeF_4). © 2001 Published by Elsevier Science B.V.

Keywords: Sputtering; Erosion; Retention

1. Introduction

Liquid materials have been considered for use in nuclear reactors for over half a century. In the late 1940s, liquid sodium was used as a high-density, low-pressure coolant in the first experimental fast breeder reactors [1]. During the next three decades, more or less in parallel with the development of liquid metal systems for fast breeder reactors, a considerable number of basic studies of the properties of liquid materials for use in nuclear environments were conducted. For fusion devices, liquid lithium was discussed as a ‘disposable’ wall coolant and as a breeding material at least as early as 1970 [2–4]. In 1972, ideas for a liquid Li-filled target chamber and for a Li-wetted first wall were proposed for inertial confinement devices [3,5].

Practical development of plasma-facing components for magnetic fusion, however, has concentrated almost exclusively on the use of solid materials, which in many respects pose less of a challenge to implement. During the past 20 years, the properties and limitations of solid systems have been intensively studied. It appears that the most studied solid plasma-facing materials, carbon, beryllium, molybdenum, and tungsten, have heat load operating limits below 30 MW/m^2. In addition, sputter erosion or neutron damage effects can render these solids unsuitable for service after short operating periods in a fusion reactor. Such limitations for solids have spurred research into the use of other types of plasma-facing materials, including liquids, solid–liquid hybrids, fluidized beds, and gaseous systems. The use of solid Cu/Li alloys, with a segregated Li layer, was proposed as a first-wall material in the 1980s [6]. However, it was found that bulk-to-surface Li transport was too slow to compensate for erosion of the Li [7]. More recently, the use of Li-wetted porous materials (e.g., W) has been proposed, and this concept appears to satisfy many of the requirements for a plasma-facing material [8,9].

Liquids have several potentially desirable properties. Foremost is the prospect of an unlimited lifetime, since replenishment can counteract erosion, neutron damage, and aid in recovery from off-normal events. Controlling the flow rate and thickness of a liquid layer across the plasma exposure region opens the possibility of adjusting the heat removal and particle retention/release characteristics of plasma-facing components. For liquids, as for all plasma-facing materials, understanding

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and controlling plasma–surface interactions (PSIs) is key to their successful application. Recently, two research programs were established in the US to study PSI in these alternate materials and to design and test prototype components built from them. These programs, the advanced limiter–divertor plasma-facing systems (ALPSs) and the advanced power extraction (APEX) studies, are exploring several long-term materials' options for pulsed and steady-state fusion plasmas [10,11].

We focus in this paper on several aspects of PSIs in liquids occurring at the atomic level. The effects considered are physical sputtering, evaporation, retention and release of the hydrogen isotopes, and helium retention. Macroscopic effects, such as wave formation, splashing, heat transport, etc., are not considered. Materials of interest in the following are the metals Li, Ga, the alloy Sn–Li, and the compound material $(LiF)_2$–BeF_2, which is called Flibe. These materials have received the most attention due their relatively low melting temperatures, neutronic properties, and availability.

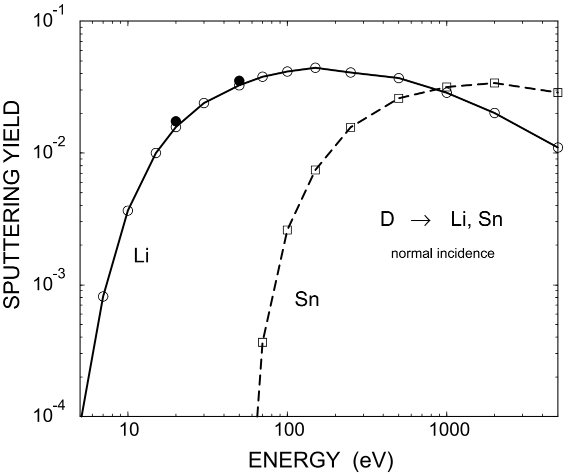

Fig. 1. Sputtering yields for D bombardment of Li and Sn at normal incidence calculated with the TRIM.SP code. The solid (open circles) and liquid (solid circles) sputtering yields for Li, shown at 20 and 50 eV, are calculated to be similar when only the difference in sublimation energy upon melting is considered.

