Calphad 60 (2018) 90–97

Contents lists available at ScienceDirect

Calphad

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

A thermodynamic description of the U − Ti − Zr system

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ARTICLE INFO

Keywords:
U − Ti − Zr ternary system
Phase diagram
Thermodynamic calculation
Solvus projection

ABSTRACT

The U − Ti − Zr system was assessed by means of the CALPHAD method for the first time. Based on a critical evaluation of experimental phase diagram data available in the literature, a thermodynamic modeling was conducted for the individual phases. The solution phases including the liquid, hcp and bcc were described by a substitutional solution model. The binary compounds, U_2Ti and UZr_2, with a ternary extension were treated as one single phase using a sublattice model of $(U,Zr)_{2/3}(Ti,Zr)_{1/3}$. There is no ternary compound in this system. A set of self-consistent thermodynamic parameters for the U − Ti − Zr system was then obtained. Comparisons between the calculated and measured phase diagrams show that the experimental information is satisfactorily accounted for by the present thermodynamic description. The solvus projection and reaction scheme were generated using the present thermodynamic parameters. The presently calculated phase diagrams of U–Zr − Ti alloys can be used for further industrial application.

1. Introduction

U-alloys have been considered to be a high potential candidate of base material for nuclear fuel due to their high fissile density and high thermal conductivity compared to conventional uranium oxide fuel [1–3]. It was reported that pure U presents a high possibility to be fissile, poor mechanical properties, and high anisotropy of physical properties [4], while the U alloys with elements such as Ti, Mo, Nb and Zr show markedly improved corrosion and oxidation resistance, ductility and strength [5,6]. Since these elements have limited solubilities in the low temperature orthorhombic α-U phase and stabilize the high temperature bcc γ-U phase, U alloys are usually heat treated in the bcc γ phase and quenched [7], thereby presenting good mechanical and high symmetry in the physical properties [8].

Moreover, U − Ti alloys exhibit many different microstructures and textures, i.e., β, α, U_2Ti and α′ [9], and some studies focused on the hydride nucleation and initial growth behavior of U − 0.7 wt%Ti alloy [10–12]. Uranium rich U − Zr alloys are of interest because they are considered as metallic fuel [13–15]. U − Zr alloys are also used as blanket seeds for fast breeder reactors. Additionally, uranium alloys with zirconium as a reactor fuel are normally preferred in as-cast condition because mechanical working may introduce texture [16–19]. Thus, a mastery of microstructure evolution during solidification and subsequent heat treatment is essential to predict the behavior of alloy under operational condition damage. As a result, it is necessary to have a reliable knowledge on the phase diagrams in uranium-based alloys.

The only intermediate phase in the U − Ti binary system, i.e. U_2Ti, and that in the U–Zr system, i.e. UZr_2, have the same crystallography. Consequently, the two binary phases share the same designation of δ in the present work. The two δ phases offer a promising field of investigation both as binary alloys and ternary alloy combinations. Although a large amount of work has been done on the binary alloys [20–23], very limited work on the ternary system has been reported in the literature.

Since the early work by Saller et al. [24], there has been only one study on the phase equilibria in the U − Ti − Zr system [25]. So far, there is no thermodynamic modeling for the ternary system. Consequently, the major aims of the present work are: (i) to critically evaluate the experimental phase diagram data for the U − Ti − Zr system in the literature, (ii) to obtain a set of self-consistent thermodynamic parameters for the ternary system over the whole composition and temperature ranges by means of CALPHAD approach, and (iii) to present a solvus projection and reaction scheme of the entire ternary system for industrial applications.

2. Evaluation of experimental information

The experimental phase diagram data for the U − Ti − Zr system

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https://doi.org/10.1016/j.calphad.2017.11.008
Received 22 September 2017; Received in revised form 20 November 2017; Accepted 30 November 2017

Table 1
The notation of the phases in the U − Ti − Zr system.

