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Full Length Article

Evidence of formation of lithium compounds on FTU tiles and dust

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ABSTRACT

Since 2006 lithium as an advanced plasma facing material has been tested on the Frascati Tokamak Upgrade (FTU). Lithium in the liquid phase acts both as plasma facing component, i.e. limiter, and plays also a role in plasma operation because by depositing a lithium film on the walls (lithization) oxygen is gettered.

As in all deposition processes, even for the lithization, the presence of impurities in plasma phase strongly affects the properties of the deposited film. During the 2008 campaigns of FTU it was observed a strong release of carbon dioxide (during disruptions), resulting in successive serious difficulty of operation. In order to find the possible reactions occurred, we have analyzed the surface of two tiles of the toroidal limiter close to the *Liquid Lithium Limiter* (LLL). The presence of molybdenum oxides and carbides suggested that the surface temperatures could have exceeded 1000 K, likely during disruptions. lithium oxides and hydroxides have been found on the tiles and in the dust collected in the vessel, confirming the presence of LiO and LiOH and a not negligible concentration of Li_2CO_3 especially at the LLL location.

On the basis of the above results, we propose here a simple rationale, based on a two reactions mechanism, which can explain the formation of Li_2CO_3 and its subsequent decomposition during disruption with release of CO_2 in the vessel. Admitting surface temperatures above 1000 K during a disruption, relatively high partial pressures of CO_2 are also predicted by the equilibrium constant for Li_2CO_3 decomposition.

1. Introduction

Since 2006 most of plasma wall interaction experiments on FTU used liquid lithium as plasma facing material. Lithium is the lightest alkali metal and it is highly chemically reactive with relevant ion species in fusion plasmas including hydrogen, deuterium, tritium, carbon, and oxygen. As such, lithium can provide strong pumping for those ions. By placing a liquid lithium surface in the path of the main wall heat flux, the lithium is evaporated from the surface. The evaporated lithium is quickly ionized by the plasma and the ionized lithium ions can provide a strongly radiative layer of plasma (vapour shield), thus could significantly reduce the heat flux to the surfaces. Liquid lithium limiter in FTU is also an active method to deposit, during the plasma discharge, a lithium film on the walls with prolonged beneficial effects: reliable operation with very clean plasmas, very low wall particle recycling, spontaneous peaking of the density profile [1].

In FTU, like in other fusion devises, during plasma operations, particles (ions, electrons, charge exchange neutrals) impacting on plasma facing materials (PFCs) cause physical sputtering, chemical erosion, melting, evaporation or sublimation. In this way, species removed from surfaces are ionized and transported along the magnetic field lines. A fraction of the transported material is pumped out but the rest is re-deposited on surfaces in different location. Eroded atoms are re-deposited together with fuel species and impurity present in the vessel (oxygen, nitrogen, water vapour etc). This process, called *codeposition*, results in the formation of mixed material layers. The continuous growth of these co-deposited layers has strong implications for the plasma operation because of the deteriorated chemical and physical properties with respect to the original plasma facing materials. Besides, in the perspective of using tritium, the codeposited film can increase the immobilized tritium inventory inside the vessel. Last, in the case of disintegration of such films, can be a potential source of dust.

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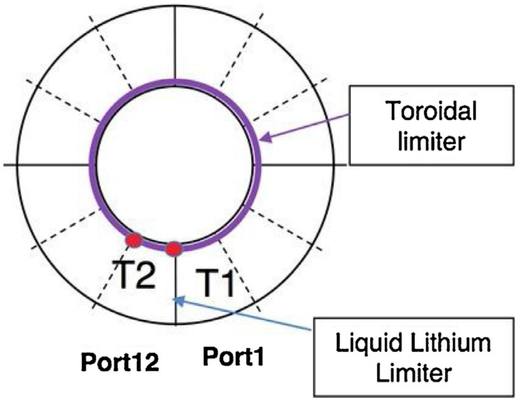

Fig. 1. Schematic layout for the toroidal localization of tile1 (T1) and tiles 2 (T2) inside the vessel of FTU.

In particular, in FTU, anomalous carbon dioxide releases were observed after disruptions and in a campaign following a long lasting venting of the machine just after a period of intensive Lithium limiter usage. The consequence was a deterioration in the plasma performance hampering the normal operation of almost the 2008 campaign. We suppose that, due to its high chemical reactivity, Lithium deposited on plasma facing components, in particular on the toroidal limiter, could have bound CO_2, O and all the reactive species during the air venting operations, leading to the formation of lithium carbonate, lithium oxide etc. During disruptions, in the following experimental campaign, the high power released on the toroidal limiter (in FTU disruptions are always characterized by a fast inboard movement of the plasma column) could have raised the surface temperature above 1000 K. At this temperature lithium carbonate can be decomposed back into metallic lithium and volatile CO_2 which can be easily condensed on the first wall of FTU, usually at very low temperature because of the liquid nitrogen cooling needed for avoiding magnet coils overheating. In the following discharge energetic ions imping the walls will immediately sputter CO_2 which still have the time to reach the core plasma and cool it by radiation inhibiting sustainment of plasma current. The premature cease of the discharge would leave the CO_2 in the exhaust and then detected by a quadrupole. In order to verify the above rationale, we have analyzed two tiles of the toroidal limiter via X Ray Photoelectron Spectroscopy (XPS), Fourier Transform Infra Red spectroscopy in combination with the Attenuated Total Reflectance (FTIR-ATR) and Secondary ion Mass Spectrometry (SIMS), dismounted during maintenance, and the dust collected on the floor of the machine via X Ray Diffraction (XRD), Neutron Diffraction (ND) and SIMS looking for lithium compounds formation.

In view of the results, we propose a study of Gibbs' free energy for lithium carbonate formation/decomposition via a two reactions mechanism which shows that above a surface temperature of 900 K the released fraction of CO_2 is no longer negligible.

2. Analysis of the tiles

A number of tiles of the toroidal limiter exposed to plasma were retrieved from the torus and transferred via air for *ex-situ* examination and subsequent cleaning. A scheduled temperature desorption analysis on these tiles by the FTU team and the requirement to minimize the number of cut tiles (to be accommodate in the chambers of surface analysis stations) have reduced the availability to two tiles T1 and T2 mounted on the toroidal limiter in the proximity of the liquid lithium limiter as depicted in the layout of Fig. 1.

Table 1
Binding Energy and relative atomic concentrations of the major constituents at the surface of T1.

Element	Position (eV)	At%
C1s	285	43.63
Na1s	1072	0.31
O1s	531	35.29
Ti2p	459	0.76
Fe2p	711	0.37
Cr2p	577	0.87
Mo3d	232	16.70
Ca2p	348	2.21

2.1. T1

The FTU tiles are made of 363 TZM alloy whose principal element is Mo with the addition of Ti, Zr, Fe, Ni and Si [2]. The whole tile ($6 \times 7 \times 2\,cm^3$, 420 g) was introduced in a XPS VG Theta Probe apparatus. Several survey spectra, not reported for brevity, on a 100 μm spot were acquired with an overall resolution of 2 eV. All spectra were referenced to the same energy scale determined by calibrating the Ag $3d_{5/2}$ line at 368.3 eV. The main elements at the surface are reported in Table 1. Li is present at trace level. Mo, Fe Ti are from the TZM alloy, Cr from sputtering and redeposition of stainless steel component while C and O are present at a very high unusual concentrations.

With the attempt to investigate the interaction of Li with the surface of the tiles, high resolution spectra have been acquired for the L1s, Mo3d, C1s and O1s core levels. The core level fitting has been performed through a Voigt profile including a Lorentzian function (accounting for lifetime broadening) and a Gaussian function (accounting for the finite instrumental resolution) (FWHM 1.3 eV).

The fitting routine included also a Shirley back-line, mimicking the secondary background. A Doniach-Sunjic's function was used to fit the C1s core level with an asymmetry factor of 0.07 to account for the Doniach-Sunjic's effect (Fig. 2a)–d)).

As one can see the Li1s at about 56 eV of binding energy is present at trace level and unfortunately close to a variety of secondary peaks. As such, to study the Li chemicals state by fitting the L1s core line can be difficult and misleading. Due to its high chemical reactivity a fresh Li film deposited can change its state at the surface very quickly with time, especially when interact with reactive species present in a fusion plasma like hydrogen or oxygen. As a matter of fact, due to the lack of data, to infer the type of bonds and their binding energies that Li forms with C, O and D when reacts with a deuterium plasma, we exploit the results of a controlled laboratory experiment using polished graphite samples coming from the NSTX experiment [3–5]. Looking at the C1s spectrum, by comparison with results reported in Refs. [3–5], we have assigned to the component at 285 eV C—O bonds and at 293.4 eV L—C—D bonds respectively. At the present we do not know yet what spiece is associated to the peak at 296.4 eV. In agreement with Ref. [6] the O1s core level have been fitted as in Fig. 2d). In particular the component at 530.4 eV has been assigned to LiO or Li_2O_2 bonds, that at 531.3 eV to MoO_3, that at 532.6 eV to Li—O—D bonds and that at 534.3 eV to OH. Therefore we assign, with a due reserve, LiO to the component at 55.9 eV and Li—C—D to that at 57.3 eV under the Li1s core level.

2.2. T2

T2 was received at IFP for analysis before TDS and therefore a sample of $19 \times 11\,mm^2$ with the most interesting morphological features on the surface could be cut out (see Fig. 3). On that surface we analyzed by XPS a $10 \times 4\,mm^2$ area using a non-monochromated Al X Ray source and hemispherical analyzer [7].