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Vaporization properties of the Sn–25 at.%Li alloy

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Abstract

This paper reports the results of mass-spectrometer experiments on the vaporization properties of pure Li and two different Sn–25 at.%Li alloys heated in a Knudsen effusion source at temperatures from 800 to 1200 K. A Li vaporization energy of 172 kJ/mol was obtained from the analysis of three combined Sn–25 at.%Li experiments. Li vapor pressures for Sn–25 at.%Li were derived from the data by comparing the *IT* (Li^+ ion current × temperature) products from Sn–25 at.%Li experiments with the measured *IT* product from a pure Li experiment at 816 K for which the vapor pressure is 1.8 Pa. The derived vapor pressures are more than three orders of magnitude below the corresponding vapor pressures for pure Li, and they are generally in good agreement with previous data obtained from a variety of different measurement techniques.

1. Introduction

In recent developments of fusion energy concepts, the use of liquid tin–lithium alloys (e.g. Sn–20%Li) has been proposed as a novel breeding material because such alloys have attractive thermo-physical properties, and they are expected to exhibit low vapor pressures at operating temperatures. Fütterer et al. [1] have evaluated the use of Sn–Li alloys as a blanket breeder material in comparison to Pb–17Li blanket concepts and concluded that Sn–Li alloys are best-suited for free surface blanket concepts because of potentially low vapor pressures. Because the vaporization data for Sn–Li alloys are somewhat limited, we have conducted a mass-spectrometric investigation on the vaporization properties of the Sn–25 at.%Li alloy heated in a Knudsen effusion source from 800 to 1200 K, and we report the principal results in this paper.

Thermodynamic properties for Sn–Li alloys have been summarized in various reviews [2–4] that include Li activity coefficients derived from measurements based on emf, calorimetry and vaporization techniques. Key emf references include: Moser et al. [5] with measurements at 775–906 K for Li mole-fractions X_{Li} varying from 0.1 to 0.6; Barsoum and Tuller [6], 593–743 K, for X_{Li} from 0.2 to 0.44; Wen and Huggins [7], 633–863 K, for X_{Li} from 0.0 to 0.86; Morachevski et al. [8], 823 K, for X_{Li} from 0.04 to 0.5; and Foster et al. [9], 800–1050 K, for X_{Li} from 0.1 to 0.65. Based on Knudsen vaporization measurements, Baradel et al. [10] report Li activity coefficients at 973 and 1123 K for X_{Li} from 0.0 to 0.70. Fischer and Johnson [11] report Li activity coefficients derived from transpiration measurements at 1473 K for X_{Li} from 0.1 to 0.9. These results indicate that the ratio of Li vapor pressure above molten Sn–25 at.%Li to that above pure Li ranges from 10^{-5} to 10^{-3} as the temperature varies from 600 to 1000 K.

2. Experimental details

2.1. Sample description

Two different batches of Sn–Li samples were studied, one type prepared at Argonne National Laboratory (ANL) [12] and the second prepared at the University of Wisconsin (UW) [13]. Both materials were prepared by reacting pure Li and Sn, with the melting and mixing operations conducted under an inert atmosphere. The

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nominal composition of the ANL material was 75 at.%Sn and 25 at.%Li. This material had a melting point of 607 K and a density of 6.36 g/cm^3 [12]. The nominal composition of the UW material was 74 at.%Sn and 26 at.%Li. Vaporization samples were obtained by fracturing cast cylinders of the UW and ANL material and by using pieces from the interior. The outer surfaces of both cast cylinders were a dull gray. Fracturing of the UW cylinder resulted in pieces that appeared shiny and facetted. In contrast, the fractured pieces of ANL material appeared a dull gray throughout, even for internal surfaces. All fracturing and sample handling of the ANL material for the mass-spectrometer measurements were done in an air environment, whereas, similar operations for the UW material were done under an inert environment. Sample masses were 100–300 mg.

Lithium metal was used to calibrate the high temperature mass-spectrometer system. This material, 99.9% Li ribbon from Aldrich Chemical, was handled in a glovebox under an inert atmosphere. Approximately 35 mg samples were cut from the ribbon, loaded into sample crucibles, and transferred under inert gas purge into the mass spectrometer.

2.2. *Mass spectrometer experiments*

We used a Nuclide model 12-90-HT-1.15 mass spectrometer for these measurements. This single-focusing instrument is equipped with (1) a Knudsen molecular-effusion source (2) an electron-bombardment ion source to ionize molecular effusing species, (3) a 30 cm radius of curvature, 90° magnetic sector mass/charge analyzer, and (4) a detector stage equipped both with a Faraday cup and a channeltron for beam current measurements. The Knudsen effusion source consisted of a 7.92 mm diameter × 13.5 mm long Mo crucible held inside a W crucible holder that was surrounded by a W-filament heating element. This assembly was surrounded by Ta heat shields and could be heated to about 2300 K. Temperature of the Knudsen crucible was measured by a thermocouple inserted into the crucible holder. Internal dimensions of the crucible were 5.06 mm diameter by 9.52 mm long and the 1.6 mm thick cover had a 0.889 mm diameter orifice. Base pressure in the mass-spectrometer system was typically about 10^{-6} Pa. Typical mass-spectrometer operating conditions were: emission current, 2 mA; electron energy, 70 eV; ion acceleration voltage, 5 kV; and detector gain, 10^5.

The approach taken in these experiments was to measure ion intensities and spectra of the effusing species as a function of sample temperature for several Sn–25 at.%Li and Li samples. For the Sn–Li vapor-pressure measurements, sufficient sample material (100–300 mg) was used to minimize the influence of compositional changes during the measurements. Typically the sample temperature was not changed in a monotonic manner, rather it was varied both up and down throughout a run. Ion intensities were measured at several temperatures for each Sn–25 at.%Li sample, and the sample was typically not run to complete depletion of the Li. However, some Sn–Li samples were heated to temperatures above 1200 K to determine the temperature at which Sn was first observed. The pure Li samples were typically run at a constant temperature throughout most of the run to maintain equilibrium conditions between the vapor and condensed phase, and the pure Li samples were run to exhaustion.

In these experiments, the predominant ion observed was $^{7}\text{Li}^+$. We saw no dimer or oxide species associated with Li. No Sn ions ($^{120}\text{Sn}^+$) were observed in Sn–Li experiments at temperatures less than 1273 K and typically this ion was not observed until the Li ion disappeared.

3. Analysis and results

The results of mass-spectrometer measurements for three portions of the UW Sn–Li sample are shown in Fig. 1. Each data point is the product of a Li$^+$ ion intensity and the corresponding temperature T in Kelvin, and it is plotted on a semi-log graph as a function of inverse temperature. The data show a typical 'second law' linear relationship [14]. The linear fit to the combined set of data gives a slope that corresponds to the heat of vaporization of Li from the Sn–25 at.%Li alloy, namely, 172 kJ/mol.

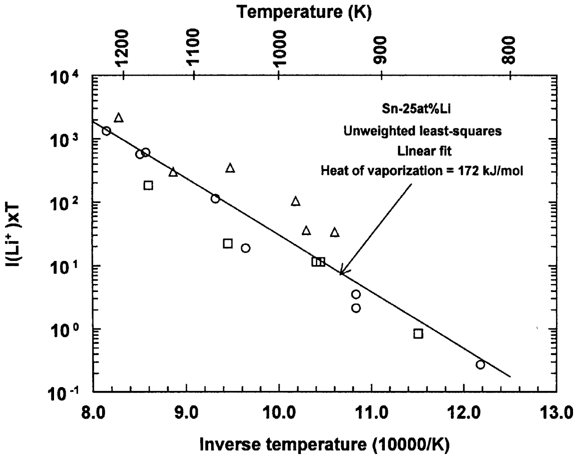

Fig. 1. Semi-log plot of the product IT (Li$^+$ ion current × temperature in K) as a function of inverse temperature for three UW Sn–25 at.%Li analyses shown by the different symbols.

Absolute vapor pressures for the Sn–25 at.%Li samples were derived by the 'method of comparing ion currents' [14]. The approach is based on the equation $p = CIT$, were p is the pressure inside the Knudsen source at an absolute temperature T, I is the ion intensity for the vaporized species, and C includes other factors such as isotopic fraction, ionization cross-section, emission current, and detector gain. Our measurements for Sn–25 at.%Li and pure Li were run with all instrument conditions identical and with measurements of the dominant ionization species, $^7\mathrm{Li}^+$, so C is the same for the individual measurements. As a result, we computed the Li vapor pressures over Sn–25 at.%Li, p_{SnLi}, using the equation $p_{\mathrm{SnLi}} = [(IT)_{\mathrm{SnLi}}/(IT)_{\mathrm{Li}}]p_{\mathrm{Li}}$, where $(IT)_{\mathrm{Li}}$ is the IT product measured for a pure Li sample at 816 K, p_{Li} is 1.8 Pa, the vapor pressure of Li at 816 K as computed using FactSage 5.0 [15], and $(IT)_{\mathrm{SnLi}}$ are IT products for Sn–25 at.%Li samples at different temperatures.

The results of the vapor pressure analyses are shown in Fig. 2. INEEL01, INEEL02, and INEEL03, identified by solid squares, solid circles and crosses, respectively, represent the data sets for the three UW sample analyses. The two solid triangle data points, INEEL04, were obtained from measurements for one ANL sample. We also show in this figure vapor pressure values derived from previous work: transpiration datum from Fischer and Johnson [11], open upward triangle at 1473 K; Knudsen vaporization measurements by Baradel et al. [10], open squares at 973 and 1123 K; and emf references: Moser et al. [5], open diamonds at 800 and 900 K; Barsoum and Tuller [6], open circles at 606–694 K; and Foster et al. [9], open downward triangles at 823 and 900 K. Typically, the results from previous work were derived from activity coefficients or partial Gibbs energies reported in the publications. Fig. 3 presents a comparison of our vaporization data and that from the previous work, with all data expressed as Li activity ($p_{\mathrm{SnLi}}/p_{\mathrm{Li}}$), where p_{SnLi} and p_{Li} are the Li vapor pressures over Sn–25 at.%Li and pure Li, respectively.

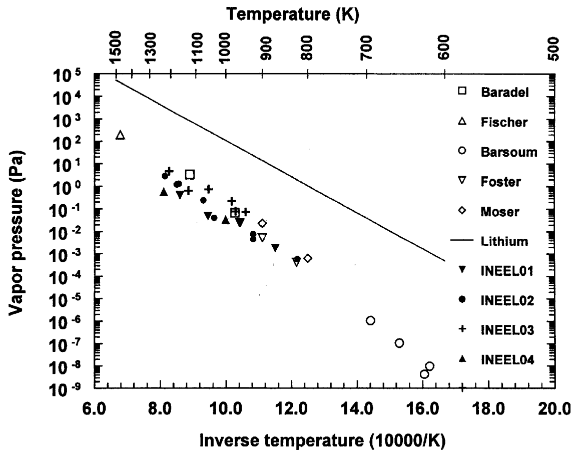

Fig. 2. Semi-log plot of Li vapor pressure over Sn–25 at.%Li alloys (experimental data) compared to vapor pressure of pure Li (straight line).

