J. Chem. Thermodynamics 92 (2016) 158–167

Contents lists available at ScienceDirect

J. Chem. Thermodynamics

journal homepage: www.elsevier.com/locate/jct

Critical evaluation and thermodynamic optimization of the (U + Bi), (U + Si) and (U + Sn) binary systems

Jian Wang [a], Kun Wang [b,*], Chunhua Ma [c], Leidong Xie [b]

[a] Center for Research in Computational Thermochemistry (CRCT), Department of Chemical Engineering, École Polytechnique, Montréal, Québec H3C 3A7, Canada
[b] Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai 201800, PR China
[c] College of Physics and Electronic Engineering, Nanyang Normal University, Nanyang 473061, PR China

ARTICLE INFO

Article history:
Received 10 July 2015
Received in revised form 18 August 2015
Accepted 21 August 2015
Available online 12 September 2015

Keywords:
Phase diagram
Nuclear materials
CALPHAD method
(U + Bi) system
(U + Si) system
(U + Sn) system

ABSTRACT

A complete literature review, critical evaluation and thermodynamic optimization of the phase diagrams and thermodynamic properties in the (U + X) (X: Bi, Si and Sn) binary systems are presented. The CALPHAD method was used for the thermodynamic optimization, the result of which can reproduce all available and reliable experimental phase equilibria and thermodynamic data of the (U + X) (X: Bi, Si and Sn) binary systems using a set of thermodynamic functions. The modified quasi-chemical model in the pair approximation (MQMPA) was used for modelling the liquid solution. The Gibbs energies of all terminal solid solutions and intermetallic compounds were described by the compound energy formalism (CEF) model. All reliable experimental results have been reproduced within measurement error limits. A self-consistent thermodynamic database has been constructed for these (U + X) binary systems; this database can be used as a guide for nuclear materials research.

1. Introduction

The use of uranium in energy production from nuclear fission has given considerable impetus to the investigation of U-based alloys in recent decades. These investigations focus not only on the U-containing compounds used in the fuels, but also on the alloys of U with common elements of structural materials and fission products [1–4]. (U + Bi) and (U + Sn) molten alloys used as mixed fuel have been investigated by many researchers because of their notable advantages such as high specific power, low costs, better neutron economy, *etc.* [5–8]. Molten Sn is used to dissolve the nitrides and oxides from liquid fuel to extract desired actinide elements and remove the fission products [8,9]. Reliable data of thermodynamic properties and phase transformations of (U + Sn) molten alloys in the extracting process are important for keeping the fuel reactor operating safely. Si, C and Si–C based alloys are candidates for the inert matrix in gas-cooled fast reactor [1,10]. For the design of optimal operation condition of fuel reactor with molten fuel containing (U + Si), a systematic knowledge of the phase equilibria and thermodynamic properties of (U + Si) alloys is required. Hence, a better approach is to study the relevant phase diagrams of these (U + X) binary systems that are vital for beginning research and development of nuclear materials. However, on account of stringent experimental conditions, the traditional methods used in much experimental work are impractical. Fortunately, thermodynamic modelling of multi-component systems by the calculation of phase diagrams (CALPHAD approach) has been shown to be a very efficient way to investigate phase equilibria and thermodynamic properties systematically [11,12]. The (U + Bi) and (U + Si) binary systems have been assessed and calculated respectively by Wang *et al.* [13] and Berche *et al.* [14]. However, further improvements are necessary for the reproduction of phase diagram and thermodynamic properties. This is because of the gaps and errors in reported experimental values. Details will be discussed in the literature review section.

Thermodynamic assessments in metallic nuclear materials systems: (U, Pu)–X (Al, Ga, Co, Fe, Se, Te, Sn, Si, Sb, Bi, Ge, Ag, Cu, Zn, Ni, W, Mn, *etc.*) [15–17] have been conducted by the present authors using the CALPHAD method in order to develop a thermodynamic database for nuclear materials development. As a part of this database, the present work focuses on comprehensive literature review, critical evaluation and thermodynamic assessments of the (U + Bi), (U + Si) and (U + Sn) binary systems.

* Corresponding author. Tel./fax: +86 21 39194119.
E-mail addresses: jian.wang@polymtl.ca (J. Wang), wangkun@sinap.ac.cn (K. Wang), mch@nynu.edu.cn (C. Ma), leidongxie@sinap.ca.cn (L. Xie).

http://dx.doi.org/10.1016/j.jct.2015.08.029
0021-9614/

2. Critical literature review

2.1. (U + Bi) binary system

The phase equilibria of the (U + Bi) binary system were first investigated by Abmann and Baldwin [18] using cooling curve analysis and microscopic examination. Two intermetallic compounds UBi and UBi_2 were reported in this binary system. Later, Ferro [19] investigated several (U + Bi) binary alloys by X-ray diffraction analysis. A new compound U_3Bi_4 with cubic Th_3P_4 ($D7_3$) crystal structure was reported. Moreover, the X-ray study by Ferro [19] confirms the existence of compounds UBi and UBi_2 with crystal structures of NaCl (B1) and Cu_2Sb (C38) types respectively. Ferro [19] also reported that the solid solubilities in terminal phase the U and Bi terminal phases as well as intermetallic compounds are insignificant at low temperature. Teite [20] re-investigated the phase equilibria of the (U + Bi) binary system in the whole composition range using thermal analysis, neutron diffraction and metallography. The existence of compounds UBi, U_3Bi_4, and UBi_2 were confirmed by Teite [20]. U_3Bi_4 and UBi_2 form in peritectic reactions: (liquid + UBi) → U_3Bi_4 and (liquid + U_3Bi_4) → UBi_2 at (1150 and 1010) °C, respectively. The formation temperature of UBi was estimated to lay in the range (1400 to 1450) °C in a syntectic reaction (liquid#1 + liquid#2) → UBi. It is noted worthy that measurements of the miscibility gap of the liquid phase were faulty in Teite's work due to the high vapour pressure of Bi above its melting temperature [20]. The solubility of U in Bi-rich liquid solution in the temperature range (515 to 960) °C was determined by Greenwood [21] using a filtration method. Bareis [22] determined the solubility of U in Bi-rich liquid solution at (271 to 700) °C using filtration and flotation methods. The results in the common temperature range from the two authors [21,22] are in good agreement.

Gross *et al.* [23] reported the activity of Bi in the equilibrated phase at 742 °C using effusion method via Bi vapour pressure measurements. The activity of Bi, enthalpies and entropies of formation of UBi, UBi_2 and U_3Bi_4 in the temperature range (725 to 875) °C were investigated by Cosgarea *et al.* [24]. They used their own vapour pressure measurements of Bi. Due to the unknown molecular weight of the Bi vapour in those experiments, an optical absorption technique was used by Gross *et al.* [23] and Cosgarea *et al.* [24] to determine the concentration of each species independently. This may cause large error in the derived thermodynamic properties of the (U + Bi) binary system. This is evidenced by differences in the *liquidus* curve (see figure 1) reported by Cosgarea *et al.* [24] in comparison with other investigators [20–22]. Rice *et al.* [25] investigated the thermodynamic properties of (U + Bi) alloys at (745 to 842) °C using the effusion method [24]. The enthalpies and entropies of formation of UBi, UBi_2 and U_3Bi_4 in the range (745 to 842) °C were derived with the use of Bi vapour pressure measurements. Lebedev *et al.* [26] studied the thermodynamic properties of (U + Bi) alloys at (496 to 788) °C using electromotive force (emf) measurements. The partial and integral thermodynamic properties (Gibbs energy, enthalpy and entropy of formation) of (U + Bi) alloys at 745 °C were derived by Lebedev *et al.* [26]. The solubilities of U in liquid Bi at various temperatures were found by Levedev *et al.* [26] from their emf measurements. Dilute (U + Bi) solutions at (400 to 600) °C were studied by Tien *et al.* [27] by emf measurements.

A thermodynamic optimization of the (U + Bi) binary system was presented by Wang *et al.* [13]. However, the important experimental values of the *liquidus* in the Bi-rich region from references [21,22,24,26] were not included in their optimizations. As a result, the calculated phase diagram of the (U + Bi) binary system was erroneous. Hence, a critical review and re-optimization of the (U + Bi) binary system are imperative for the purpose of improvement of the overall ((U, Pu) + X) system.

