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Review

Thermodynamic properties of actinides and fission products in liquid bismuth

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ABSTRACT

A critical review on the fundamental properties (solubility, activity coefficients and stable metallic compounds) of actinides and rare earth fission products in liquid bismuth is conducted in this study. The available data are summarized and analyzed. New temperature-dependent correlations, which extend the available data to a broader range of applications, are developed based on existing data from different sources when multiple measurements are available. Analysis of the data shows the strong correlations between some properties (solubility and activity coefficients) and the atomic numbers of the elements.

1. Introduction

Liquid Bi has broad applications in pyropocressing in both the processing of used nuclear fuels and the partitioning of minor actinides and long-lived fission products arising out of the back-end of nuclear fuel cycles (Kinoshita et al., 1999). It can be used as a liquid electrode in electrorefining or electrolysis or as a liquid solvent in liquid–liquid extraction between liquid metal and molten salt for the separation of actinides (e.g. Inoue et al., 2011) or for rare earth drawdown (e.g. Simpson et al., 2012). Liquid bismuth was also used as a cleanup solvent in molten slat reactors (MSRs) (Rosenthal et al., 1970). The lithium-activated bismuth metal contacting system has been found to be good technology to remove rare earth contaminants in MSRs. Most recently, a liquid bismuth contacting system was proposed to be used as the coolant cleanup system for cleaning the fission product contaminants due to fuel failures in a fluoride salt-coolant high-temperature reactor (Holcomb et al., 2013).

All these applications require the fundamental behaviors of actinides and fission products in liquid bismuth. The present study conducts a critical review on data of the thermodynamic properties of actinides and rare earth metals in liquid bismuth. The review focuses on the solubility, the activity coefficients, and the stable metallic compounds of actinides and rare earth metals in liquid bismuth. These properties are key thermodynamic fundaments that determine or partially determine behaviors, such as the separation factors between the liquid metal and molten salt phases of the elements considered in the liquid metal. Considering the applications and the available data, the review focuses on Bi-rich regions of liquid binary alloys. The collected data are analyzed, and overall correlations are developed based on the all the data collected when multiple data sources are available for one element. The analysis shows that the properties have strong correlations with the atomic numbers of the elements, which makes it possible to predict the unknown properties of an element based on the known properties of other elements. Such strong correlations were also reported for the thermodynamic properties of rare earth metals in other metals, for example, in solid Fe (Norgren, 2000) and liquid Cd (Johnson, 1962). Finally, the future research directions are proposed based on the available data and the needs of the applications.

2. Relationships between solubility, activity coefficient and Gibbs free energy of formation metal compound

When a metal dissolves into a liquid metal (M), the activity coefficient of the metal in the liquid metal (here, the liquid metal is liquid Bi) can be expressed by:

$$RT \ln \gamma_M = \Delta G_M^{ex} \quad (1)$$

where γ is the activity coefficient, R is the gas constant, and T is the temperature in K. ΔG^{ex} is the partial molar excess Gibbs energy

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which can be expressed in terms of partial molar enthalpy of mixing (ΔH_M^{mix}) and the partial molar excess entropy (ΔS_M^{ex}) by:

$$\Delta G^{ex} = \Delta H_M^{mix} - \Delta S_M^{ex} T \quad (2)$$

Therefore, activity coefficient of the metal M in the liquid metal can be calculated by:

$$\ln \gamma_M = \frac{\Delta H_M^{mix}}{RT} - \frac{\Delta S_M^{ex}}{R} = A_{M,\gamma} + \frac{B_{M,\gamma}}{T} \quad (3)$$

where

$$A_{M,\gamma} = -\frac{\Delta S_M^{ex}}{R};\ \ B_{M,\gamma} = \frac{\Delta H_M^{mix}}{R}$$

For infinite dilution, $A_{M,\gamma}$ and $B_{M,\gamma}$ are constant.

When the dissolved metal reaches its saturation limit, either solid metal or metal compounds can precipitate out of the solution, which depends on the operation temperature. For the case of metal precipitation, the reaction can be expressed by:

$$M(s) \leftrightharpoons M(soln) \quad (4)$$

At equilibrium:

$$RT \ln(\gamma_M X_{M,s}) = 0 \quad (5)$$

where $X_{M,s}$ is the M solubility in the liquid Bi in mole fraction, M(s) represents the solid metal, M(soln) represents the dissolved metal, and $\gamma_M X_{M,s}$ is the activity of M. Therefore:

$$\ln X_{M,s} = -A_{M,\gamma} - \frac{B_{M,\gamma}}{T} \quad (6)$$

For the case of metal compound (MBi_n) precipitation, the reaction can be expressed by:

$$M(soln) + nBi(l) \rightleftharpoons MBi_n(s) \quad (7)$$

At equilibrium:

$$RT \ln(\gamma_M X_{M,s}) = \Delta G_{MBi_n} = \Delta H_{MBi_n} - \Delta S_{MBi_n} T \quad (8)$$

where ΔG_{MBi_n} is the Gibbs free energy of formation of the metal compound, ΔH_{MBi_n} and ΔS_{MBi_n} are the corresponding enthalpy and entropy. Equation (8) is obtained based on the reasonable assumption that the activity of Bi is 1 because the solution is infinite dilution.