2. Physical sputtering

A large body of experimental data and calculations exists for physical sputtering yields, S_y, of solid materials, but not for liquids [12,13]. A fundamental question immediately arises: is physical sputtering significantly different in the liquid phase? If not, then the literature available for solids, such as that which exists for Li and Ga, can be utilized [14]. If physical sputtering in liquids and solids is not similar, then a considerable amount of work will be needed to characterize this basic aspect of PSI. The question has been addressed from at least two points of view. Behrisch and Eckstein [15] considered the effect on S_y of crossing the solid–liquid phase boundary. They reasoned that the main effect must come from any change in the binding energy of surface atoms. Using tabulated thermodynamic data on sublimation energies, they found, using Ag as an example, that the change in S_y in crossing the phase boundary is small, increasing only by a few percent. Similar results have been obtained for the sputtering yield of Li, which is shown in Fig. 1.

Another approach has been taken by Morgan, who considered the surface structure of liquid metals [16]. Substantial evidence has accumulated, primarily from X-ray scattering measurements, that a general property of liquid surfaces, ranging from metals to water, is a density stratification or layering of atoms in the vicinity of the interface [17–19]. This characteristic property, which lowers the average coordination number of near-surface atoms, may affect the physical sputtering yield. In one classical dynamics simulation of a model high-Z liquid metal surface, an enhancement in the value of S_y was predicted for the stratified liquid surface compared to a uniform surface model [16]. At incident energies below 500 eV, the enhancement factor for self-sputtering exceeded a factor of 2. A stratified model for Ga exists, but not for other liquids being considered as plasma-facing materials [20]. Realistic model calculations of physical sputtering are needed and will require the development of detailed surface models, derived from experiment or from ab initio methods [18,21]. In the meantime, S_y values for solids must be considered as lower-bound estimates to the liquid S_y values.

A separate fundamental question concerning the physical sputtering of liquids is: what is the composition of the liquid surface? This question is important in assessing plasma contamination levels, since the majority of sputtered particles originate at the surface. In many current fusion experiments, the dominant plasma impurity is carbon sputtered from wall surfaces. However, because diffusion rates in liquids can be rapid, segregation effects may be important in a device with a large liquid surface area facing the plasma. In the case of pure materials, such as Li and Ga, segregation of bulk impurities to the surface may occur. In the case of alloys and compounds, segregation of the bulk components is also a possibility. Atoms that lower surface tension tend to segregate, and many common impurities (e.g, O, F) have this property [22]. The process often follows a Gibbsian segregation rule and leads to a large difference in the surface and bulk compositions. For example, the surface of a liquid Ga–In eutectic alloy is >94% atomic In, in contrast to the bulk value of 17% atomic In [20]. Oxygen has been found to segregate to liquid Li surfaces and Li has been observed to segregate to liquid Sn–Li surfaces [23]. Fluorine is expected to segregate to liquid

Flibe surfaces, but no experimental data are yet available.

The altered layer composition affects the sputter flux composition, at least initially. In contrast to preferential sputtering, in which the surface layer composition adjusts to produce an equilibrium sputter flux corresponding to the bulk composition, continuous segregation can lead to a sputter flux substantially different than the substrate composition. If the segregation rate exceeds the sputter rate, the segregated component will be present in the sputter flux, until the segregating species is exhausted from the material. Diffusion rates are high in most liquids. Measurements in liquid Li indicate that the self-diffusivity is of the order of 10^{-4} cm^2/s at 375°C [24]. Solvent species are expected to have similar values. At high sputter rates, the effect is transient, leading to an equilibrium sputter flux more closely resembling the bulk composition. This situation is also encountered in some solid materials with a strongly segregating component, such as Li–Al [25] and Cu–Li [7,26].

Of particular interest are self-sputtering rates. If surface properties change significantly upon melting, calculations based on a solid model may underestimate the yield. TRIM.SP calculations, using a planar solid surface model, indicate that Li self-sputtering yields exceed unity at incident energies above 100 eV and impact angles >60° [14]. Further, higher reflection of projectiles from the more massive atoms in a liquid metal alloy (e.g., Sn in Sn–Li) will enhance the partial yield of the lighter component. This effect is shown in Fig. 2 for the case of D bombardment of Sn–Li. In compounds, two effects contributing to the sputter yield must be considered. First, preferential sputtering of some constituents will lead to an altered surface layer of different composition than the bulk. Departures from ideal stoichiometry increase the surface energy, leading to decreased surface binding and increased partial sputter yields of the constituent surface atoms. Second, for compound materials composed of molecular components (e.g, LiF and BeF_2 in Flibe) intermolecular binding is usually weaker than intramolecular binding forces [27]. As projectile energy dissipates in collision cascades, the point is reached where the transferred energy is less than the intramolecular binding, but greater than the intermolecular binding. This would lead to sputtering of intact molecular units from the liquid surface. This mechanism is not considered in binary collision models, but classical dynamics codes may provide some insight.

Only limited experimental data presently exist for fusion-relevant liquid self-sputtering rates. Indirect measurements of Hg and Ga self-sputtering suggest a yield enhancement compared to solid self-sputtering data, but the results are not definitive. Recent ion beam measurements of the self-sputtering of Li indicate a higher yield on the liquid surface than on the solid surface [28]. Further work is needed, as high self-sputtering rates would profoundly affect PSI. Some experimentation in magnetically confined plasma devices has been conducted. A Ga system was studied in a plasma chamber, which showed efficient transport of Ga throughout the device [29]. A liquid Li sample has been exposed to the divertor plasma in DIII-D, with transport of Li observed in the $J \times B$ direction [30]. The mechanism of transport was not identified, but evaporation as well as sputtering could both have occurred.

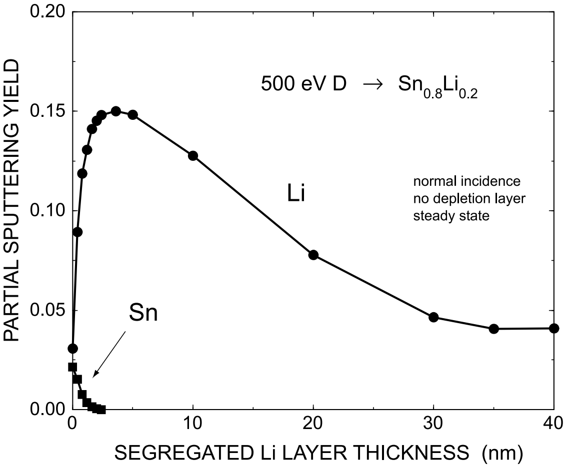

Fig. 2. Sputtering yields of a Sn–Li alloy by deuterium as a function of the segregated Li layer thickness. The yields are calculated for the initial surface composition, before any depletion of the Li layer by preferential sputtering or evaporation occurs. In the Sn–Li system, the $Sn_{0.8}Li_{0.2}$ composition has the chemical short-range order parameter closest to 0, indicating a random distribution of atoms in the material [37].

