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Investigation of the Pu–U phase diagram

Yoshihiro Okamoto, Atsushi Maeda, Yasufumi Suzuki and Toshihiko Ohmichi
Japan Atomic Energy Research Institute, Tokai-mura, Naka-gun, Ibaraki-ken 319-11 (Japan)

Abstract

The Pu–U phase diagram was investigated by differential thermal analysis. The transition temperatures for solid phases were consistent with the widely accepted diagrams. However, a very narrow solidus–liquidus gap was found in the present work. The obtained data for the solidus and liquidus temperatures were well reproduced in the thermodynamic analysis.

1. Introduction

Understanding the Pu–U binary alloy phase diagram is important in investigating metallic fuel behaviour. At present the phase diagram for this system by Peterson and Foltyn [1] is widely accepted as being correct. It is mainly based on thermal, dilatometric, metallographic and X-ray diffraction data from Ellinger *et al.* in 1959 [2]. Recently, thermodynamic modelling of the Pu–U alloy was performed by Leibowitz *et al.* [3,4] and Ogawa [5]. The solidus and liquidus curves reported by Ellinger *et al.* could not be reproduced with their models. The calculated solidus and liquidus curves from the established thermodynamic data for pure U and Pu resulted in a significantly narrower solidus–liquidus gap than the experimental gap. In the present work, differential thermal analysis (DTA) was performed and the data were analysed by the Gibbs free energy minimizer code ChemSage [6] to investigate the above discrepancy.

2. Experimental details

The DTA measurements were carried out using a model DT7000RH (Sinku Rikou Corp.) analyser as described in the work on Pu–Zr binary system [7]. The Pu–U alloys of seven compositions, 11, 20, 42, 61, 70, 78 and 89 at.% U, were prepared by direct melting of pure Pu and U metal chips in a Y_2O_3 cell (0.5 mm in wall thickness) in the DTA apparatus. Characterization of the Pu and U metals used is described elsewhere [7, 8]. Alloying was monitored by DTA. For the purpose of comparison, a sample of 80 at.% U alloy, which had been vacuum melted in a graphite crucible and characterized in Harwell Laboratory, was also used. In the measurements, the samples were kept at a slightly lower temperature than each transition point in order to achieve thermal equilibrium and then heated at a rate of 5 or 10 K min^{-1}. The above procedure was repeated several times until a reproducible transition temperature was obtained. Sample preparations and the DTA measurements were performed in highly purified argon gas [9].

3. Results

Transition points obtained from the DTA measurements are superimposed on the diagram by Peterson and Foltyn [1] in Fig. 1. The data for the 80 at.% U alloy (Harwell Laboratory) were similar to those for the 78 at.% U alloy prepared in the present work. The outline of the Pu–U system from the present DTA measurements is similar to the previously reported diagram. For instance, the obtained solidus at 11 at.% U is 892 K, which corresponds well to the minimum of the solidus in the vicinity of 12 at.% U by Peterson and Foltyn [1]. Differences were observed in solidus and liquidus temperatures for alloys with more than 20 at.% U; the solidus temperatures were slightly higher, while the liquidus curve was lower by 30 K or more.

4. Discussion

A significantly narrower solidus–liquidus gap compared with the published diagram [1] is noticeable, as shown in Fig. 1. The solidus–liquidus gap in this work is also slightly narrower than that reported by Mound Laboratory [10]. The magnitude of our solidus–liquidus gap was comparable with the gap calculated by Leibowitz *et al.* [3] and Ogawa [5], although the measured solidus

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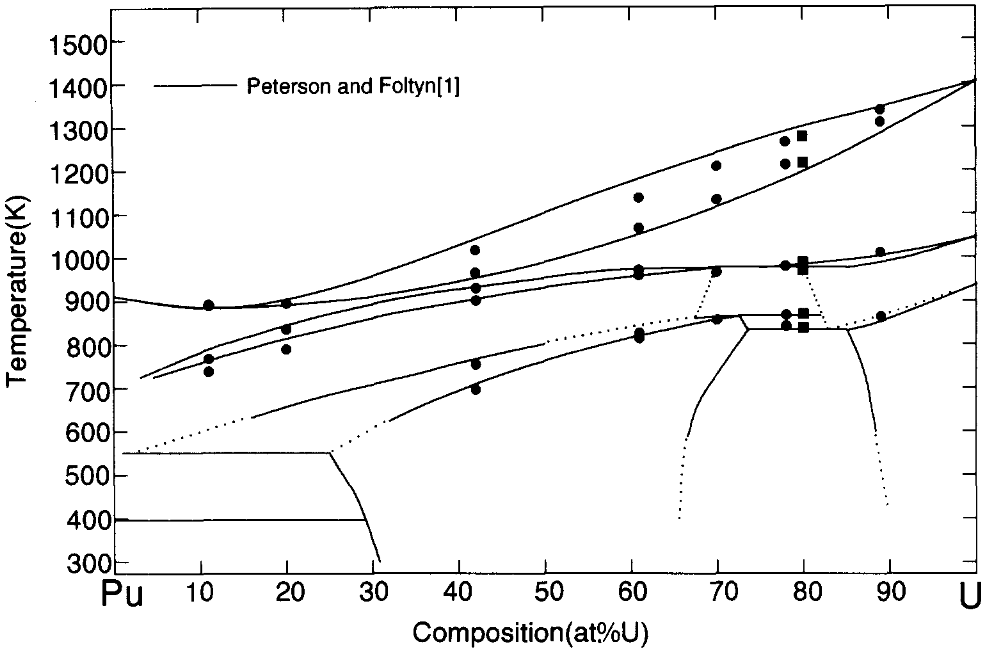