Therefore, the solubility can be expressed by:

$$\ln X_{M,s} = \frac{\Delta H_{MBi_n} - \Delta H_M^{mix}}{RT} + \frac{\Delta S_M^{ex} - \Delta S_{MBi_n}}{R} \quad (9)$$

Equations (6) and (9) can be written into a uniform formula as:

$$\ln X_{M,s} = A_{M,s} - \frac{B_{M,s}}{T} \quad (10)$$

where $A_{M,s}$ and $B_{M,s}$ are constant.

All the data collected in the present article used Equation (3) for activity coefficient and Equation (10) for solubility of metal in liquid Bi to fit the experimental data. Therefore, in the present article, Equation (10) is applied to analysis and fit the multiple available data for solubility and Equation (3) is applied to analysis and fit the multiple available data for activity coefficient to get the overall correlations based on available data from multiple data sources which are recommended correlations.

3. Actinides in liquid bismuth

3.1. Solubility

The phase diagram of the Bi-rich Bi–Th system has been developed (Chiotti et al., 1982). The solubility of Th in liquid Bi has been determined by different authors (e.g. Schilling and Ferris, 1970; Smith, 1972a; von Goldbeck, 1975). The available experimental data were summarized in Chiotti et al. (1982). Based on all the experimental points, a temperature-dependent correlation for the solubility of Th in liquid Bi was recommended (Chiotti et al., 1982) and is given in Table 1. The phase diagram of the Bi-rich Bi–U system has also been developed (Elliott, 1965). The solubility of U in liquid Bi has been measured (Schweitzer and Weeks, 1961a; Lebedev et al., 1966). The Actinide Binary Alloys (1981) recommended two correlations for different temperature ranges, both of which are given in Table 1. The phase diagram of the Bi-rich Bi–Pu system can be found in Elliott (1965). The solubility of Pu in liquid Bi was measured (Lebedev et al., 1969). A correlation was recommended (The Actinide Binary Alloys, 1981; Shirai et al., 2001) and is given in Table 1.

For Np in liquid Bi, no temperature-dependent correlation was developed. However, the solubility was found to be 0.34, 0.61, and 1.06 at% at 673, 723, and 873 K, respectively (Sakamura et al., 2000). Based on these three points, one can obtain a correlation for the solubility of Np in liquid Bi using Equation (10). It was found that the constants are $A_{Np,s} = 3.017$ and $B_{Np,s} = 5857$ K which are given in Table 1. The obtained correlation predicts the solubility to be 0.3394, 0.6195, and 1.0462 at% at 673, 723, and 873 K. All these calculated values agree well with the experimental measurements.

The solubility of Am in liquid Bi is not available.

3.2. Activity coefficient

In the present article, the solid metal is selected as the standard state. For concentrated solution, the activity coefficient of an element in a liquid metal is believed to be a concentration-dependent parameter. However, the concentration-dependent activity coefficients of actinides in liquid bismuth have not been well reported. Therefore, the present article still focuses on the infinite dilution for which the activity coefficient of one element does not depend on the concentration.

For thorium, the activity coefficients at 913 K and 1023 K were reported to be 2.65×10^{-8} and 6.46×10^{-7}, respectively (Moriyama et al., 1987). The activity coefficient can be calculated based on the distribution coefficient of thorium between molten salt and liquid

Table 1
Solubility (mole fraction) of actinides in liquid bismuth.

Actinide	Solid in equilibrium with the liquid	$\ln X_s = A - (B/T)$		Temperature range (K) (T_{min}, T_{max})	Reference
		A	B		
Th	$ThBi_2$	3.4837	8332	688–1373	(Chiotti et al., 1982)
U	UBi_2	1.2178	5158	543–753	(The Actinide Binary Alloys, 1981)
U	UBi_2	2.7778	6318	753–998	(The Actinide Binary Alloys, 1981)
Np	$NpBi_2$	3.017	5857	673–773	(Sakamura et al., 2000)
Pu	$PuBi_2$	4.332	6788	650–1070	(The Actinide Binary Alloys, 1981; Shirai et al., 2001)