Gibbs energies of formation of the intermetallic compounds of U–Sn system

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ABSTRACT

Gibbs energies of formation of the intermetallic compounds, USn_3, U_3Sn_7, USn_2, and USn were determined by using high temperature molten salt galvanic cells: $U(s)//UCl_3$ in LiCl–KCl (eutectic)//U–Sn alloy, where pure uranium was used as one of the electrodes and a two phase alloy of uranium and tin as the other. The two phase alloys used in cells I, II, III and IV as the electrodes were $\langle USn_3 \rangle + \{Sn\}$, $\langle U_3Sn_7 + USn_3 \rangle$, $\langle USn_2 + U_3Sn_7 \rangle$ and $\langle USn + USn_2 \rangle$, respectively. The Gibbs energies of formation ($\Delta_f G^0$) of USn_3, U_3Sn_7, USn_2 and USn with respect to α-U and liquid Sn, in the temperature range 682–905 K, were determined to be given by

$$\Delta_f G^0(USn_3)(\text{kJ mol}^{-1}) = -172.8 + 0.061T \ (\text{K}),$$
$$\Delta_f G^0(U_3Sn_7)(\text{kJ mol}^{-1}) = -527.8 + 0.200T \ (\text{K}),$$
$$\Delta_f G^0(USn_2)(\text{kJ mol}^{-1}) = -174.9 + 0.073T \ (\text{K}),$$
$$\Delta_f G^0(USn)(\text{kJ mol}^{-1}) = -176.9 + 0.064T \ (\text{K})$$

The Gibbs energy of formation for U_3Sn_7, USn_2 and USn have been obtained for the first time.

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1. Introduction

Molten tin process is looked upon as a potential alternative for the aqueous reprocessing of the oxide and carbide fuels. In this process, the spent fuel is dissolved in liquid tin and then subsequently subjected to nitriding and oxidation to extract the desired actinide elements leaving the fission products behind. The thermodynamic properties of U–Sn alloys are thus relevant to the liquid tin process [1], Since alloys of U and Pu with Sn and noble metal fission products have been reported to be found in the irradiated (U,Pu) mixed oxide fuels [2], thermodynamic data of the U–Sn system is important. The U–Sn phase diagram has been studied by Rough et al. [3], Sheldon et al. [4], and Palenzona et al. [5]. The former two have reported the presence of USn_3, U_3Sn_5, and U_3Sn_2 phases. However, except for USn_3, the accurate compositions of the other two phases have not been reported due to the pyrophoricity of these compounds. The examination by Palenzona et al. [5] using differential thermal analysis, metallography, X-ray diffraction and electron microscopy has shown the presence of five intermetallics, viz, USn_3, U_3Sn_7, USn_2, USn and U_5Sn_4 [5]. Johnson et al. [6] have reported the $\Delta_f G^0$ values of USn_3 and Alcock et al. [7] have reported the $\Delta_f G^0$ values of USn_3, U_3Sn_5, and U_3Sn_2 in the U–Sn system. Subsequently, Johnson [8] reviewed the thermodynamic data pertaining to U–Sn system. The review by Palenzona et al. [5] of the

system revealed that some of the phase fields including U_3Sn_5 and U_3Sn_2 phases considered in the earlier studies [7,8] are irrelevant. In view of the above, there is a need to re-examine the data reported in references [6,7] for USn_3 and to determine the Gibbs energies of formation ($\Delta_f G^0$) of other intermetallic compounds for which no thermodynamic data are available. Hence the experimental determination of the $\Delta_f G^0$ of the intermetallics in U–Sn systems by using molten salt emf method was undertaken. In this paper, the Gibbs energy of formation of USn_3 is reported in the temperature range 682–905 K and discussed in comparison with those reported in literature. The Gibbs energies of formation of U_3Sn_7, USn_2 and USn in the temperature ranges, 693–843, 692–892 and 692–892 K, respectively, are also reported in this paper for the first time.

2. Experimental

2.1. Raw materials

Nuclear grade uranium metal (99.99%) was obtained from BARC, Mumbai and spectroscopic grade high purity (99.99%) tin metal was procured from M/s. BDH, Poole, U.K. Anhydrous LiCl (>99%) from M/s. Fluka, Switzerland, analytical grade KCl (99.8%) from M/s. Glaxo Laboratories, India and anhydrous $CdCl_2$ (99%) from M/s. Merck, Germany were used for preparing the molten salt electrolyte.

2.2. Preparation of alloys

The intermetallic compounds were prepared by melting stoichiometric amounts of the constituents under argon atmosphere in an arc melting furnace (Tri-arc, M/s. Centorr, USA). The buttons thus prepared were wrapped in tantalum foils

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and were sealed in quartz ampoules after several cycles of evacuation and purging with high purity argon. The samples were annealed at 800 K for 240 h in a furnace. The X-ray diffraction patterns of the annealed sample confirmed the presence of two phase alloys.

