Ceramics International 42 (2016) 13738–13747

Contents lists available at ScienceDirect

Ceramics International

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

Thermodynamic evaluation of the BaO-ZrO_2-$YO_{1.5}$ system

Chongmao Lin [a], Shusen Wang [a], Guangyao Chen [a], Kun Wang [b], Zhiwei Cheng [a], Xionggang Lu [a,c], Chonghe Li [a,c,*]

[a] State Key Laboratory of Advanced Special Steel & Shanghai Key Laboratory of Advanced Ferrometallurgy & School of Materials Science and Engineering, Shanghai University, Shanghai 200072, China
[b] Center for Research in Computational Thermochemistry (CRCT), Department of Chemical Engineering, Ecole Poly technique, Montréal, Québec, Canada H3C 3A7
[c] Shanghai Special Casting Engineering Technology Research Center, Shanghai 201605, China

ARTICLE INFO

Article history:
Received 1 April 2016
Received in revised form
26 May 2016
Accepted 26 May 2016
Available online 27 May 2016

Keywords:
E. Refractories
Thermodynamic modeling
CALPHAD method
BaO-ZrO_2-$YO_{1.5}$
Phase diagram

ABSTRACT

Based upon the experimental data available in the literature and present measurements, thermodynamic reassessments were initially performed on the binary BaO-ZrO_2, BaO-$YO_{1.5}$ systems, and the resultant thermodynamic parameters were then merged in combination with that of the previous ZrO_2-$YO_{1.5}$ system to derive a self-consistent thermodynamic description for the ZrO_2-BaO-$YO_{1.5}$ ternary system with limited ternary thermodynamic parameters. The Gibbs energies of all the liquid and terminal solid solution phases were treated by the substitutional solution model, the BZ phase featured by second solid solution described by the compound energy formalism (CEF) model, and the stoichiometric compound BZY424 and Ba_2YZrO_{6-d} modeled following the Neumann-Kopp rule. The calculated results agree well with the isothermal sections at 1600 °C and 1750 °C (1873 K and 1923 K) from both of the previous and present measured phase diagrams. This demonstrates that the thermodynamic parameters derived in the present work could be applicable to compositional optimizations of novel refractories for melting titanium alloys on the basis of this ternary oxide system.

1. Introduction

Titanium and titanium alloys are high-chemically active metals, which can react with almost all refractory materials in the molten state [1]. $BaZrO_3$ is viewed as a possible candidate for melting titanium alloys, and also successfully used to refine Ti-Ni alloys [2]. However, great challenges still exist in using $BaZrO_3$ to manufacture the alloys with high-concentrated titanium, for example, the $BaZrO_3$ crucible would be reactive with high Ti alloys; the structure of $BaZrO_3$ crucible would be damaged after melting high Ti alloys; the Ba and Zr elements would diffuse to Ti alloys. Nevertheless, doping Y_2O_3 into $BaZrO_3$ is a tentative step to improve the compatibility of $BaZrO_3$ refractory with the titanium alloys. Moreover, $BaZrO_3$ has attracted particular attention among the candidate proton conducting electrolyte materials for electrochemical applications because of its chemical stability and high bulk proton conductivity. The development of protonic conductors based on this material, however, has been hampered by the high resistance of grain boundaries, due to limited grain growth during sintering and the high number density of such boundaries [3]. In order to resolved these issues, many researchers reported that the Y-doped $BaZrO_3$ is one of the most promising candidate as protonic conductor in view of its high protonic conductivity [3–15] and significant stability against reaction with CO_2 [7,8]. Yamasaki [3] investigated that $BaZr_{0.8}Y_{0.2}O_{3-\delta}$ possesses total high conductivity based on the sol-gel synthesis of nanocrystalline precursor materials and reactive sintering. Pergolesi [4] verified that the yttrium-doped barium zirconate films are provided with high proton conductivity in grain-boundary. The Y-doped $BaZrO_3$ is also used in solid oxide fuel cells (SOFCs) to improve the electrochemical performance [16–22]. The Ba_2ZrYO_{6-d} is suggested as a good substrate material for the deposition of $YBa_2Cu_3O_7$ films [23,24], and the optical properties are potentially applied to warming coatings, solar control, antireflection coatings and window layer in solar cells [25].