Symbol (this work)	Symbol in Ref. [25]	Pearson's symbol, Space group	Phase description
(αU)	α	*oS*4, *Cmcm*	Solid solution based on αU
(βU)	β	*tP*30, $P\bar{4}n2$	Solid solution based on βU
hcp	δ	*hP*2, $P6_3/mmm$	Solid solution based on α(Ti,Zr)
bcc	γ	*cI*2, $Im\bar{3}m$	Solid solution based on γ(U,Ti, Zr)
UZr_2	ε	*hP*3, *P6/mmm*	Intermediate compound based on UZr_2
U_2Ti	U_2Ti	*hP*3, *P6/mmm*	Intermediate compound based on U_2Ti

were critically reviewed in the present work. To facilitate reading, the symbols denoting the phases in the system are summarized in Table 1.

Saller et al. [24] investigated the phase relationship along the vertical section between δ-U_2Ti and δ-UZr_2 by means of metallography, X-ray diffraction (XRD), and differential thermal analysis (DTA) methods. At 900 °C, they found a continuous solid solution between the bcc (U,Ti) and (U,Zr). At 575 °C, the bcc phase finally disappeared via a eutectoid decomposition to δ-U_2Ti or δ-UZr_2, and a maximum solubility of 1.4 at% Zr in δ-U_2Ti at 575 °C and a maximum solubility of 0.7 at% Ti in δ-UZr_2 at 500 °C were determined.

Using XRD and optical microscopy methods, Howlett [25] constructed nine isothermal sections in U-rich side at 1000, 850, 800, 750, 700, 662, 650, 650 and 575 °C. The observed phases at these sections are listed in Table 2. No ternary compound was found in their work. After homogenization at 1000 °C for four weeks, only the single bcc phase over the examined composition range was found. A two-phase region of bcc + U_2Ti was detected at 850 and 800 °C. At 700 °C, a narrow bcc + (βU) + U_2Ti three- phase field was observed, which originates from the eutectoid reaction of bcc = (βU) + U_2Ti along the U-Ti side at 723 °C. The addition of Ti tends to narrow the miscibility gap for bcc#1 and bcc#2 phases extending from the U − Zr binary system and finally close to a single bcc phase. At 662 °C, the bcc phase disappears in the binary system, but it still exists in the ternary with the shape of narrow tongue approximately parallel to the U − Zr system. Between 662 and 650 °C, there was no marked change for the phase relations. The δ-UZr_2 phase was detected at 575 °C, and the three-phase-region, bcc + δ-UZr_2 + U_2Ti, was constructed. However, the vertical section of $U_{26}Zr_{74} - U_{66}Ti_{34}$ presented by Saller et al. [24] differs from that [25] with respect to the three-phase-region although there is a general agreement on the topology of the phase diagram. Critical assessment was done to exclude the data of Saller et al. [24] from the thermodynamic optimization for the following reasons:

1) the longest annealing time for the alloys investigated by Saller et al. [24] was only 24 h, which was substantially shorter in comparison with the investigation by Howlett [25], resulting in discrepancies from true equilibria, 2) little experimental information concerning the sample preparation, e.g. the impurity of raw materials, the weight loss after melting, and the crucible materials used, was mentioned in the report by Saller et al. [24], while Howlett [25] described the experimental information in detail. Therefore, the isothermal sections reported by Howlett [25] are used in the present modeling, while the experimental values for the vertical section from Saller et al. [24] are given a lower weight in the thermodynamic modeling.

Table 2
The experimental phase region for the U − Ti − Zr system from Howlett [25].