Fig. 1. The transition points for the Pu–U system. Data for the samples made by direct melting in the present work (●) and vacuum melting at Harwell Laboratory (■) are shown.

and liquidus exhibited poor agreement with their calculated curves.

The obtained solidus and liquidus were thermodynamically analysed by the Gibbs free energy minimizer code, ChemSage [6], to elucidate the above discussion. In this code, some thermodynamic models are prepared to handle a non-ideal solution. In this work, a model in which the free energy ΔG_{mix} of mixing is expressed by the following Redlich–Kister–Muggianu type formula was used.

$$\Delta G_{\mathrm{mix}} = X(1-X)\sum_{i=1}^{m} A_i(1-2X)^{i-1} + RT[X\ln X-(1-X)\ln(1-X)] \qquad (1)$$

where X is the atomic fraction of uranium, A is an interaction parameter defined as $A_i = H_i - S_iT$ and m is the order of the interaction. The following recommended values of ΔG (J mol^{-1}) summarized by Oetting *et al.* [11] were used in the present calculation as well as values by Leibowitz *et al.* [3]:

$$\Delta G(\mathrm{Pu},\ \epsilon \longrightarrow \text{liquid}) = -3290.2 + 49.261T - 6.7T\ln T \qquad (2)$$

$$\Delta G(\mathrm{U},\ \gamma \longrightarrow \text{liquid}) = -5437.6 + 79.111T - 10.4T\ln T \qquad (3)$$

In the calculation of the solidus and liquidus, ideality in the solid state (b.c.c. phase) and regularity and first-order interaction in the liquid state were at first assumed taking account of a speculation by Chiotti *et al.* [12] using data for the Pu–Mg system. The excess free energy ΔG^{E} of mixing is then written as follows:

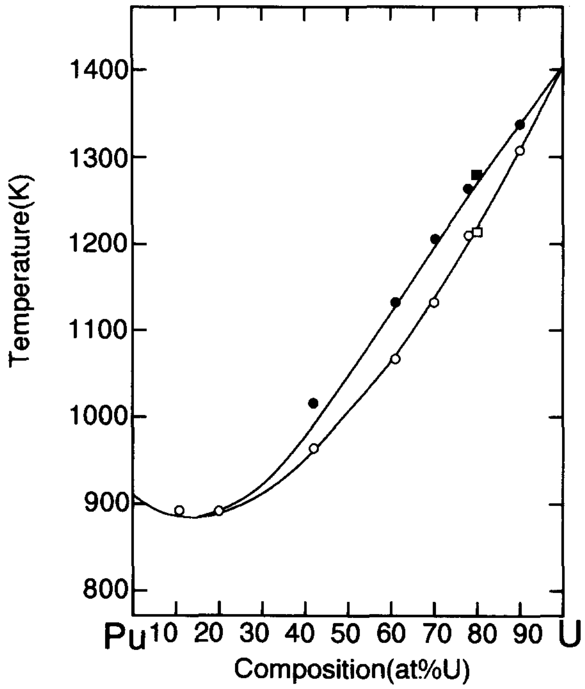

Fig. 2. The calculated solidus and liquidus curves for the Pu–U system by the ChemSage code. The experimental data from Fig. 1 are also shown: ○, □, solidus; ●, ■, liquidus.

$$\Delta G^{\mathrm{E}}_{\mathrm{sol.}} = 0 \qquad (4)$$

$$\Delta G^{E}_{\mathrm{liq.}} = X(1-X)[H_1 + H_2(1-2X)] \qquad (5)$$

Thus, solidus and liquidus curves are determined by two parameters H_1 and H_2 in this model.

Calculated solidus and liquidus curves using the values $H_1 = -3000$ J mol^{-1} and $H_2 = 100$ J mol^{-1} are in good agreement with the experimental data shown in Fig. 2. Leibowitz *et al.* [3] suggested from their thermodynamic modelling that either the solidus given by Ellinger *et al.* should be modified or the enthalpy of fusion of pure U is higher than the value recommended by the International Atomic Energy Agency. Our analysis implies that the former suggestion is probably true.

5. Conclusion

As the result of the DTA measurements of the Pu–U alloys, a diagram similar to that given by Peterson and Foltyn [1] was established, except for the magnitude of the solidus–liquidus gap. The gap determined in the present work was considerably narrower than in previously reported values. The obtained solidus and liquidus temperatures were well reproduced by thermodynamic calculations using the recommended thermodynamic data of pure Pu and U. The present analysis suggests that the published solidus and liquidus should be modified.

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