In order to facilitate the search for the suitable chemical compositions among $BaZrO_3$ based materials for their specific applications, it is of primary importance to investigate the phase equilibria and thermodynamic behavior of the BaO-ZrO_2-MO_x (M: Metal elements) systems. For instance, there are three prerequisites for developing novel refractories in the process of titanium smelting, which are high melting point, high chemical stability (not react with liquid titanium), and good thermal shock

* Corresponding author at: State Key Laboratory of Advanced Special Steel & Shanghai Key Laboratory of Advanced Ferrometallurgy & School of Materials Science and Engineering, Shanghai University, Shanghai 200072, China.
E-mail address: chli@staff.shu.edu.cn (C. Li).

http://dx.doi.org/10.1016/j.ceramint.2016.05.172
0272-8842/

resistance. These demands for designing refractories could be satisfied by the provided phase equilibria and thermodynamic properties of the corresponding systems. The conventional approach on the basis of experimental measurements is expensive, time-consuming and hence unrealistic. Thanks to the great development of the CALPHAD method, it is now very effective and fast in obtaining phase diagrams and thermodynamic properties of multicomponent systems and limited amount of experimental data are just needed to verify the calculated accuracy.

The aim of this paper is to derive a set of self-consistent thermodynamic functions for credibly describing solid phase relations (isothermal sections at 1600 °C and 1750 °C) in the BaO-ZrO_2-$YO_{1.5}$ ternary system. The three binary subsystems were initially reproduced or optimized based upon the available experimental data in the literature, and then all the binary model parameters for the relevant phases were merged with simultaneously introducing of necessary ternary parameters to accurately treat the ternary phase equilibria in formation reported in the literature and the present measurements. The final calculated results are in good agreement with all the available experimental data within the error limits, which demonstrate the derived thermodynamic database could be safely used to optimize and design $BaZrO_3$ based refractories for melting titanium and its alloys.

2. Review of the literature information

2.1. ZrO_2-$YO_{1.5}$ system

The first phase diagram of the ZrO_2-$YO_{1.5}$ system was published in 1951 by Duwez [27]. The first thermodynamic evaluation of the ZrO_2-$YO_{1.5}$ system was conducted by Degtyarev [28]. Du [29] reassessed this system by using the simple substitutional solution model for describing the various solid solutions and the liquid phase based on the available phase diagram data. Subsequently, this system has been reassessed by Yokokawa [30], Fabrichnaya [31], Jacobson [32] and Chen [33] using the ionic sublattice model. Recently, Wang [34] also reassessed the ZrO_2-$YO_{1.5}$ system by using an updated lattice stability parameters of ZrO_2, showing an improved calculation of the phase equilibria on the ZrO_2 side. The present work adopted the relative parameters reported by Wang [34] to derive a set of self-consistent thermodynamic database for the BaO-ZrO_2-$YO_{1.5}$ system. Fig. 1 shows the calculated ZrO_2-$YO_{1.5}$ phase diagram based upon the optimized parameters by Wang [34].

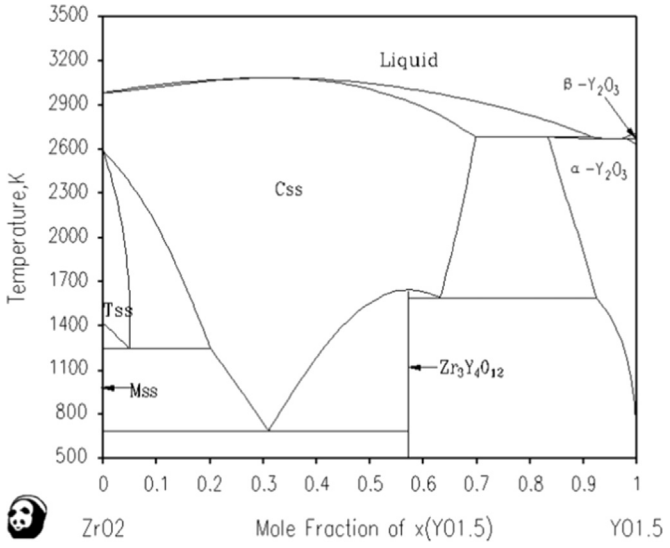

Fig. 1. Calculated phase diagram of the ZrO_2-$YO_{1.5}$ system.