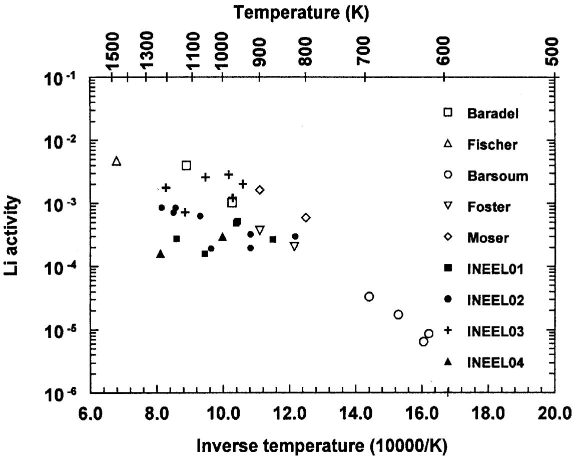

Fig. 3. Semi-log plot comparing Li activities derived from present experiments (INEEL01–INEEL04) with activities reported in previous studies.

4. Discussion

These Knudsen vaporization experiments have demonstrated that the vapor above molten Sn–25 at.%Li in the temperature range 800–1200 K is predominately Li, and that the Li vapor pressure is at least three orders of magnitude below that of pure Li. In general, vapor pressures measured over the UW material are in good agreement with previously published data up to 1000 K but are somewhat smaller than other data above 1000 K. We suspect that one reason for this difference above 1000 K could be a change in the Li vaporization coefficient, α, at higher temperatures ($\alpha < 1$ would result in lower measured ion intensities). We also note that the vapor pressure results for the ANL test material were typically lower than the other data, especially at the highest temperature. Again, this could be due to a reduced α for Li in this temperature regime or to oxidation of the test material during sample handling operations in air. In our experiments, we derived a Li heat of vaporization of 172 kJ/mol for the Sn–25 at.%Li material. This value is between that for pure Li, 136 kJ/mol, and that for pure Sn, 293 kJ/mol, and accounts for the reduction in Li vaporization rate for the Sn–Li alloy. In conclusion, the vaporization results from these experiments confirm the benefit of using Sn–25%Li for free-surface blanket concepts in fusion systems because it has low vapor pressures at relevant temperatures.

Acknowledgements

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References

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

[2] W. Gasior, Z. Moser, Archiv. Metall. 44 (1999) 83.

[3] J. Sangster, C.W. Bale, J. Phase Equil. 19 (1998) 70.

[4] J.F. Smith, Z. Moser, J. Nucl. Mater. 59 (1976) 158.

[5] Z. Moser, W. Gasior, F. Sommer, G. Schwitzgebel, B. Predel, Metall. Trans. B 17B (1986) 791.

[6] M.W. Barsoum, H.L. Tuller, Metall. Trans. A 19A (1988) 637.

[7] C.J. Wen, R.A. Huggins, J. Electrochem. Soc. 128 (1981) 1181.

[8] A.G. Morachevski, L.N. Gerasimenko, A.I. Demidov, O.A. Drozdova, Electrokhimiya 8 (1972) 1622.

[9] M.S. Foster, C.A. Crouthamel, S.E. Wood, J. Phys. Chem. 70 (1966) 3042.

[10] P. Baradel, A. Vermande, I. Ansara, P. Desre, Rev. Int. Hautes Temp. Refract. 8 (1971) 201.

[11] A. Fischer, S.A. Johnson, J. Chem. Eng. Data 17 (1972) 280.

[12] K. Natesan, W.E. Ruther, Fabrication and properties of a Tin-Lithium alloy, in Fusion Materials Semiannual Progress report for the Period ending 31 December 1999, DOE/ER-0313/27, 2000.

[13] M. Anderson, University of Wisconsin, private communication, March 20, 2001.

[14] V.L. Stolyarova, G.A. Semenov, in: J.H. Beynon FRS (Ed.), Mass Spectrometric Study of the Vaporization of Oxide Systems, John Wiley, New York, 1994, p. 23.

[15] C.W. Bale, FACT Sage 5.0, THERMFACT Ltd., 447 Berwick, Mount-Royal, Montreal, Quebec, Canada, 2001.