Thermodynamic properties of uranium in gallium–aluminium based alloys

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ABSTRACT

Activity, activity coefficients and solubility of uranium was determined in gallium-aluminium alloys containing 1.6 (eutectic), 5 and 20 wt.% aluminium. Additionally, activity of uranium was determined in aluminium and Ga–Al alloys containing 0.014–20 wt.% Al. Experiments were performed up to 1073 K. Intermetallic compounds formed in the alloys were characterized by X-ray diffraction. Partial and excess thermodynamic functions of U in the studied alloys were calculated.

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1. Introduction

Pyrochemical reprocessing is considered as a possible alternative to the existing solvent extraction technology for treating spent nuclear fuels, especially when dealing with fuels from fast neutron reactors or high burn-up fuels, particularly with low cooling times. Separation of fissile materials and fission products can be performed in a "molten salt – liquid metal" system using various low melting metals. Thermodynamic estimates show that aluminium is the most efficient low-melting metal for partitioning actinides and lanthanides [1,2]. For example, thermodynamically possible separation factor of U and La on liquid aluminium in a 3LiCl–2KCl eutectic based melt is around 10^8, which is four orders of magnitude higher than for the nearest competitor – gallium. However, of all the low melting metals, aluminium has the highest melting point (933.45 K) that limits its application to relatively high temperatures. Separation of An and Ln on a solid aluminium electrode can be achieved but Cassayre et al. [2] noted that a periodic melting the cathode

assisted the diffusion of deposited actinides from the surface and therefore allowed increasing loading of aluminium with actinides. High temperature chlorination of Al-An alloys is suggested as one of the ways of their subsequent reprocessing [3].

Binary and ternary metal eutectic alloys can be employed to lower working temperatures in the same way as eutectic salt mixtures are used to decrease melting point of the salt electrolytes. Addition of gallium to aluminium allows obtaining alloys with low melting points. Binary Ga–Al system has the eutectic melting at 298.8 K but it contains around 1.6 wt.% (4.2 at%) Al. Increasing aluminium content raises the melting point of the alloy.

Ternary systems containing an f-element and two low-melting metals are very little studied. Previous investigation of Ga–In eutectic based alloys with uranium, lanthanum and praseodymium [4–6] showed that addition of indium to gallium had little influence on the f-element behaviour. It was therefore of interest to study whether the behaviour of uranium in Ga–Al alloys would be different from the alloys with gallium. There is no information concerning the ternary U–Ga–Al system but the corresponding binary systems are sufficiently well studied.

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Binary U—Al phase diagram was studied employing a variety of techniques. Earlier works were reviewed by Kassner et al. [7]. Subsequent studies [8,9] clarified the situation concerning UAl_4 phase and currently three intermetallic compounds, UAl_2, UAl_3 and UAl_4 (or $U_{0.9}Al_4$) are reported for U—Al system. UAl_2 melts at 1893 K, UAl_3 UAl_4 are stable to 1624 K and 1004 K, respectively [8]. Thermodynamic modelling of U—Al binary system and *ab-initio* calculations [8,10—12] showed good agreement with the experimental data, although there is still some controversy concerning the structure and nature of UAl_4 phase.

Thermodynamic properties of solid and liquid U—Al alloys were studied using electromotive force (EMF) measurements [13,14], and activity of uranium in liquid U—Al alloys was measured at 913—1143 K. Activity coefficients of uranium in liquid aluminium based alloys were also determined at 934—1147 K using EMF method [14], and the reported values exceeded the results obtained earlier from the measurements of uranium equilibrium distribution between liquid aluminium and cadmium [15]. Solubility of uranium in liquid Al at 913—1143 K [14] agrees well with the liquidus line in U—Al phase diagram [16]. Of the ternary systems containing uranium and aluminium, U—Al—Mo is, perhaps, the best studied owing to its importance for predicting the behaviour of U—Mo fuel in aluminium matrix [17,18].

Wang et al. [19] reviewed the available data on U—Ga phase diagram and thermodynamics of uranium—gallium intermetallic compounds (IMCs), and performed calculations of U—Ga system using CALPHAD method. Uranium activity, activity coefficients and solubility in liquid alloys with gallium were studied employing various experimental methods [4,19—25].

The present work was aimed at studying the effect of Al content in Ga—Al mixtures on thermodynamic properties of uranium in U—Ga—Al alloys. To achieve this, uranium activity and solubility were experimentally determined in the alloys containing up to 20 wt. % aluminium and uranium activity coefficients were calculated from the difference of temperature dependencies of activity and solubility.