3. Evaporation

The evaporation rate is an important parameter in considering the PSI of liquids. Fig. 3 shows the evaporation rates into vacuum for various liquid materials as a function of temperature. At high temperatures, the evaporation flux can be significant and can surpass physical sputtering as the dominant material release mechanism. This is illustrated in Figs. 4 and 5, which plot the point at which the evaporation flux and the sputter flux are equal, as a function of the incident particle energy and substrate temperature for various incident particle species and fluxes. The curves mark the boundary between evaporation and sputtering dominated regions. For Li, which has a vapor pressure >0.1 Pa above 450°C [31], evaporation dominates in most cases above this temperature. Ga and Sn have significantly lower vapor pressures and the situation for Sn–Li

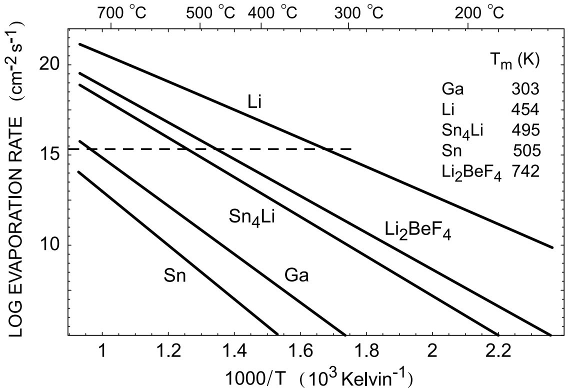

Fig. 3. Evaporation rates for Li, $(LiF)_2$–BeF_2, Sn_4Li alloy, Ga, and Sn. The horizontal dashed line corresponds to an evaporation rate of 1 monolayer/s.

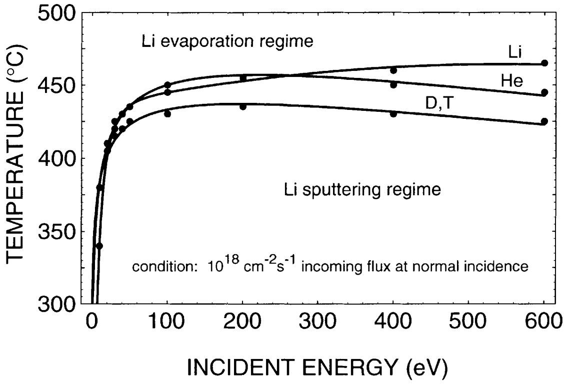

Fig. 4. Lines of equal sputtering and evaporation rates of Li for a bombarding flux of 10^{18} cm^{-2} s^{-1} of various particles at normal incidence. The curves mark the boundary between evaporation and sputter dominated regimes. Above ≈450°C, evaporation dominates sputtering regardless of the incident particle species or energy.

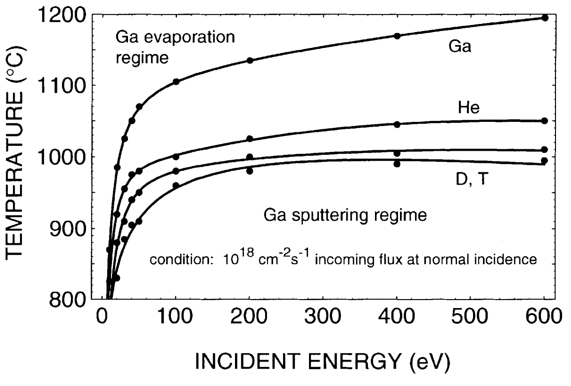

Fig. 5. Lines of equal sputtering and evaporation rates of Ga for a bombarding flux of 10^{18} cm^{-2} s^{-1} of various particles at normal incidence. Below 1100°C, Ga self-sputtering exceeds evaporation except at energies <100 eV.

and Flibe is intermediate. This comparison assumes that sputtering and evaporation are independent processes, but this is not the case for high incident particle fluxes, where the deposited energy to the surface cannot be neglected. Recent data from the PISCES experiment indicate that the emitted flux of Li, at temperatures slightly above the melting point, is greater than what can attributed to the sum of independent sputter and evaporation fluxes [32]. A more realistic model is needed to match the data, akin to the radiation-enhanced sublimation model in solids [33], at least in the region where the sputtering and evaporation fluxes are comparable.

4. Process dynamics

The processes of sputtering, segregation, and evaporation will occur together for a liquid surface exposed to a plasma. To understand how these processes interact, an approach used by Kirchheim and Hofmann [34] in developing a model for surfaces undergoing simultaneous sputtering, segregation, and adsorption can be of use with some modification. The relevant balance equation for the surface coverage, θ, of a particular species is $d\theta/dt = J_d - J_s - J_e$, where J_d is the diffusion flux from the bulk to the surface of the material, J_s the sputter flux, and J_e is the evaporation flux. Solving this equation yields the time dependence of the surface coverage for the species of interest:

$$\theta(t) = \frac{e^{-k_1 t}(k_2\sqrt{k_1} + k_3\,\mathrm{Erf}(\sqrt{k_1 t}))}{\sqrt{k_1}},$$

where $k_1 = (S_y J_i + J_e)/\theta_0$ is a term that incorporates sputtering and evaporation rates, $k_2 = \theta(0)$ gives the initial condition, and $k_3 = c_0\sqrt{D}$ is a diffusion term accounting for surface segregation. J_i is the incident particle flux, θ_0 the surface density, and c_0 is the bulk concentration of the species. Fig. 6 plots the surface coverage of Li in a Sn–Li alloy for various conditions of particle flux and temperature that might be encountered in a fusion reactor divertor. In all cases, the surface coverage of Li decreases with time. If a fresh surface moves across the plasma region, as would happen in a flowing divertor, the maximum allowable residence time can be determined for a given criterion. For example, if at least 50% of the surface must remain Li, the maximum residence time is about 25 ms for $J_i = 10^{18}/cm^2$ s at 500°C or $J_i = 10^{17}/cm^2$ s at 600°C. It is seen that at high temperatures, evaporation is always the main loss mechanism. At 700°C, the time dependence of the Li surface coverage is almost independent of the incident particle flux at this scale. Fig. 7 shows the time dependence of Li coverage as a

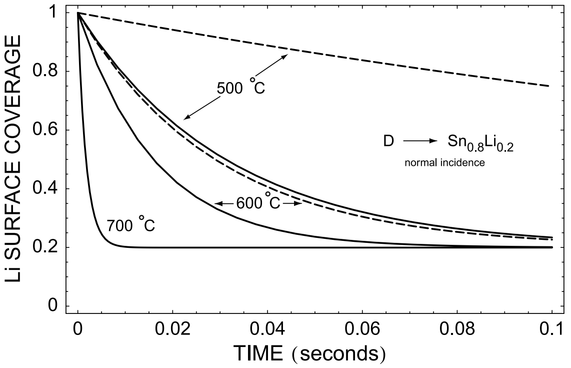

Fig. 6. Surface coverage of Li in a Sn–Li alloy as a function of exposure time to 500 eV D bombardment for two temperatures (indicated) and incident particle fluxes (dashed lines: 10^{17} cm^{-2} s^{-1}; solid lines: 10^{18} cm^{-2} s^{-1}). Initially, the alloy surface is covered by 1 monolayer of Li.

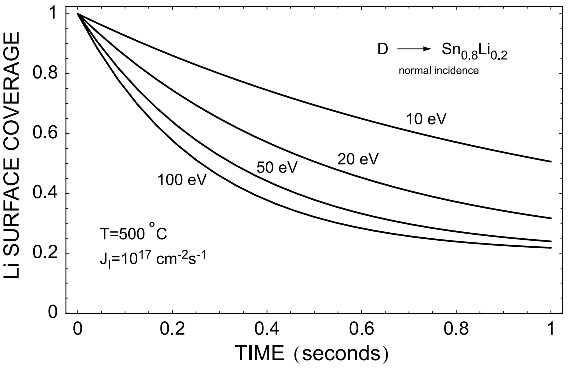

Fig. 7. Surface coverage of Li in a Sn–Li alloy as a function of exposure time to D bombardment at a flux of 10^{17} cm^{-2} s^{-1} for various incident particle energies at 500°C. Initially, the alloy surface is covered by 1 monolayer of Li.

function of the incident D energy. The Li segregated surface may persist in certain circumstances. At 10 eV the coverage remains high (>50%) for times greater than 1 s.

5. Retention and release of H isotopes

Recycling of hydrogen isotopes from plasma-facing surfaces directly affects particle energies and densities in the boundary plasma layer. Recycling from solids is an intrinsic materials' property, which can be modified only through considerable effort (e.g., H isotope removal from carbon by He glow discharge cleaning). Liquids that efficiently trap hydrogen offer the possibility of 'tunable' recycling. In the case of Li, the metal strongly retains incident hydrogen until a saturated LiH layer forms throughout the implantation zone [31,35]. By adjusting the flow rate of liquid Li across the plasma-facing surface, the recycling behavior might be varied from high retention at high flow rates to low retention at low flow rates, where saturation occurs during exposure. Several methods for moving liquid sheets or droplets across the plasma region have been proposed, ranging from mechanical pumping and nozzle spray to electromagnetic drive schemes. These concepts have not yet been tested in a large-scale fusion experiment. One complication is that the liquid flow rate is not a freely adjustable parameter, since process dynamics and heat removal requirements will dictate a minimum flow velocity. For non-hydride forming liquids, e.g., Ga, only a high recycling operating mode is possible. In Flibe, the solubility of the hydrogen isotopes is low, but the formation of hydrogen-isotope fluorides, which have appreciable solubilities, will influence the hydrogen isotope retention and release characteristics of the material [27]. Tritium recovery is another issue for plasma-facing liquids. Hydride forming materials, e.g., Li, and Sn–Li may have unacceptably high T inventories unless efficient T removal procedures are used. Ga and Flibe materials should have lower T inventories, but would still require active T removal methods.

6. Helium retention and release

Managing He exhaust from burning fusion plasmas requires an efficient pumping method. Liquids have been suggested as a possibly effective collection medium, since the He implanted zone could be rapidly transported away from the plasma chamber. But He retention in liquids depends on entrainment, bubble production, or the formation of bound complexes, rather than trapping at lattice defects, as in the case of solids. Some evidence exists that He is retained, at least for short periods, in liquid Li and Ga [29]. However, more detailed measurements of He retention, transport, and release must be obtained before the feasibility of liquids for He removal from fusion plasmas can be assessed. A theoretical analysis by Hassanein of He implantation in liquid Li indicates that the effective pumping coefficient is expected to be of the order of 1% for 1 keV He implanted into a liquid Li sheet moving at a velocity of 10 m/s [36]. This value is tantalizingly close to the minimum pumping coefficient needed to make the method feasible. For this calculation, the diffusivity of He in Li was assumed to equal the self-diffusivity of liquid Li. If the He diffusivity is in fact lower, larger effective pumping coefficients are predicted. Should this be the case, the use of liquids to remove He may be an option if transport systems capable of handling large volumes are practical.

7. Conclusions

Considering the fundamental processes of sputtering, evaporation, segregation and particle retention place boundaries on the operating conditions suitable for using liquids as plasma-facing materials. For Li, its high evaporation rate appear to limit its use to temperatures below 450°C. For Sn–Li, its lower vapor pressure should allow operation at higher temperatures, but only for a limited exposure time to the plasma. The lower Li content and the enhanced reflectivity of hydrogenic particles may make this material an option for high recycling operation, although a higher sputtering yield also results. For Ga, the low evaporation and sputtering yield are attractive features, but plasma contamination from this higher-Z material may be unacceptable. Flibe is interesting as a hydrogen compatible insulating material, but its sputtering properties and degradation during particle bombardment are problematic. At this time, no liquid material is clearly suitable for use as a plasma-facing material. Further model development and experimental verifications of predicted properties are needed before a definite feasibility assessment can be made.

Acknowledgements

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