Annealed temperature °C	Phases
1000	bcc
850	bcc, bcc + U_2Ti
800	bcc, bcc + U_2Ti
750	bcc, (βU), bcc + U_2Ti, (βU) + bcc
700	bcc, (βU) + U_2Ti, bcc + U_2Ti, (βU) + bcc, (βU) + bcc + U_2Ti, bcc#1 + bcc#2
662	bcc, (βU) + U_2Ti, bcc + U_2Ti, (βU) + bcc, (βU) + bcc + U_2Ti
650	bcc, (αU) + U_2Ti, bcc + U_2Ti, (αU) + bcc, (αU) + bcc + U_2Ti
625	bcc, (αU) + U_2Ti, bcc + U_2Ti, (αU) + bcc, (αU) + bcc + U_2Ti
575	(αU) + U_2Ti, bcc + U_2Ti, UZr2 + U_2Ti, (αU) + UZr2 + U_2Ti, bcc + UZr2 + U_2Ti, (αU) + U_2Ti

3. Thermodynamic models

In the present modeling, the Gibbs energy functions for U, Ti and Zr were taken from the SGTE compilation by Dinsdale [26]. The present work is based on the most recent evaluations of the binary systems of U–Ti [27], U–Zr [28], and Ti–Zr [29]. The calculated binary phase diagrams are presented in Fig. 1(a), (b) and (c).

3.1. Solid solution phase

The bcc phase is described with a two-sublattice model as (U, Ti, $Zr)_1(Va)_3$ by means of the Redlich-Kister polynomial [30]. In this model, the U, Ti and Zr atoms can substitute for each other in the metal sublattice and the vacancy (Va) in the interstitial sublattice. The standard element reference (SER) state [26], i.e. the stable structure of the element at 25 °C and 1 bar, is used as the reference state of the Gibbs energy. For one formula unit(U, Ti, $Zr)_1(Va)_3$, the molar Gibbs is given by:

$$\begin{aligned} {}^0G_m^{bcc.a2} &= x_U\,{}^0G_U^{bcc.a2} + x_{Ti}\,{}^0G_{Ti}^{bcc.a2} + x_{Zr}\,{}^0G_{Zr}^{bcc.a2} \\ &\quad + RT(x_U \ln x_U + x_{Ti} \ln x_{Ti} + x_{Zr} \ln x_{Zr}) + x_U x_{Ti} L_{U,Ti:Va}^{bcc.a2} \\ &\quad + x_{Ti} x_{Zr} L_{Ti,Zr:Va}^{bcc.a2} + x_U x_{Zr} L_{U,Zr:Va}^{bcc.a2} + {}^{ex}G_{U,Ti,Zr:Va}^{bcc.a2} \end{aligned} \quad (1)$$

where R is the gas constant, and x_U, x_{Ti} and x_{Zr} are the mole fractions of Ti, U and Zr, respectively. The parameters denoted as $L_{U,Ti:Va}^{bcc.a2}$, $L_{Ti,Zr:Va}^{bcc.a2}$ and $L_{U,Zr:Va}^{bcc.a2}$ are the interaction parameters from the binary systems. The ternary excess Gibbs energy is expressed as follows:

$${}^{ex}G_{U,Ti,Zr:Va}^{bcc.a2} = x_U x_{Ti} x_{Zr}(x_U\,{}^0L_{U,Ti,Zr:Va}^{bcc.a2} + x_{Ti}\,{}^1L_{U,Ti,Zr:Va}^{bcc.a2} + x_{Zr}\,{}^2L_{U,Ti,Zr:Va}^{bcc.a2}) \quad (2)$$

in which the parameters ${}^0L_{U,Ti,Zr:Va}^{bcc.a2}$, ${}^1L_{U,Ti,Zr:Va}^{bcc.a2}$ and ${}^2L_{U,Ti,Zr:Va}^{bcc.a2}$ are ternary interaction parameters to be optimized in the present work.

For the other phases such as liquid, (αU) and hcp, the models and the parameters come from [27–29].

3.2. Phases extending into the ternary system

In view of the same crystallography for the two binary compounds, i.e. δ-U_2Ti [27] and δ-UZr_2 [28], the two separated δ phases are described with one sublattice model of $(U,Zr)_{2/3}(Ti,Zr)_{1/3}$. The Gibbs energy of the δ phase per mole atom is expressed as follows: