Thermochimica Acta 657 (2017) 185–196

Contents lists available at ScienceDirect

Thermochimica Acta

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

Review Article

Phase equilibria in the ternary B-Ce-Cu system with a thermodynamic reassessment of the binary B-Ce system

Milena Premović[a,b,*], Yong Du[a,*], Fan Zhang[a], Bo Sundman[c], Duško Minić[b], Biao Hu[d]

[a] State Key Laboratory of Powder Metallurgy, Central South University Changsha, China
[b] University of Priština, Faculty of Technical Science, Kos. Mitrovica, Serbia
[c] CIRIMAT, UPS/CNRS/ENSIACET, 116 Route de Narbonne, 31077 Toulouse, France
[d] School of Materials Science and Engineering, Anhui University of Science and Technology, Huainan, Anhui 232001, China

ARTICLE INFO

Keywords:
Thermodynamic assessment
The B-Ce system
The B-Ce-Cu system
CALPHAD method
Experimental investigations

ABSTRACT

In order to provide new phase relations for a thermodynamic modeling, eight binary B-Ce alloys were experimentally examined by means of differential thermal analysis, electron probe microanalyzer and X-ray diffraction methods Reassessment of the binary B-Ce system was then performed based on the experimental data from this work and literature data by using the CALPHAD method. Reasonable agreement between experimental data and the calculated phase diagrams has been reached. Subsequently, the phase equilibria of the B-Ce-Cu system was calculated based on the present thermodynamic description of the B-Ce system, the previous descriptions for the B-Cu and Ce-Cu systems as well as the experimental data from the literature. The isothermal sections at 400 and 600 °C, liquidus projection with invariant reactions were calculated and presented in this work.

1. Introduction

The borides of rare earth metals (B-REM) have attracted significant attention [1–3] over the last few decades due to the unique properties. Some of the unique B-REM properties are a high melting point [4], low work function [5–7], fluctuating valence [8–10], magnetic properties [11], superconductivity and semiconductivity [12–15], metal insulator transition [16] and many others. Due to the mentioned properties, B-REM possesses a great technical importance. For the example, LaB_6 and CeB_6 are used as an electron source with high brightness and longevity [17]. One of the important tasks in the way of searching for possible application of alloys is knowledge of phase diagram. Well defined phase diagram by using a powerful tool CALPHAD method [18] will give the opportunity to design preferred alloy efficiently, reduce time and cost during the development of materials.

The purpose of this work is to present the phase equilibria of the ternary B-Ce-Cu system with a reassessment of the binary B-Ce system by means of the CALPHAD method. The previous description of binary B-Ce phase diagram [19] did not include thermodynamic properties of two B_6Ce and B_4Ce intermetallic compound and computed liquidus line is extrapolated without any experimental data. Based on this fact, the liquidus line in the Ce-rich part is experimentally investigated in this work by using differential thermal analysis (DTA). Besides DTA analysis, electron probe micro-analyzer (EPMA) and X-ray diffraction (XRD) method were employed as experimental techniques. The composition of alloys and composition of presented phases were determined by using electron probe micro-analyzer (EPMA) and identification of phases by using X-ray diffraction (XRD) method. Experimentally obtained data from this work and literature data are used in thermodynamic optimization of the B-Ce system.

Thermodynamic descriptions of binary systems were combined into a ternary description used for calculations of phase equilibria in the ternary system B-Ce-Cu. The accepted binary descriptions were from the present work for the B-Ce system, from Wang et al. [20] for B-Cu and from Bo et al. [21] for Cu-Ce system. Up to now two isothermal sections at 400 and 600 °C of the ternary B-Ce-Cu system were investigated by Bilonizhko [22].

