Journal of Nuclear Materials 396 (2010) 170–175

Contents lists available at ScienceDirect

Journal of Nuclear Materials

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

Thermodynamic assessments of the Al–Th and Th–Zn systems

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ARTICLE INFO

Article history:
Received 8 August 2009
Accepted 31 October 2009

Keywords:
Nuclear reactor materials
Phase diagrams
Thermodynamic modeling

ABSTRACT

The phase diagrams of the Al–Th and Th–Zn systems have been evaluated by using the Calculation of Phase Diagrams (CALPHAD) method with the experimental data including the phase equilibria and thermodynamic properties. The Gibbs free energies of the liquid, bcc and hcp phases were described by the subregular solution model with the Redlich–Kister equation, and those of the stoichiometric compounds of the Th_2Al, Th_3Al_2, ThAl, Th_2Al_3, $ThAl_2$, $ThAl_3$, Th_2Al_7, Th_2Zn, $ThZn_2$, $ThZn_4$ and Th_2Zn_{17} were described by the two-sublattice model. The calculated phase equilibria and thermodynamic properties are in good agreement with the experimental data.

1. Introduction

Nuclear energy is a new kind of important energy, and the nuclear materials are the important fundamental guarantee to develop a safe nuclear reactor with high efficiency [1–3]. Thorium (Th) is an abundant element in nature with multiple advantages as a nuclear fuel for future reactors of all types [4]. The traditional methods of materials researches with many experimental tries are unsuitable in the nuclear materials researches because of the rigorous experimental conditions. Thus, the investigation on the phase diagrams of nuclear materials systems is very important for development of new nuclear materials. Our goal is to develop the thermodynamic database of the phase diagrams in nuclear material system. The present authors have made some thermodynamic assessments of nuclear material system [5–11]. As a part of this thermodynamic database, the purpose of the present work is to carry out thermodynamic assessment of the phase diagrams in the Al–Th and Th–Zn systems based on the Calculation of Phase Diagrams (CALPHAD) method by means of the available experimental data.

2. Thermodynamic models

The information of the stable solid phases and the used models in the Al–Th and Th–Zn systems are presented in Table 1.

2.1. Solution phases

Gibbs free energies of the solution phases (liquid, hcp, fcc and bcc phases) in an A–B system, corresponding to the Al–Th, and Th–Zn systems, are described by the subregular solution model. The molar Gibbs free energy of each solution phase in A–B system is given as follows:

$$G_m^\phi = \sum_{i=A,B} {}^0G_i^\phi x_i + RT\sum_{i=A,B} x_i \ln x_i + {}^EG_m^\phi, \tag{1}$$

where ${}^0G_i^\phi$ is the molar Gibbs free energy of pure component i in the respective reference state with the ϕ phase, which is taken from the SGTE pure element database [12]. R is the gas constant, and T is the absolute temperature. The x_i denotes the mole fraction of component i. The term ${}^EG_m^\phi$ is the excess Gibbs free energy, which is expressed in the Redlich–Kister polynomials [13] as:

$${}^EG_m^\phi = L_{A,B}^\phi x_A x_B, \tag{2}$$

where $L_{A,B}^\phi$ is the interaction energies in a hypothetical binary system denoted by A–B, which is expressed in the following forms:

$$\begin{aligned} L_{A,B}^\phi &= {}^0L_{A,B}^\phi + {}^1L_{A,B}^\phi(x_A - x_B) + {}^2L_{A,B}^\phi(x_A - x_B)^2 + \cdots \\ &= \sum_{m=0}^{n} {}^mL_{A,B}^\phi (x_A - x_B)^m, \end{aligned} \tag{3}$$

$${}^mL_{A,B}^\phi = a + bT, \tag{4}$$

where the parameters of a and b were evaluated based on the experimental data in binary systems, respectively.

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0022-3115/$ - see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.jnucmat.2009.10.068

Table 1
The stable solid phases and the used models in the Al–Th and Th–Zn systems.

System	Phase	Prototype	Crystal system	Modeling phase	Used models
Th–Al	αTh	Cu	fcc	(Al, Th)	SSM
	βTh	W	bcc	(Al, Th)	SSM
	(Al)	Cu	fcc	(Al, Th)	SSM
	Th_2Al	Al_2Cu	bct	$(Th)_{0.667}(Al)_{0.333}$	SM
	Th_3Al_2	U_3Si_2	Tetragonal	$(Th)_{0.6}(Al)_{0.4}$	SM
	ThAl	CrB	Orthorhombic	$(Th)_{0.5}(Al)_{0.5}$	SM
	$ThAl_3$	–	Tetragonal	$(Th)_{0.4}(Al)_{0.6}$	SM
	$ThAl_2$	AlB_2	Hexagonal	$(Th)_{0.333}(Al)_{0.667}$	SM
	$ThAl_3$	$SnNi_3$	Hexagonal	$(Th)_{0.25}(Al)_{0.75}$	SM
	Th_2Al_7	–	Orthorhombic	$(Th)_{0.222}(Al)_{0.778}$	SM
Th–Zn	αTh	Cu	fcc	(Th, Zn)	SSM
	βTh	W	bcc	(Th, Zn)	SSM
	(Zn)	Mg	hcp	(Th, Zn)	SSM
	Th_2Zn	Al_2Cu	bct	$(Th)_{0.667}(Zn)_{0.333}$	SM
	$ThZn_2$	–	Hexagonal	$(Th)_{0.333}(Zn)_{0.667}$	SM
	$ThZn_4$	$BaAl_4$	bct	$(Th)_{0.2}(Zn)_{0.8}$	SM
	Th_2Zn_{17}	Th_2Zn_{17}	Rhombohedral	$(Th)_{0.105}(Zn)_{0.895}$	SM

SSM: subregular solution model and SM: sublattice model.