2. Experimental

The experiments were performed in aluminium and gallium—aluminium alloys containing 1.6 (eutectic), 5 and 20 wt.% Al. Pure Ga (99.9999%) and Al (99.999%) were used as the staring materials and the alloys containing below 6 wt.% Al were prepared by dissolving the required amount of aluminium in liquid gallium at 323 K in an argon filled dry box (MBraun Unilab 1200/780) using the procedure employed previously for making Ga—In alloys [4]. For the experiments involving Ga-20 wt.% Al alloys, the necessary amounts of individual metals were loaded into the experimental cells without preliminary fusing. Activity of uranium was determined by the electromotive force (EMF) method using the experimental cell and procedures described previously [4]. In addition to the Ga—Al alloys mentioned above, uranium activity measurements were also performed in the alloys based on pure aluminium and Ga—Al mixtures containing 0.014, 0.032, 0.145, 0.363, 4.75 and 5.2 wt.% Al. Beryllium oxide ceramic was used throughout this work as the material for all the items contacting with uranium containing metallic alloys or U(III) containing salt melts.

Aluminium can react with U(III) containing chloride melts [26]. Cassayre et al. [27] studied the formation of U—Al alloys by electrodepositing uranium on aluminium cathodes and detected UAl_4 and UAl_3 phases. The same compounds were formed on the surface of an aluminium plate after a prolonged immersion into a UCl_3 containing chloride melt as a result of U(III) reduction by Al metal. In the present study, aluminium-gallium alloys were used for determining uranium activity. In the experiments, the alloys contacted $LiCl—KCl—CsCl—UCl_3$ melts. Chemical analysis of the alloy samples after the experiments did not show appreciable changes in Ga-to-Al ratio, showing that aluminium was not noticeably oxidised by U(III) ions. Diluting aluminium with gallium and having the alloys oversaturated with uranium perhaps suppressed or significantly slowed down the possible reaction of Al and U(III) chloride (at least over the timescale of the experiments, not exceeding 48 h).

Solubility of uranium in gallium-aluminium alloys was determined by direct physical methods: sedimentation of excess intermetallic compounds (IMCs), filtration and centrifuging supersaturated alloys. Experimental cells and procedures employed for the measurements were described previously [28]. In addition, solubility of uranium in Ga—Al eutectic alloy was determined from the difference of experimentally measured activity and activity coefficients using the procedure described previously [4]. Activity coefficients of uranium were obtained from the electrochemical measurements of dilute homogeneous alloys [4] or calculated from the difference between experimentally determined activity and solubility values.

Concentration of uranium (and gallium and aluminium when desired) was determined in the samples of the alloys after the experiments. The samples were dissolved in a mixture of concentrated hydrochloric and nitric acids, and the solutions obtained were analysed using ICP spectrometry.

3. Results and discussion

3.1. Potentiometric study of uranium—gallium—aluminium alloys

The electrode potentials of U—Ga—Al alloys were measured *vs.* pure metallic uranium employing the following galvanic cell:

$$(-)\ U|LiCl - KCl - CsCl - UCl_3|U - Ga - Al\ (+). \qquad (1)$$
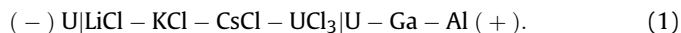
If the alloy is oversaturated with uranium, then the EMF value of the cell (1) is determined by the activity of uranium in the alloy. In this case the EMF value should not depend on uranium content providing that the alloy remains a two-phase system, *i.e.* liquid phase saturated with uranium in contact with the solid uranium IMC, and the example of the results obtained in Ga—Al eutectic based system at 573—1073 K are presented in Fig. 1(a). Alloys containing between 3.311 and 0.056 at% uranium were used and showed good reproducibility of data upon decreasing and increasing temperature. Samples containing more than 0.3 at% U remained two-phase in the entire temperature range, more dilute alloys at higher temperatures became homogeneous. The change of EMF of the cell (1), containing two-phase U-Ga-Al alloys, with temperature was not monotonous. Upon lowering the temperature, the EMF increased (as could be expected) but then after reaching a certain maximum began to decrease. Previous measurements of the potentials of U—Ga—In alloys *vs.* uranium at various Ga-to-In ratios always showed monotonous change of EMF of the corresponding galvanic cells with temperature [4,28]. To check reproducibility of such behaviour, the potentials of two-phase U—Ga—Al alloys with various Ga—to—Al ratios were measured and the results are presented in Fig. 1(b). Aluminium content in the Ga—Al alloys was varied from 0.014 to 20 wt.%. In addition, the potentials of two-phase U—Ga and U—Al alloys were also measured. The obtained results show that for U—Ga and U—Ga—Al alloys (containing 0.014 and 0.032 wt.% Al) the EMF of the cell (1) monotonously changes with temperature. For the alloys containing 0.145 wt.% Al and above, temperature dependencies of the EMF have maxima and the position of the maximum shifts to higher temperature with increasing aluminium content. Temperature range of the