Solubility of uranium in liquid gallium, indium and their alloys

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Pyrochemical reprocessing of spent nuclear fuels (SNF) employing molten salts and liquid metals as working media is considered as a possible alternative to the existing liquid extraction (PUREX) processes. Liquid salts and metals allow reprocessing highly irradiated high burn-up fuels with short cooling times, including the fuels of fast neutron reactors. Pyrochemical technology opens a way to practical realization of short closed fuel cycle.

Liquid low-melting metals are immiscible with molten salts and can be effectively used for separation (or selective extraction) of SNF components dissolved in fused salts. Binary or ternary alloys of eutectic compositions can be employed to lower the melting point of the metallic phase. However, the information on SNF components behaviour and properties in ternary liquid metal alloys is very scarce.

In the present study solubility of uranium (primary fissile material) were determined in liquid Ga, In and their alloys (containing 21.8, 40 and 70 wt. % In) over 800 degrees range. The alloy containing 21.8 % In represents the eutectic composition with the lowest melting point of 289 K (16 ^{o}C) in the binary Ga–In system. Solubility of uranium was determined using four different techniques: from the difference of activity and activity coefficients determined by electromotive force measurements; by filtering supersaturated alloys; by precipitation of intermetallic compounds from supersaturated alloys; and by centrifuging supersaturated alloys.

Solubility of uranium in individual liquid gallium and indium is presented in Fig. 1. The proposed liquidus line in the Ga-rich region of Ga-U binary phase diagram [1] gives considerably higher uranium solubility than was obtained from the results of experimental measurements in the present work. In-U binary phase diagram is not known and there is only a part of liquidus line from the indium side [1]. Fig. 1 shows that the proposed line agrees well with the results obtained in the present work. Solubility of uranium (in molar fractions) in Ga and In can be expressed by the following equations.

Gallium based alloys:

$$\lg X_{U(Ga)} = 0.4074 - 2954.2 / T \quad (600\text{–}1073\ K)$$
$$\lg X_{U(Ga)} = -2.5051 - 1218.4 / T \quad (296.5\text{–}600\ K)$$

Indium based alloys:

$$\lg X_{U(In)} = 3.2059 - 6445.7 / T \quad (780\text{–}1069\ K)$$
$$\lg X_{U(In)} = -0.3722 - 3610.7 / T \quad (607\text{–}780\ K)$$

Solubility of uranium in Ga-In alloys depends on the alloy composition, Fig. 2. Increase of indium content in the alloy results in lowering uranium solubility. Solubility of uranium in the studied alloys is described by the following equations.

Ga-21.8 wt.% In:

$$\lg X_U = -0.1693 - 2839.3 / T \quad (530\text{–}1076\ K)$$
$$\lg X_U = -3.8033 - 930.85 / T \quad (297\text{–}530\ K)$$

Ga-40 wt.% In:

$$\lg X_U = 2.1594 - 5253.8 / T \quad (710\text{–}985\ K)$$
$$\lg X_U = -3.3337 - 1380.3 / T \quad (446\text{–}710\ K)$$

Ga-70 wt.% In:

$$\lg X_U = -0.229 - 3793.9 / T \quad (680\text{–}1060\ K)$$
$$\lg X_U = -4.8354 - 635.8 / T \quad (470\text{–}608\ K)$$

X-ray diffraction analysis of the intermetallic compounds precipitated from the Ga-In alloys showed that all of them were isostructural with UGa_3 phase. Increasing indium content in the starting allow to 70 wt.% (58.6 at.%) resulted in a very minor change of the lattice parameter from 4.251 Å for the phase formed in Ga to 4.255 Å for the phase formed in Ga-70 wt.% In alloy. For comparison, the lattice parameter of UIn_3 phase (also isostructural with UGa_3) is 4.601 Å. This indicates that uranium in Ga-In alloys predominantly interacts with gallium.
To check this assumption activity of uranium was measured in liquid gallium, indium and Ga-In alloys. The results are presented in Fig. 3. Activity of uranium in liquid indium is considerably higher than in gallium and Ga-In alloys. Moreover, uranium activity in Ga-In alloys containing up to 40 wt.% indium is very close to that in pure gallium. Only in Ga-70 wt.% In alloy activity of uranium is somewhat higher at higher temperatures (above 670 K); on lowering the temperature this difference becomes smaller and below 600 K activity of uranium in Ga and studied Ga-In alloys becomes virtually identical. This again confirms predominant interaction of uranium with gallium.