2. Literature review

The crystal structure data for the solid phases in the ternary B-Ce-Cu system are listed in Table 1. The binary B-Ce system consists of six phases, i.e. liquid phase, two intermetallic compounds B_6Ce and B_4Ce, and three solid solution phases δ(Ce), γ(Ce) and β(B). The binary B-Cu system consists of two solid solutions β(B) and (Cu) and liquid phase. The Cu-Ce system is complex in comparison with B-Cu and B-Ce, and it consists of three solid solutions δ(Ce), γ(Ce) and (Cu), five intermetallic compounds Cu_6Ce, Cu_5Ce, Cu_4Ce, Cu_2Ce, CuCe, and liquid phase.

* Corresponding authors at: State Key Laboratory of Powder Metallurgy, Central South University Changsha, China.
E-mail addresses: milena.premovic@gmail.com (M. Premović), yong-du@csu.edu.cn (Y. Du).

http://dx.doi.org/10.1016/j.tca.2017.10.006
Received 1 September 2017; Received in revised form 1 October 2017; Accepted 6 October 2017
Available online 07 October 2017
0040-6031/

Table 1
Crystal structure data for the solid phases in the B-Ce-Cu system.

Thermodynamic database name	Phase name	Space group	prototype	Pearson's symbol	Lattice parameters			ref.
					a	b	c	
BETA_RHOMBO_B	β(B)	$R\bar{3}m$	βB	*hR*105	1.017	1.017	α = 65.12	[23]
BCC_A2	δ(Ce)	$Im\bar{3}m$	W	*cI*2	4.12	4.12	4.12	[24]
FCC_A1	γ(Ce) Cu	$Fm\bar{3}m$	Cu	*cF*4	5.161	5.161	5.161	[25]
					3.615	3.615	3.615	[26]
B4CE	B_4Ce	*P4/mbm*	ThB_4	*tP*20	7.2034	7.2034	4.1006	[27]
B6CE	B_6Ce	$Pm\bar{3}m$	CaB_6	*cP*7	4.1403	4.1403	4.1403	[28]
CUCE	CuCe	*Pnma*	FeB-b	*oP*8	7.3	4.3	6.36	[29]
CU2CE	Cu_2Ce	*Imma*	KHg_2	*oI*12	4.43	7.05	7.45	[30]
CU4CE	Cu_4Ce	–	–	*oP*20	4.54	8.1	9.19	[31]
CU5CE	Cu_5Ce	*P6/mmm*	$CaCu_5$	*hP*6	5.147	5.147	4.1072	[32]
CU6CE	Cu_6Ce	*Pnma*	Cu_6Ce	*oP*28	8.1088	5.1004	10.1621	[33]

Table 2
Summary of the available literature data in the binary B-Ce system.

Reaction and reaction type	Temperature	The composition of the respective phase, at.% B			Rreference
L → β(B) Melting point	2042 ± 20	100	100		[35]
	2074 ± 19	99.6	99.6		[34]
	2075	100	100		[19,40][a]
	2092	100	100		[36,37]
	2290	100	100		[39]
	2300	100	100		[38]
L → δ(Ce) Melting point	798	0	0		[19,37,40–44][a]
L → B_6Ce congruent	2330	85.7	85.7		[19,42,44][a]
	2545	85.7	85.7		[38]
	2190	85.7–89.6	85.7–89.6		[45,46]
δ(Ce)					+ B_4Ce → γ(Ce) peritectoid
	726	80	0	0	[41–44][a]
726.8	80	0	0	[19][a]	
L → B_4Ce + δ(Ce) eutectic	≈785	≈1	≈0	≈80	[56]
	790	≈1	≈0	≈80	[41,43,44][a]
	790.3	0.6	0	80	[19][a]
	798	1	0	80	[42]
L + B_6Ce → B_4Ce peritectic	2164.8	74.4	85.7	80	[19][a]
	2165	74	85.7	80	[42][a]
	2370	74.2	85.7	80	[39]
	2375	74.4	85.7	80	[38]
L → B_6Ce + β(B) eutectic	1990	99.0	85.7	100	[42]
	2000	96.0	85.7	≈100	[55][a]
	2000	96.7	85.7	100	[19][a]
	2025	≈99.0	85.7	100	[43,44]
	2200	99.0	85.7	100	[38]

[a] Data used in our study.