2.2. BaO-$YO_{1.5}$ system

The complete phase diagram of the BaO-$YO_{1.5}$ system was measured by Lopato [35] using DTA method. This system includes the liquid phase, two intermediate compounds (BaY_2O_4 and $Ba_3Y_4O_9$), three terminal solid phases (α-Y_2O_3 with cubic structure at low temperature, β-Y_2O_3 with hexagonal structure at high temperature and BaO in halite). Based upon the reported data by Lopato [35], the BaO-$YO_{1.5}$ phase diagram was calculated by Lysenko [36] and Horsak [37] using simple computer programs. However, their calculations were not well consistent with the updated experimental data by Lopato [35] and Zhang [38], especially the compositions and temperatures appeared on both of the eutectic points (Liquid ↔ BaOss + $Ba_3Y_4O_9$ and Liquid ↔ $Ba_3Y_4O_9$ + α-Y_2O_3). Thus, it is interesting and necessary to re-optimize this system based on the recently published data as illustrated in the literature [39].

The information on the thermochemical data of BaO-$YO_{1.5}$ system was rarely reported, the only available thermodynamic data was mainly focused on the intermediate compounds BaY_2O_4 and $Ba_3Y_4O_9$. The standard formation enthalpies of BaY_2O_4 from simple oxides were measured by Azad [40], Kale [41], Skolis [42], Marushkin [43], Brosha [44] and Konkova [45], remarkable deviations can be found, from −120 kJ/mol to −128 kJ/mol by Azad [40] and Kale [41], from -30.9 ± 9 to -46 ± 11 kJ/mol by Skolis [42], Marushkin [43] and Brosha [44], in their publications. The experimental data about the thermodynamic properties of BaY_2O_4 and $Ba_3Y_4O_9$ are listed in Table 1.

2.3. BaO-ZrO_2 system

Paschoal [46] and Shevchenko [47] were responsible for the major contributions to understanding the liquidus in the BaO-ZrO_2 phase diagram. By means of optical microscopy, XRD and DTA techniques, Paschoal [46] measured the BaO-rich side liquidus. Using the DTA method, Shevchenko [47] constructed a series of the phase diagrams of ZrO_2/HfO_2-based systems, and paid attention to the ZrO_2-rich side. Several groups [48–53] investigated thermodynamic properties of the BaO-ZrO_2 system. The Gibbs energy of formation of $BaZrO_3$ relative to the pure oxides in the temperature range from 960 to 1210 K, and from 1180 to 1320 K were determined by Jocab [48] and Levitskii [49] using electron motive force, respectively. Muromachi [50] reported the enthalpy of formation of $BaZrO_3$ from the component oxides at 1060 K, which agrees well with the value in the temperature range from 960 to 1210 K reported by Jocab [48]. Odoj [51] also investigated the evaporation and standard enthalpy of formation of $BaZrO_3$ from1647 to 2118 K by high temperature mass spectrometry. Due to the reference state of BaO used by Odoj [51] with gas state is different from that by Jocab [48] and Muromachi [50] with the halite structure solid state, the enthalpy of formation of $BaZrO_3$ of Odoj [51] is also different with the value of Jocab [48] and Muromachi [50]. In present optimization, the thermodynamic data of Jocab [48], Levitskii [49] and Muromachi [50] were adopted to optimize the parameters of $BaZrO_3$. For the compounds Ba_2ZrO_4 and $Ba_3Zr_2O_7$, the enthalpies of formation from elements at 298 K were determined by Dash [52,53]. These data were compared with the calculated results.

2.4. Ternary System

The BaO-ZrO_2-$YO_{1.5}$ ternary phase diagram was investigated by several groups. Paulose [23] firstly reported that a new compound Ba_2YZrO_{6-d} exists after sintering at 960 °C and subsequent cooling down of ZrO_2(5 wt%)-doped $YBa_2Cu_3O_7$. Paulose [23] also synthesized Ba_2YZrO_{6-d} from its oxide mixtures heated at 1450 °C for 10 h by the solid-state reaction method, proving that Ba_2YZrO_{6-d} is