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Assessment of corrosion phenomena in liquid lithium at T < 873 K. A Li(d,n) neutron source as case study

J. Knaster[a],[*], P. Favuzza[b]

[a] IFMIF/EVEDA Project Team (F4E), Rokkasho, Japan
[b] ENEA, Firenze, Italy

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ABSTRACT

The corrosion induced by alkali metals in steels has been the subject of long decades of intense studies under both nuclear fission and fusion research programs. Li or its eutectic Pb-17Li is the liquid metal coolant choice for fusion blankets due to the tritium breeder capability of Li. Non-metal impurities enhance corrosion, but only N becomes potentially a problem given its high solubility in liquid Li and the depletion of Cr through ternary nitrides Li-Cr-N. The low solubility of C and O allow its cold trapping to values <10 wppm, however N can only be hot trapped demanding temperatures typically of 873 K. The inherent difficulties of experimentation on physicochemical kinetics related with alkali metals lead to a confusing divergence of results available in the literature; however, the understanding of the corrosion phenomena of RAFM steels exposed to flowing Li up to 873 K is mature. Next decade, 14 MeV neutrons will be available for fusion materials testing through Li(d,n) nuclear reactions. In such a facility, a concave RAFM steel backplate will be channelling 523 K flowing Li in the region where the 40 MeV deuteron beam will be impacting. If RAFM steels are considered, two main concurrent mechanisms will take place: a) mass transport of alloying elementsalong the loop and b) depletion of Cr through formation of Li_9CrN_5. Fortunately, the mass transport phenomena of Cr within the $\Delta T = 350$ K in the loop is limited due to the poor solubility of Cr in liquid Li (0.21 wppm at 873 K). In turn, at 523 K Li the activity of N to form the ternary compound is negligible. However, the high solubility of Ni in Li (2144 wppm at 873 K), suggests the presence of mass transport phenomena of Ni from the stainless steel piping; unfortunately, the physicochemical kinetics are not fully understood. Lifus 6, in operation in Brasimone (ENEA) since the end 2015, will close in a definitive manner remaining open questions.

1. Introduction

The corrosion induced by alkali liquid metals (namely Na, Li) in steels has been subjecting of decades-long intense studies under both nuclear fission and fusion research programs. Liquid alkali metals are excellent coolants due to their wide liquidus temperature ranges (Li exhibits a melting point at 453.69 K and boiling point at 1620.00 K), high heat capacity, high thermal conductivity combined with low vapour pressure and high surface tension, which for identical flow parameters, enhances heat transfer coefficients. Another distinguishing feature of alkali liquid metals is their high heat of vaporization, low viscosity and density, which allows their use in power engineering equipment at high temperatures and low pressure, thus alleviating solution of mechanical strength problems and enhancing thermal efficiencies [1–4]. Whereas Na is the coolant chosen for fast reactors due to its low neutron absorption cross section and poor moderator properties that optimize hard neutrons availability, Li or its eutectic Pb-17Li is the choice for fusion blankets due to the tritium breeder potential of Li, mainly through

$$^{6}_{3}Li + {}^{1}_{0}n + {}^{4}_{2}He + {}^{3}_{1}H$$

The thermal efficiency of a power plant correlates with the coolant temperature, being affected by the highest possible operating temperature; however the higher the temperatures, the lower the mechanical properties of structural materials. The unprecedented Maxwell stresses induced by the cyclic electromagnetic forces in future fusion reactors, where magnetic fields in the order of 10 *T* will interact with currents in the order of tens of *kA* and $^{dI}/_{dt}$ in the order of *kA/s*, demands a careful assessment of the materials to be used. Neutron damages above 20 dpa/year will lead to the severe radiation induced degradation of most exposed components that shall withstand thermal loads >10 MW/m^2 [5]. These materi-

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[*] Corresponding author.
E-mail address: juan.knaster@ifmif.org (J. Knaster).

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als should work at the highest possible temperatures, thus liquid Li is an optimal candidate as coolant reinforced by its breeding properties. However, corrosion phenomena are enhanced at high temperatures, where both the solubility of the alloying elements of the structural materials in Li, and the chemical reactions kinetics are exponentially increased.

The inherent difficulties of experimentation on physicochemical kinetics related with alkali metals lead to a confusing divergence of results available in the literature. However, the understanding of the corrosion phenomena related with flowing Li up to 873 K is mature. In turn, about the future uses of Li in the world fusion programme, the most mature understanding relates with the four decades old technological efforts towards a fusion relevant neutron source. In IFMIF, the International Fusion Materials Irradiation Facility [4], two D^+ beams at 40 MeV yielding 5 MW power each will impact on a Li screen flowing at 523 K to generate the desired neutron flux [5], increasing its temperature by ~164 K [6]. To prevent the known corrosion enhancement caused by the presence of Nitrogen (N) in Li, it is foreseen to remove this non-metal 'hot trapping' it at 823–873 K. This thermal gradient in the Li loop will enhance mass transfer phenomena. The absence of magneto-hydrodynamic effects in a Li(d,xn) fusion relevant neutron source, conversely as will be faced in the cooling Li in future tokamaks induced by its high electrical conductivity, makes such a facility to be a suitable case study. Also, the potential remaining open questions will be closed thanks to the experiments in the Lithium for Fusion 6 (Lifus 6) facility, in operation since the end of 2015. Lifus 6 is the purpose-built experimental Li loop constructed under IFMIF/EVEDA project [4] in Brasimone ENEA to assess corrosion-erosion phenomena under a Li(d,xn) neutron source relevant conditions [7].