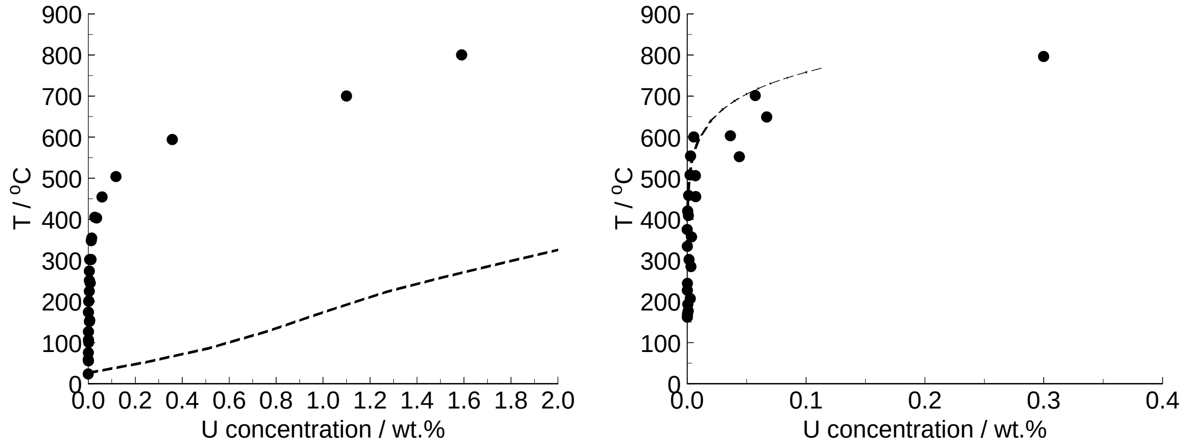

Fig. 1. Solubility of uranium in liquid gallium (left) and indium (right). Symbols show experimental data obtained in the present work, lines – proposed liquidus lines in U-Ga and U-In binary systems [1].

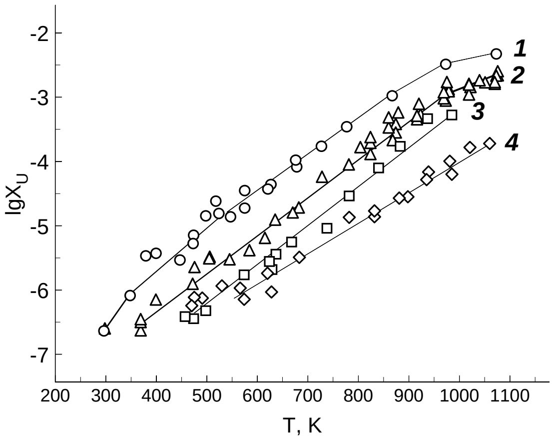

Fig. 2. Solubility of uranium in liquid gallium (1) and Ga-In alloys (2–4). Indium content of the alloys, wt.%: 21.8 (2), 40 (3), 70 (4).

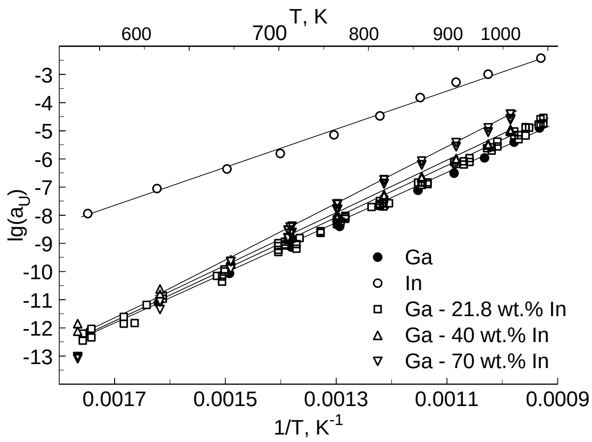

Fig. 3. Activity of uranium in liquid gallium, indium and Ga-In alloys (composition is shown for each set of data)

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References
[1] ASM Binary Phase Diagrams. ASM International (1996).