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Vaporization of liquid Pb-Li eutectic alloy from 1000K to 1200K - A high temperature mass spectrometric study

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ABSTRACT

Liquid lead-lithium eutectic will be used as a coolant in fusion reactor blanket loop. Vapor pressure of the eutectic is an important parameter to accurately predict its in-loop behavior. Past measurements of vapor pressure of the eutectic relied on indirect methods. In this paper, we report for the first time the in-situ vaporization behavior of the liquid alloy between 1042 and 1176 K by Knudsen effusion mass spectrometry (KEMS). It was seen that the vaporization occurred by independent evaporation of lead and lithium. No complex intermetallic vapor was seen in the mass spectra. The partial pressures and enthalpy of vaporization of Pb and Li were evaluated directly from the measured ion intensities formed from the equilibrium vapor over the alloy. The activity of Li over a temperature range of 1042–1176 K was found to be 4.8×10^{-5} to that of pure Li, indicating its very low activity in the alloy.

1. Introduction

Eutectic lead lithium ($Pb_{83}Li_{17}$) alloy is being considered as a coolant, neutron multiplier and tritium breeder for International Thermonuclear Experimental Reactor (ITER) and Fusion Power Reactors (FPR) [1–5]. In ITER and FPR, the coolant $Pb_{83}Li_{17}$alloy is maintained at an operating temperature of 400–550 °C (673–823 K) for more than 10000 h [6].

Problems of evaporation of liquid metals like sodium in fast reactors [7] are well known. The aerosols are known to result in heat loss and usually deposit in cooler portions [7] far away from the evaporating surface. In liquid metals like eutectic lead lithium ($Pb_{83}Li_{17}$) alloy, owing to its lower vapor pressure compared to sodium [7,8], the aerosol problem is less pronounced. However, as the ITER and future FBR will operate for long durations, activation products from lead/lead-lithium eutectic is expected to build up [9] and any aerosols due to the vaporization of the liquid alloy can cause high dose rates [7]. Feuerstein et al. [10] reported that during reactor operations lithium in the eutectic will be eventually used up by burn-up, reaction with air, and by evaporation. Preferential loss of Li from $Pb_{83}Li_{17}$ liquid eutectic may lead to change in the composition of eutectic and might lead to partial crystallization of liquid into solid lead/PbLi solid [10], the amount dictated by the equilibrium phase diagram of Pb-Li [11]. It is thus seen that the vapor pressure of liquid metallic coolant is an important parameter to accurately predict its in-loop behavior. Accurate measurement of vapor pressure for liquid metals/alloys at high temperatures are difficult due to the limitations of technique [12]. Hence even at a given temperature, the data reported may vary by orders of magnitude, from one investigator to the other [12]. In the standard data base of Pb-Li eutectic reported by Mas de les Valls et al. [8], it could be seen that the accepted data for the vapor pressure of Pb-Li eutectic is an unique entry from the work of Feuerstein et al. [7,10]. The measurement technique used by Feuerstein et al. [7] was to heat the eutectic in a Mo crucible and condense its aerosols on a long quartz tube. The amount of Pb/Li in the condensed surface was determined by ICP-AES technique. It was thus an indirect technique. High-temperature experimental thermodynamic studies of Pb-Li alloys using EMF methods has been reported by Gasior et al. [13]. In their work, the excess free energy of Li in the alloy for ($0.025< x_{Li} <0.965$) was measured. However, the authors have reported that for a reactive alloy like Pb-Li, measurement by EMF technique introduces certain uncertainty due to the reaction of the alloy with moisture, oxygen and nitrogen [13]. In this paper, we report for the first time the in-situ vaporization behavior of Pb-Li eutectic using a Knudsen Effusion Mass Spectrometry (KEMS). Using the technique, the vapor pressure of the evaporating species

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were calculated, its heat of vaporization calculated and the activity of lithium in Pb-Li eutectic was derived using partial pressure data. Additionally, high vacuum in the chamber (10^{-11} MPa) ensured that the measurement was unaffected by the presence of moisture, oxygen and nitrogen. The data obtained from KEMS was compared with the reported data in literature to check its consistency and credibility.

Mass spectrometry in conjunction with the Knudsen effusion method, commonly referred to as Knudsen Effusion Mass Spectrometry (KEMS) [14], enables identification as well as measurement of vapor pressures of gaseous species in a wide dynamic range of ~10 Pa to ~ 10^{-7} Pa [14]. It is interesting to note that most of the well established vapor pressure data in JANAF tables have been recorded using this technique [15].

2. Experimental

Commercial Pb-Li eutectic alloy solid pieces (wt. 2.8 gm) (Chempur GmbH, Germany) was used for the experiments. The composition of the eutectic was measured using ICP-AES and was found to contain 16.8 at% ±0.1 at% of Li. Measured oxygen content by inert gas fusion technique was 50 ppm. Differential Scanning Calorimetry of the sample was done in Mettler Toledo DSC1upto 773 K in high pure helium atmosphere at a pressure of 0.2 MPa with heating rate of 2 K/min using standard alumina crucible with the lid pierced. The above parameters for DSC was selected based on Jauch et al. [16]. The calibration of Mettler Toledo DSC1 was done using standard internationally accepted reference materials using Indium (Melting point 429.6 K) and Zinc (melting point: 692.5 K). The melting point of the sample was found at 505 K ± 1 K (Fig. 1) with no other endothermic peaks, which indicates that the sample was of near eutectic composition [8]. Table 1 shows the purity of metals and alloys used in this study.

