Thermodynamic stability of oxide, nitride, and carbide coating materials in liquid Sn–25Li

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Abstract

Tin–lithium (Sn–Li) has been identified as a candidate liquid metal coolant for fusion power reactors. Sn–Li coolants offer a number of advantages compared with pure lithium. The vapor pressure of Sn–25Li (0.25 Li mol fraction) is a factor of ∼1000 lower than that of pure Li, which allows an increase in coolant temperatures by as much as 450 K. Experimental data of the stability of ceramic materials in Sn–Li is scarce. The thermodynamic stability of various oxides, carbides, and nitrides in Sn–Li is estimated as a function of lithium composition and temperature at saturated solute concentrations by evaluating the Gibbs free energy of reaction, ($\Delta_r G$). At 773 K most of the studied nitrides, carbides, and some oxides were found to be stable ($\Delta_r G > 0$). However, oxides of Fe-based alloys, such as Cr_2O_3 and Fe_2O_3 were found to be unstable ($\Delta_r G < 0$) for all lithium compositions.
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1. Introduction

Following the proposal of tin–lithium (Sn–Li) as a liquid-metal coolant for free surface cooled fusion reactor internals [1,2] alloys of Sn–25at.%Li (Sn–25Li) were fabricated and thermo-physical properties reported by Natesan and Ruther [3]. Bastasz and Eckstein [4] and Rognlien and Rensink [5] investigated plasma Sn–Li interactions, and Allain et al. [6] detailed sputtering measurements of Sn–Li.

At that time the advantages of using Sn–Li coolants were based on thermo-physical properties: Sn–25Li has a factor of 1000 lower vapor pressure relative to pure lithium at 1000 K, 2.5 times higher thermal conductivity relative to Pb–17Li ($Pb_{83}Li_{17}$) at 623 K, and 55% lower density compared with Pb–17Li at 500 K [1,3,7,8]. However, Fütterer et al. [9] assessed Sn–Li alloys as breeder material for blanket applications and concluded that the low breeding ratio offsets the low vapor pressure advantage of Sn–Li coolants. It was further concluded

that lack of corrosion and compatibility data would require substantial R&D efforts to reach confidence levels comparable to other liquid metal coolants [9].

We report here the results of thermodynamic calculations to estimate the chemical stability of ceramic materials in liquid Sn–Li as a function of temperature and composition of Sn–Li coolants. The model was applied to a wide range of oxide, nitride, and carbide ceramics. Some of these could serve as magneto-hydrodynamic (MHD) mitigating coatings [10–12], although most metal carbides do not have sufficient electrical resistivity. Experimental data on the compatibility of ceramic materials with liquid Sn–Li are note available. Some stability measurements of graphite, quartz, alumina, beryllia, and SiC in pure liquid Sn were made in 1950s [13,14]. In static liquid Sn these ceramics were shown to be compatible up to 900 °C, except for beryllia, which was found to be unstable at any temperature.

2. Chemical activities

The density of Sn–25Li was measured recently [3] to be 6.36 g/cm³ with a melting temperature of 334 °C [15]

Table 1
Activity–temperature relationships of Li [$\ln a_{Li} = A + B$ $(T/K)^{-1}$] for Sn–Li alloys ($0.1 < x_{Li} < 0.9$) based on chemical activity measurements at 1200 °C

x_{Li}	Li-activity[a] at 1200 °C	Sn-activity[a] at 1200 °C	A[b]	B[b] (Pb–Li)	B (Sn–Li)	T[c] (K)
0.1	0.00109	0.895	−0.522	−7071	769	>523
0.2	0.00289	0.758	−0.151	−6624	222	>573
0.3	0.00987	0.486	0.415	−6378	−611	>673
0.4	0.0198	0.332	1.058	−6209	−1558	>723
0.5	0.0377	0.194	1.652	−5996	−2433	>729
0.6	0.0775	0.078	2.109	−5618	−3107	>781
0.7	0.186	0.0155	2.284	−4951	−3364	>973
0.8	0.354	0.00216	2.068	−3874	−3046	>1056
0.9	0.739	0.0000257	1.346	−2264	−1983	>853

[a] Measured at 1200 °C [16].
[b] Based on measurements in Pb–Li [18]; see Section 2.
[c] Temperature limits to avoid intermetallic compound formations [15].