2.2. Stoichiometric intermetallic compounds

In the Th–Me (Me: Al or Zn) system, the intermetallic compounds (Th_2Al, Th_3Al_2, ThAl, Th_2Al_3, $ThAl_2$, $ThAl_3$, Th_2Al_7, Th_2Zn, $ThZn_2$, $ThZn_4$ and Th_2Zn_{17}) are stoichiometric compounds. The Gibbs free energy for per mole of formula unit Th_pMe_q can be expressed as:

$$\Delta^0 G_f^{Th_pMe_q} = G_m^{Th_pMe_q} - p^0 G_{Th}^{ref} - q^0 G_{Me}^{ref} = a' + b'T, \quad (5)$$

where the $\Delta^0 G_f^{Th_pMe_q}$ indicates the standard Gibbs free energy for the formation of the stoichiometric compound from pure elements, and the parameters of a' and b' were evaluated in the present paper.

3. Experimental information

3.1. The Al–Th binary system

The phase diagram in the Al–Th system consists of four solution phases (liquid, αTh, βTh, (Al) phases), and seven intermetallic compounds (Th_2Al, Th_3Al_2, ThAl, Th_2Al_3, $ThAl_3$, $ThAl_2$, Th_2Al_7 phases). The phase diagram in the Al–Th system has been investigated by many researchers [14–19]. Murray [17] studied the phase diagram in the Al–Th system by thermal analysis, X-ray diffraction and metallographic methods, and found that the Th_2Al, Th_3Al_2 and $ThAl_2$ compounds are directly formed from the liquid phase, while the ThAl, Th_2Al_3 and $ThAl_3$ compounds are formed by the peritectic reactions (Th_2Al_3 + L ↔ ThAl, L + $ThAl_2$ ↔ Th_2Al_3 or L + $ThAl_2$ ↔ $ThAl_3$). Murray [17] reported that the Th_3Al_2 and Th_2Al_3 compounds eutectoidally decompose at 1075 °C and 1100 °C, respectively, and the solid solubilities of Al in the αTh and βTh phases are 0.4 at.% at 1000 °C and 0.85 at.% at 1300 °C. However, the liquidus of the Al–Th binary system around the Th-corner has not been determined. The phase diagram in the Al–Th system reviewed by Kassner et al. [20] is shown in Fig. 1.

In addition, the enthalpies and entropies of formation of the Th_2Al_7 and $ThAl_3$ compounds in the temperature range from 673 °C to 807 °C were determined by Poyarkov et al. [19] on the basis of Electromotive Force (EMF) measurements. And the enthalpy formation of $ThAl_2$ was measured calorimetically by Wang et al. [21].

3.2. The Th–Zn binary system

The phase diagram in the Th–Zn system consists of four solution phases (liquid, αTh, βTh, (Zn) phases), and four intermetallic

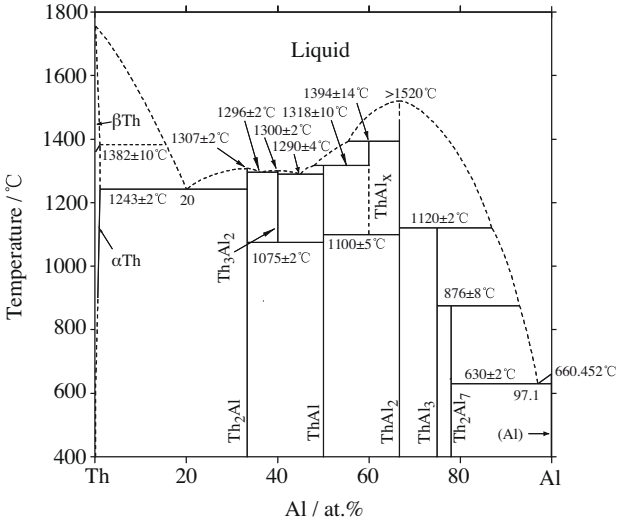

Fig. 1. The phase diagram of the Al–Th system reviewed by Kassner [20].

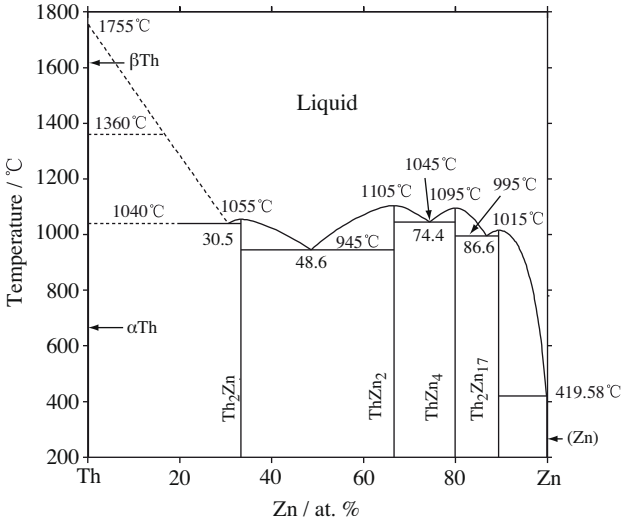

Fig. 2. The phase diagram of the Th–Zn system reviewed by Okamoto [27].