The vapor pressure measurements were carried out with an indigenously made Knudsen effusion mass spectrometer system (KEMS). The KEMS system consists of two chambers, one containing the Knudsen cell furnace assembly and the other compartment having the quadruple mass spectrometer (QMS) chamber. A vacuum-isolation valve is located in between the two chambers, to connect and disconnect the chambers as and when required. During experimentation, the residual pressure in mass spectrometer chamber was 2×10^{-13} MPa and the sample chamber had a pressure of 5×10^{-11} MPa.

The Knudsen cells made of graphite (with dimensions - inner dia: 7.5 mm, outer dia: 10.0 mm, height: 10.0 mm) was used to hold the samples. The cell was provided with a lid having knife edged effusion orifices of 0.2 mm diameter. The graphite with the sample was kept inside a tantalum cup with a tight-fitting lid made of tantalum and having a 2 mm diameter circular hole collinear with the Knudsen cell orifice. The tantalum cup (Knudsen cell) was heated by radiation and electron bombardment (EB) by two independent tungsten filaments that encircled it. Radiation shields, made of tantalum, were placed all around the filaments (as well as at the top and bottom) which aided the temperature stability of the Knudsen cell. Temperatures were measured by sighting the infrared pyrometer onto a blackbody hole drilled at the bottom of the Knudsen cell assembly. Pyrometer was calibrated by melting high pure metals Cu, Ni, Ti, V, Ag etc.

The QMS in the machine was made by Hiden Analytical (UK) having mass range upto 500 amu. In the QMS, the ions were generated by electron impact with energy of 70 eV. As mentioned above, a metallic valve separated the ion source of QMS from the Knudsen cell chamber. This is vital for accurate vapor pressure measurement. In practice, the valve does not lead to a decrease of sensitivity due to the slight increase of the distance between the ion source and the Knudsen cell. Its principal advantage is that it permits the changing of sample without breaking the vacuum level in the ion source chamber.

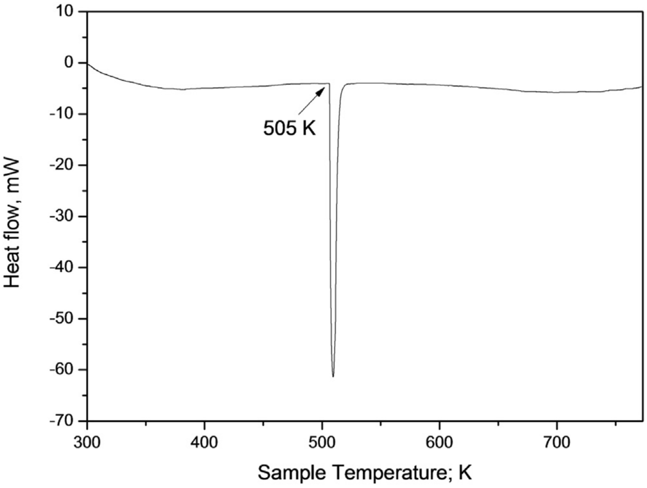

Fig. 1. DSC of the Pb-Li eutectic alloy upto 773 K in helium atmosphere.

The measured ion intensities in QMS were converted into partial pressures by means of the standard mass spectrometric relation:

$$p_i = \frac{kT}{\sigma_i A_b^i} \sum_j I_{ij} \tag{1}$$

where T is the temperature; k is the general pressure calibration constant; p_i, σ_i and are the partial pressure, the ionization cross section and isotopic abundance of species i respectively; and I_{ij} is the ion intensity of ion j originating from species i.

A constant $k_x = k/\sigma_x$ was determined by means of experiments on pure x both before and after the experiments with the actual alloys. For the current study, electrolytic grade copper (99.99% pure) was taken to be pure x (calibration material). Next, pure titanium 99.9% was vaporized and its vapor pressure was calculated using the value of k_x. This was compared with the standard vapor pressure data, to verify the correctness of k_x. The detailed methodology is described in the next section of this paper. It need to be mentioned that the calibration data obtained from Cu has also been checked in calculating the vapor pressure of silver (Ag) in the same temperature range used in this study and has given acceptable results.

k_x thus calculated was then used in calculating the partial pressures over the alloy samples. Because the calibration procedure was always performed with pure Cu, the vapor pressures over the alloy samples (here Pb-Li eutectic) can be expressed as follows

$$p_{cu} = k_{cu} I_{cu}^{+} T \tag{2}$$

$$p_{pb} = k_{pb} I_{pb}^{+} T \tag{3}$$

$$p_{Li} = k_{Li} I_{Li}^{+} T \tag{4}$$

From equations (1-4), and rearranging, we get the partial pressure of Pb in terms of copper

$$p_{pb} = k_{Cu} \frac{\sigma Cu}{\sigma Pb} \frac{A_b^{Cu}}{A_b^{pb}} I_{pb}^{+} T \tag{5}$$