2.3. Preparation of the electrolyte salt

The eutectic mixture of LiCl (58.5 mol.%) and KCl (41.5 mol.%) was prepared by using a procedure described elsewhere [9]. In a typical experiment, appropriate quantities of these salts were accurately weighed in a glove box having argon atmosphere, loaded into an alumina crucible and placed inside a quartz tube. This assembly was then taken out of the glove box and kept in a furnace well. This salt mixture was then purified by passing a stream of chlorine gas at 673 K and was subsequently melted, cooled and then remelted under chlorine atmosphere. UCl_3 was loaded into this melt by the following procedure. A known amount of $CdCl_2$ was added to the melt and the latter was equilibrated with pure uranium metal in an alumina crucible at 773 K under flowing argon in a glove box. The amount of uranium was so chosen that it was in excess of the stoichiometric amount required by Eq. (1).

$$2U + 3CdCl_2 \rightleftharpoons 2UCl_3 + 3Cd \tag{1}$$

Thus it was ensured that no $CdCl_2$ remained in the molten electrolyte. The unreacted uranium and the cadmium formed by the reaction (1) were left in the crucible, while the salt loaded with UCl_3 was decanted. The amount of uranium in the LiCl–KCl eutectic was determined by using a potentiometric technique based on the Davis and Gray method [10] and the concentration of UCl_3 in the salt was found to be about 3 wt.%. The salt thus prepared was stored in an argon atmosphere glove box until further use. However, before using the salt for electromotive force measurements, Cd in salt was estimated by inductively-coupled plasma atomic emission spectroscopy and was found to be below 10 ppm.

2.4. The galvanic cell and the emf measurement

A schematic diagram of the whole emf measurement system is shown in Fig. 1. The cell essentially comprises a cylindrical vessel made of stainless steel fitted with a knife edged flange having provisions for gas entry and exit, electrode leads and a thermocouple well. The electrolyte was contained in an alumina crucible that was placed inside this stainless steel vessel. The metal/alloys that were used as the electrodes were kept in tantalum cups which were welded to tantalum wires of 1.5 mm diameter. The tantalum wires were drawn through 3/8″ dia. 4-bore alumina rod for electrical insulation. The alumina rod was attached through veeco couplings on the
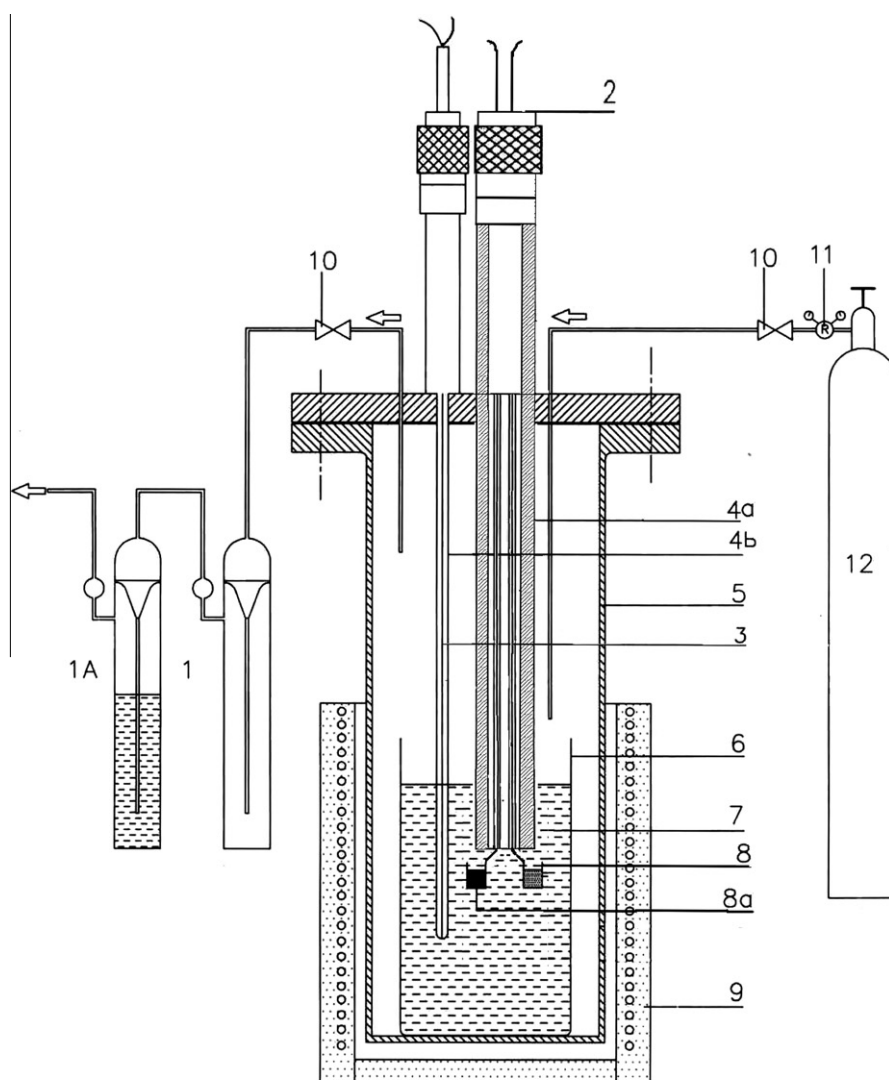
1,1A	GAS BUBBLER
2	ELECTRODE LEADS
3	THERMOCOUPLE
4a	FOUR BORE ALUMINA TUBE
4b	ALUMINA THERMO WELL
5	STAINLESS STEEL VESSEL
6	ALUMINA CRUCIBLE
7	ELECTROLYTE SALT
8	METAL ELECTRODE
8a	ALLOY ELECTRODE
9	FURNACE
10	NEEDLE VALVES
11	GAS REGULATOR
12	ARGON GAS CYLINDER

Fig. 1. Schematic of the experimental set up.