to avoid formation of the solid intermetallics. The activities (a_{Li} and a_{Sn}) of Li and Sn in Sn–Li were measured as a function of lithium concentration at 1200 °C [16]. Table 1 shows the activity of both Li and Sn to be very low, which are representative of similarly low activities of Li and Pb in Pb–Li [17,18]. At 1200 °C the composition-based (x_{Li}) activity relationship for Li in Sn–25Li can be approximated as

$$\ln a_{Li} = -8.1442 + 14.097 x_{Li} - 11.371 x_{Li}^2 + 6.0259 x_{Li}^3, \tag{1}$$

where x_{Li} is the Li-content in at.%. To assess the stability of ceramics in Sn–Li at fusion relevant temperatures (<773 K), the activity of Li and Sn has to be known as a function of temperature. For Pb–Li systems the activity–temperature relationship is of the form [17,18]:

$$\ln a_{Li} = A + B/T. \tag{2}$$

The same activity–temperature form is assumed for Sn–Li. Because Li and Sn have low activities similar to those of Pb and Li in Pb–Li and because Sn–Li have similar activity–concentration relationships (Eq. (1)), the Pb–Li constant A is assumed to determine B for Sn–Li. Table 1 shows the estimated activity–temperature relationships for Li in Sn–Li alloys. In lieu of lack of experimental data these activities values are used to determine the stability of potential ceramic materials.

3. Thermodynamics of dissolved solutes

The compatibility of ceramics with Sn–Li can be determined from the corresponding free energy of reaction ($\Delta_r G$) as a function of temperature, lithium concentration, and non-metal solute concentration. To evaluate $\Delta_r G$, the activity of the solutes, O, C, N, and H

have to be known, which depend on the standard free energy of formation, $\Delta_f G$, of corresponding Li-salts (Li$_2$O, Li$_3$N, Li$_2$C$_2$, and LiH).

The activity relationships for oxygen, nitrogen, carbon, and hydrogen in Sn–Li can be established using equilibrium conditions of saturated solutions. Equations for Li$_2$O are given below, while similar expressions are used for Li$_3$N, Li$_2$C$_2$, and LiH:

$$2\text{Li(Sn–Li)} + \text{O(Sn–Li)} \overset{\Delta_f G^0(\text{Li}_2\text{O})}{\rightleftarrows} \text{Li}_2\text{O}, \tag{3}$$
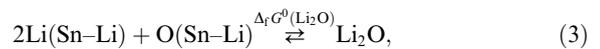
where $\Delta_f G$ is evaluated at temperature T (K) using

$$\Delta_f G^0(\text{Li}_2\text{O}) = RT \ln K_e = RT \ln\{a_{\text{Li}_2\text{O}}/a_{\text{Li}_2} \cdot a_O\}, \tag{4}$$

where R is the gas constant, a_i is chemical activity of specie i and K_e is the equilibrium constant, expressed by the RHS of Eq. (4). The activity of Li$_2$O is very low, thus Eq. (4) can be solved for the oxygen activity:

$$\ln a_O = \{-\Delta_f G^0(\text{Li}_2\text{O})/RT\} - 2\ln a_{Li}. \tag{5}$$

The standard energy of formation of the salts, Li$_2$O, Li$_3$N, Li$_2$C$_2$, and LiH are taken from the JANAF Thermochemical Tables [20]. The estimated chemical activities of Li, O, C, N, and H in Sn–Li at 773 K are shown in Fig. 1. Most oxides are unstable in liquid lithium due to the stability of Li$_2$O (large negative $\Delta_f G^0(\text{Li}_2\text{O}) = -497.3$ [kJ/mol] at 773 K). Fig. 1 shows a strong negative activity of oxygen in Sn–Li for all values of x_{Li}. In contrast, for x_{Li} below 0.6, 0.74, and 0.87 the activities of C, N, and H are respectively positive. This indicates that carbides and nitrides would be stable in Sn–25Li and LiH formation is suppressed at 773 K. Calculations at higher temperatures showed that the activity of oxygen remains negative even at 1773 K, thus Li$_2$O would be stable at elevated temperatures. The zero activity lines ($\ln a_i = 0$; $i = $ C, N, H) for Li$_2$C, LiN, and LiH are shown in Fig. 2. At 500 °C
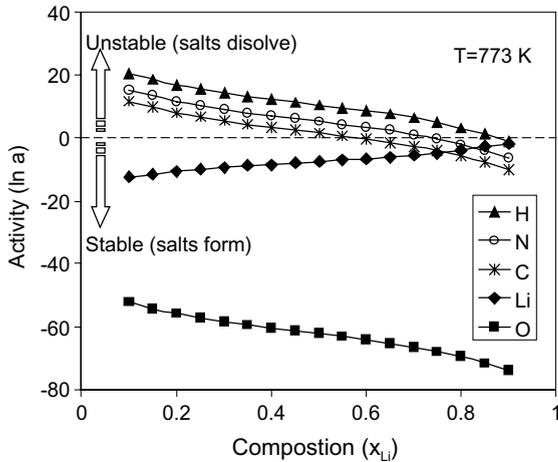
Fig. 1. Activity–composition relationship of Li, O, H, N, and C in saturated Sn–Li at 773 K.
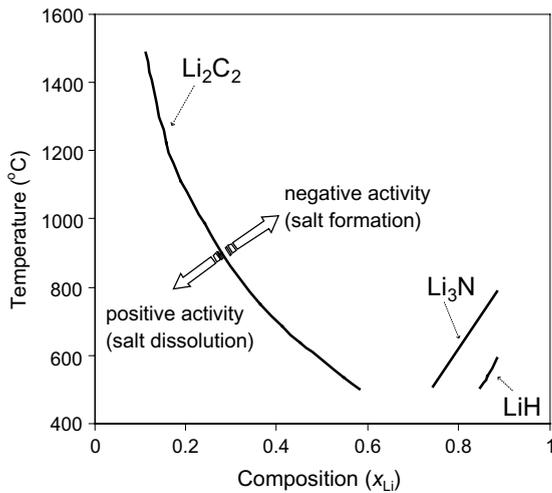

Fig. 2. Zero-activity-composition lines (ln $a_i = 0$; i = C, N, or H) for Li_2C_2, Li_3N, and LiH in Sn–Li; right and left sides of the zero-activity lines indicate stable and unstable regimes for salt formation, respectively.

LiH and Li_3N form if Li contents are above 0.85 and 0.75, respectively. For LiH and Li_3N to be stable at higher temperatures, the Li content has to increase. However, the stability of Li_2C_2 increasing with rising temperatures. The maximum operating temperature would be ∼900 °C to avoid forming Li_2C_2.

4. Thermodynamics of ceramics

The stability of ceramic coatings in liquid Sn–Li can be inferred from the free energy change of reaction ($\Delta_r G$)

[17], which depends on the reduction reaction of the ceramic in Sn–Li. For oxide ceramic (M_xO_y) the associated free energy of change of the reaction is expressed as

$$\Delta_r G = \frac{1}{x}\{y\overline{G_O}(\text{Sn–Li}) - \Delta_f G^0(M_xO_y)\}, \qquad (6)$$

where $\overline{G_O}(\text{Sn–Li})$ is the solute free energy in Sn–Li, in this case of oxygen, and $\Delta_f G^0$ is the metal oxide formation energy. The oxide ceramic reduction reaction is evaluated using

$$M_xO_y \xrightarrow{\text{liquid Sn–Li}} yO(\text{Sn – Li}) + xM. \qquad (7)$$
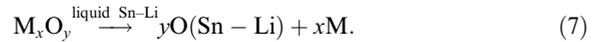
Eq. (6) represents a relative equilibrium state between the oxygen solute free energy and the Gibbs free energy of the metal oxide formation, which by definition is the thermodynamic driving force $\Delta_r G$. For a smaller $\Delta_f G^0$ relative to $\overline{G_O}(\text{Sn–Li})$ the oxide is more stable than the oxygen in solution with Sn–Li. This would indicate that an oxide ceramic would be thermodynamically compatible with Sn–Li. To evaluate $\Delta_r G$ for oxides, nitrides, and carbides, the Gibbs free energy of formation and the free energy of the associated solutes need to be known. The formation energies are tabulated [20], while the solute free energies are evaluated from solubility data using

$$\begin{aligned} G_O(\text{Sn–Li}) &= RT\ln a_O = RT\ln a_O^* + RT\ln(x_O/x_O^*) \\ &= \Delta_f G^0(Li_2O) - 2\overline{G_{Li}}(\text{Li}) + RT\ln(x_O/x_O^*), \end{aligned} \qquad (8)$$

where a_O^* is the oxygen activation at saturation, x_O is the oxygen concentration, and x_O^* is the oxygen concentration at saturation, and $\overline{G_{Li}}$ ($= RT\ln a_{Li}$) is the partial free energy of dissolved lithium. Of the four salts (LiH, Li_3N, Li_2C_2, and Li_2O) only Li_2O is sufficiently stable to form in Sn–Li at any temperature, the others decompose to saturated non-metals in solution at Li-concentrations of $x_{Li} < 0.65$ at 773 K.

The solubility of oxygen in Pb–17Li has been measured ($x_O \sim 3.256 \times 10^{-4}$ at 743 K) and is found to be a factor of ∼10^3 and ∼10^4 lower than in Pb ($x_O \sim 3.14 \times 10^{-5}$ at 743 K) or Li ($x_O \sim 5.34 \times 10^{-4}$ at 743 K) [17]. The solubility of oxygen in Sn is also very low and comparable to that in Pb (at 809, 873, and 973 K the solubility limits are 6×10^{-6}, 2×10^{-4}, and 6×10^{-4} at.%, respectively [21]). Because of lack of solubility data in Sn–Li and because of similar low solubility limits of oxygen in Pb and Sn, the solubility of oxygen in Sn–Li will be approximated using the well established solubility data in lithium. For H and N the solubilities are driven by their partial pressures. However, the current analysis assumes saturated solute levels only. Thus for O, N, and H the following Li solubilities for O, N, and C are used [17–19]:

$$\ln x_O = 1.428 - 6659 \ (T/K)^{-1},$$
$$\ln x_N = 2.976 - 4832 \ (T/K)^{-1}, \tag{9}$$
$$\ln x_C = -1.100 - 5750 \ (T/K)^{-1}.$$

Because of its low solubility in Sn, oxygen is assumed to be maintained at the saturated level in regardless of the level of purification. Furthermore, because the lithium salts LiH, Li_3N, and Li_2C_2 decompose readily (at $x_{Li} < 0.65$; $T = 773$ K), a simplified expression can be derived for the solute free energies:

$$G_O(\text{Sn–Li}) = \Delta_f G^0(Li_2O) - 2\overline{G_{Li}}(Li). \tag{10}$$

Using Eqs. (6) and (8) the free energy of change of reaction for oxide ceramic materials can be evaluated by

$$\Delta_r G = \frac{1}{x}\{y[\Delta_f G^0(Li_2O) - 2\overline{G_{Li}}(\text{Sn–Li})]$$
$$- \Delta_f G^0(M_xO_y)\}. \tag{11}$$

4.1. Free energy changes of reaction of ceramics

Fig. 3 shows the calculated free energy changes of reaction ($\Delta_r G$) of several oxides in Sn–Li at 773 K. Fe_2O_3, Cr_2O_3, and NiO have negative $\Delta_r G$ values in liquid Sn–25Li for all compositions of Sn–Li, which indicates dissolution. $LiCrO_2$ is stable up to about 50 at.% Li, for compositions with higher lithium content $LiCrO_2$ would unstable. Based on these free energy calculations Li_4SiO_4 and Y_2O_3 are stable in Sn–25Li at 773 °K over the entire Li-composition range.
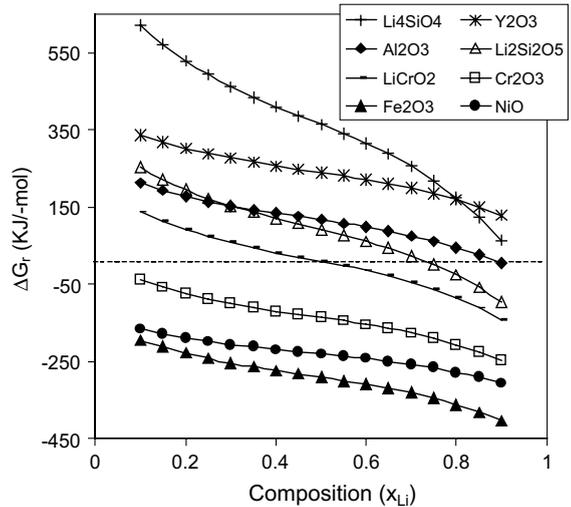

Fig. 3. Energy of reaction ($\Delta_r G$) of several oxides ceramics in solute saturated Sn–25Li at 773 K.
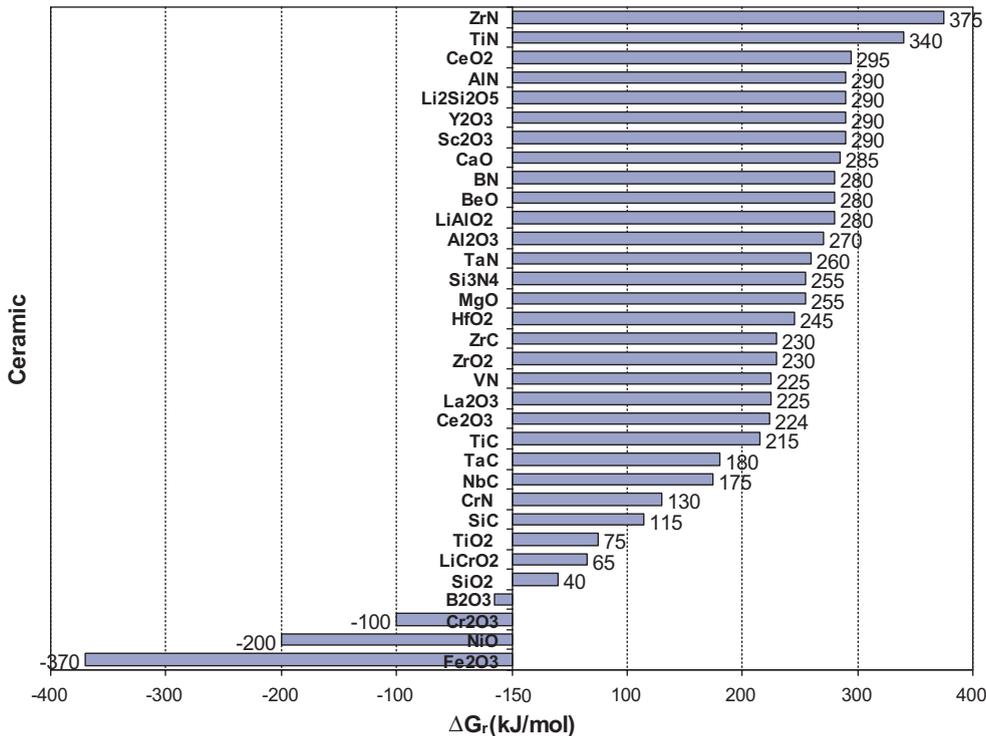

Fig. 4. Energy of reaction ($\Delta_r G$) of selected ceramic materials in solute (O, N, C) saturated Sn–25Li at 773 K.

Fig. 4 summarizes the stability ($\Delta_r G$) of various ceramics in Sn–25Li at 773 K. Most nitrides and carbides would be stable in liquid Sn–25Li at 773 K, with ZrC and TiC being the most stable carbides. Based on the energy of reaction the stability of nitride, oxide, and carbide-based coatings can be categorized as follows: (1) the nitrides, ZrN, TiN, AlN, BN, TaN, VN, CrN, and Si_3N_4 are quite stable with ZrN being the most stable one; (2) the carbides ZrC, TiC, TaC, NbC, and SiC hold promise to be stable with ZrC being the most stable one; and (3) among the oxides the free energy changes of reaction ($\Delta_r G$) of Fe_2O_3, Cr_2O_3, and NiO are negative for all compositions of Sn–Li, which would indicate dissolution of these oxides. B_2O_3 was found to be stable up to about 0.2 Li, for compositions with higher lithium content B_2O_3 would not be stable. SiO_2 and TiO_2 are only marginally stable in Sn–25Li at 773 K. Sc_2O_3 and Y_2O_3 are the most stable oxides, while the other oxides Al_2O_3, La_2O_3, Ce_2O_3, ZrO_2, HfO_2, CeO_2, BeO, MgO, CaO, $LiAlO_2$, $LiCrO_2$, $Li_2Si_2O_5$, Li_2SiO_3, and Li_4SiO_4 hold promise to be stable in Sn–25Li at 773 K.