2.1. The B-Ce binary system

Reported literature data about the melting point of pure boron β(B) shown different values from different studies. Kimpel and Moss [34] reported that melting point of boron within the nominal purity range of 99–99.6% boron varies from 2056 °C to 2074 ± 19 °C, respectively. The values were obtained by using four methods (powder specimens, solid specimens, disappearing hole and piston movement). Later Mar [35], reported a different temperature 2042 ± 20 °C, which is significantly lower than previously reported ones. Holcombe et al. [36] and Massalski [37] reported a melting point of β(B) of 2092 °C. Also from the proposed B-Ce phase diagram, a different value for the melting point of β(B) is noticeable. The melting temperature for β(B) according to Stecher et al. [38] is 2300 °C, Benesovsky et al. [39] 2290 °C, Wang et al. [19] and the SGTE-Pure database [40] compilation 2075 °C. The melting point of δ(Ce) in all studies [19,37,40–44] showed to be at the same temperature 798 °C. The solid solution phase γ(Ce) is an allotropic modification of δ(Ce), and according to the literature this solid solution forms [19,37,41–44] at 726 °C. To the best of our knowledge, there is no data about the solubilities of B in δ(Ce) or γ(Ce) and of Ce in β(B) in the literature. According to all available literature data, intermetallic compound B_6Ce melts congruently, but the melting temperature is ranging from 2190 to 2545 °C according to different authors. Stecher et al. [38] reported a temperature of 2545 °C and composition of 85.71 at.% B. Samsonov and Paderno [45] and von Stackelberg and Neumann [46] reported a significantly lower temperature of 2190 °C. Both temperatures are suspected since other studies [19,42,44] detected that the temperature of formation of B_6Ce is 2330 °C. Von Stackelberg and Neumann [46] and Allard [47] reported composition range of B_6Ce compound from 85.7–89.6 at.% B. Other studies did not confirm the existence of this composition range.

Muratov et al. [48] measured enthalpy increment of the B_6Ce by means of the mixing method in temperature range from 450 to 1100 °C and from 1150 to 2300 °C by vacuum calorimetric equipment. Experimental data for the enthalpy increment were approximated by using Mayer-Kelly equation and temperature dependent parameters for enthalpy increment were estimated. Based on these parameters the authors calculated temperature dependence of heat capacity and entropy for the B_6Ce compound. The total error of enthalpy is 1.5% and 5% for both heat capacity and entropy in the entire temperature range. The formation enthalpies of the B_6Ce phase were measured by Samsonov and Grodstein [49], Gordienko et al. [50], and Ames and McGrath [51] to be −48.4 ± 9.6 kJ/mol atom [49], −11.6 ± 6 kJ/mol atom [50], and −30.6 ± 27 kJ/mol atom [51], respectively. In all studies, the mass spectrometry method was used but a big difference in results was obtained. Another intermetallic compound B_4Ce is formed by a peritectic reaction at temperatures such as 2164.8 °C [19], 2165 °C [42], 2370 °C [39] and 2375 °C [38]. In all studies, detected composition of the B_4Ce compound is 80 at.% B and 20 at.% Ce without any homogeneity ranges. Following the same method as that by Muratov et al. [48], Bolgar et al. [52] presented an approximate equation for the temperature dependences of heat capacity, entropy, and enthalpy increment from 298.15 K to melting point of B_4Ce. Meschel and Kleppa [53] measured standard enthalpy of formation of the B_4Ce compound to be −53.5 + 1.5 kJ/mol-atom by direct synthesis calorimetry. Liquid phase has not been investigated and present liquidus curves in all literature are speculative.

In the binary B-Ce system, four invariant reactions occur: one peritectic, two eutectics, and one peritectoid. A peritectic reaction L + B_6Ce → B_4Ce corresponds to the formation B_4Ce compound, and according to the critical review [54], the temperature for this reaction