2. Solubility and chemistry of non-metallic impurities in liquid Li: why is N relevant?

The dissolution of metals enclosing a liquid is caused by the rupture of the short-range bonds of the alloying atoms in the metal lattice and ensuing formation of more stable bonds in the solvent. The dissolution process lasts until the chemical potential of the element in the solid phase matches the one in the liquid phase. The solubility of metals in a liquid metal solvent is strongly related to the energy of these short-range bonds of the structural alloys, increasing with the solvent temperature. Physicochemical estimations are theoretically feasible, but thermodynamic data coping with all possible scenarios is unavailable.

The compatibility of the materials directly in contact with the liquid alkali metals for an optimal cooling efficiency is strongly influenced by the non-metallic impurities present in the solvent. Furthermore, the physical properties of both Li and Na are impacted by them. Their presence, if sufficiently relevant, can increase the apparent solubility of the solid metal driven by chemical reactions that selectively depletes alloying elements at the surface. Related chemistry is complex; thus accurate predictions at given conditions are in general not possible without specific experimentation. Estimation of the stoichiometry and thermal stability of the ternary compounds that can often form is experimentally difficult with many variables influencing uncertainties remaining.

Among the non-metallic impurities, C, N, and O play a crucial role since form stable compounds with most of the alloying elements of steels [8–10]. Their impact is strongly linked to their solubility at the operating temperatures in both Na and Li. C and O are the most relevant in corrosion processes for liquid Na, while the extremely low solubility of N makes it irrelevant corrosion wise. In turn, Li does not form stable compounds directly with metals, and conversely, the high solubility of N (970 wppm at the melting temperature of Li) makes it the main corrosion inducing non-metallic element in liquid Li.

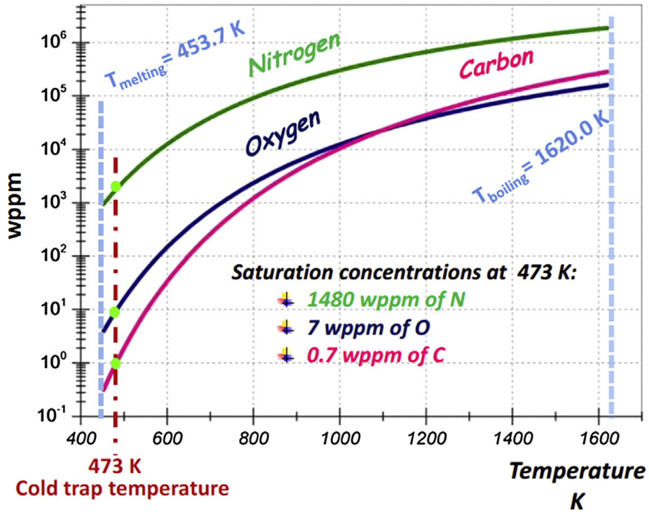

Fig. 1. Solubility (wppm) of N, O and C in liquid Li with respect to Temperature (K). Minimum achievable concentrations at cold trapping temperatures are indicated following the recommended expressions by the IUPAC-NIST Solubility Data Series [14].

2.1. Solubility of non-metallic impurities in liquid Li

The solubility of non-metallic elements in Li follows an Arrhenius equation. Doubtful data available led to strong historical discrepancies in the literature that were only overcome in the late 70 s thanks to the careful experiments developed by Yonco [11–13]. His work allowed reliable thermodynamics and phase data resulting in the ensuing years in a better understanding of the reaction kinetics. A compilation of the solubility of non-metallic elements in alkali liquid metals has been recently carried out under IUPAC-NIST coordination [14]. The recommended expressions for the solubility in liquid Li of the three relevant impurities aforementioned is as follows:

$$\text{ForC : } \log x_c = 3.221 - {}^{3741}\!/_{T}$$

$$\text{For N : } \log x_N = 3.246 - {}^{2072}\!/_{T}$$

$$\text{ForO : } \log x_O = 2.628 - {}^{2896}\!/_{T}$$

Where x_i is the molar fraction in% and T is the absolute temperature. These solubilities were obtained based on the dependence on temperature of the concentrations at saturation of each of the impurities binary compound with Li (namely, Li_2C_2, Li_3N and Li_2O respectively), i.e. in equilibrium on the processes of dissolution of the element and precipitation of the compound.

The low solubility of C and O close to the Li melting temperature, $T_{melting}$, together with their strong dependence on temperature, allows their efficient cold trapping at temperatures close to the melting point of Li (see Fig. 1), typically 473 K. Conversely, this is not feasible for N, whose trapping demands a more complex approach by means of its high reactivity with Ti at high temperatures (823–873 K) [15].

Yonco in his study determined the melting point of Li_3N at 1086 K; thus it might be present as a solid precipitate in practical liquid Li operational temperatures of cooling circuits [12] if N concentration lies beyond equilibrium concentration.