5. Conclusions

Thermodynamic analysis was used to evaluate the stability of potential ceramic materials in Sn–25Li at 773 K. Several assumptions had to be made due to lack of experimental data: (1) the activity of lithium was extrapolated using Pb–Li activity data, (2) the solubility of the solutes (O, C, N, H) was based on their solubility in pure lithium, and (3) the Sn–Li contains saturated solution of the solutes.

The actual lithium activity in Sn–Li varies from that in Pb–Li, which has to be determined experimentally. The solubility of the solutes (O, N, C, H) in Sn–Li was assumed to be dominated by the solubility in lithium, because of their very low solubility in pure Sn. The third assumption may have very significant implications on the stability of candidate ceramic coatings. Purification of Sn–Li may be advantages because of radioactivity control, tritium extraction, or minimizing bi-metallic loop material transport, however it could adversely affect the thermodynamic stability of ceramic coatings in liquid Sn–Li.

At 773 K the energy of reaction ($\Delta_r G$) between solute-saturated liquid Sn–25Li and selected nitrides, carbides, and oxides, indicates that nitrides are the most stable followed by carbide and then oxide ceramics. The most stable nitride, carbide and oxide ceramics were found to be ZrN, ZrC, and CeO_2 respectively.

References

[1] D.K. Sze, R.F. Mattas, Z. Wang, E.T. Cheng, M. Sawan, S.J. Zinkle, K.A. McCarthy, Presented at the 9th International Conference on Fusion Reactor Materials, 9–15 October 1999, Colorado Springs.

[2] M. Abdou et al., Fusion Eng. Des. 54 (2001) 181.

[3] K. Natesan, W.E. Ruther, J. Nucl. Mater. 307–311, Part 1 (2002).

[4] R. Bastasz, W. Eckstein, J. Nucl. Mater. 290–293 (2001) 19.

[5] T.D. Rognlien, M.E. Rensink, J. Nucl. Mater. 290–293 (2001) 312.

[6] J.P. Allain, D.N. Ruzic, M.R. Hendricks, J. Nucl. Mater. 290–293 (2001) 33.

[7] D.K. Sze et al., APEX Interim Report, University of California Los Angeles Report, Nov. 1999, vol. 2, UCLA-ENG-99-206.

[8] S. Sharafat, N. Ghoniem, University of California Report, Mech. & Aero. Engr. Dept., October 2000, UCLA-UCMEP-00-31. Available from <http://www.fusion.ucla.edu/APEX/interim_report.html>.

[9] M.A. Fütterer, G. Aiello, F. Barbier, L. Giancarli, Y. Poitevin, P. Sardain, J. Szczepanski, A. Li Puma, G. Ruvutuso, G. Vella, J. Nucl. Mater. 283–287, Part 2 (2000) 1375.

[10] R.F. Mattas et al., Fusion Eng. Des. 49 (2000) 127.

[11] B.A. Pint, J.R. DiStefano, P.F. Tortorelli, Fusion Sci. Technol. 44 (2) (2003) 433.

[12] A. Suzuki, T. Muroga, B.A. Pint, et al., Fusion Eng. Des. 69 (1–4) (2003) 397.

[13] R.N. Lyon, Liquid Metals Handbook, The Atomic Energy Commission, 1952.

[14] E.L. Reed, J. AcerS 37 (1954) 146.

[15] D.M. Bailey et al., JLCM 64 (1979) 233.

[16] M. Abdou et al., APEX, Interim Report, vol. 2, University of California Los Angeles, 1999, p. 8.

[17] P. Hubberstey, J. Nucl. Mater. 247 (1997) 208.

[18] P. Hubberstey, T. Sample, J. Nucl. Mater. 248 (1997) 140.

[19] P. Hubberstey, A.J. Dadd, P.G. Roberts, in: H.U. Borgstedt (Ed.), Material Behavior and Physical Chemistry in Liquid Metal Systems, Plenum Press, New York, 1982.

[20] J. Phys. Chem. Ref. Data, 14 (Suppl. 1) (1985).

[21] T.N. Belford, Trans. Faraday Soc. 61 (1965).