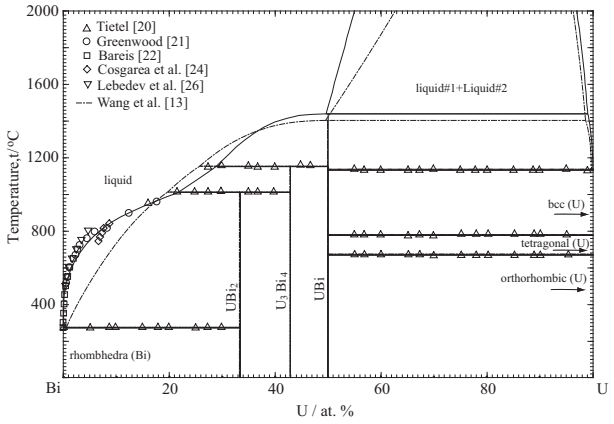

FIGURE 1. The calculated phase diagram of the (U + Bi) binary system with experimental values [20–22,24,26] and calculated result from Wang *et al.* [13].

2.2. (U + Si) binary system

The phase equilibria of the (U + Si) binary system were first investigated by Cullity [28] using thermal analysis, microscopy and X-ray analysis. Four terminal solid solutions, with very small solid solubilities, and six intermetallic compounds were reported. These latter were ε, U_5Si_3, USi, U_2Si_3, USi_2, and USi_3. The ε compound forms at 930 °C in a peritectic reaction: (bcc (U) + U_5Si_3) → ε. Kaufmann [29] and Kaufmann *et al.* [30] re-investigated the phase equilibria of the (U + Si) binary system in the whole composition range using thermal analysis, X-ray analysis, and microscopy. Six intermetallic compounds (ε, U_5Si_3, USi, U_2Si_3, USi_2 and USi_3) were confirmed by Kaufmann and Kaufmann *et al.* [29,30]. Therein, U_5Si_3 and USi_2 melt congruently at (1665 and 1700) °C respectively [29,30]. Later, these six compounds were re-examined by Zachariasen [31] using X-ray analysis. Some compounds were differently identified by Zachariasen [31], who designated "ε" to be "U_3Si", and "U_5Si_3" to be "U_3Si_2. Moreover, "U_2Si_3" is a polymorphic form of "USi_2". Brown and Norreys [32,33] studied some (U + Si) binary alloys at compositions around 33.3 at.% Si using X-ray analysis and metallography. The highest stable temperature of USi_2 was confirmed as 450 °C by Brown and Norreys [33]. Furthermore, a new intermetallic compound $USi_{1.88}$, with very high melting temperature, was observed by Brown and Norreys [33]. In order to resolve these contradictions, Vaugoyeau *et al.* [34] re-investigated the phase equilibria of the (U + Si) binary system in the composition region (34.5 to 55.6) at. % U using high and low temperature X-ray analysis. The existence of compounds USi, U_3Si_5, U_3Si_2 and $USi_{1.88}$ was confirmed. U_3Si_5 melts congruently at (1770 ± 10) °C. USi forms in a peritectic reaction, (liquid + U_3Si_5) → USi at (1580 ± 10) °C, according to the measurements of Vaugoyeau *et al.* [34]. This is consistent with the result of 1575 °C reported by Kaufmann *et al.* [30]. The temperature of eutectic reaction: liquid → (USi + U_3Si_2) was reported as (1540 ± 10) °C by Vaugoyeau *et al.* [34], which is about 20 °C lower than that reported by Kaufmann *et al.* [30]. Finally, the melting temperature of $USi_{1.88}$, reported by Brown and Norreys [33], was also measured by Vaugoyeau *et al.* [34]. $USi_{1.88}$ melts in a peritectic reaction: (liquid + U_3Si_5) → $USi_{1.88}$ at (1710 ± 10) °C. The solid solubilities of Si in U terminal phases bcc (U), Tetragonal (U) and Orthorhombic (U) were reviewed by Katz and Rabinowitch [35] and Shunk [36]. Dwight [37] reported that U_3Si undergoes an