CALPHAD: Computer Coupling of Phase Diagrams and Thermochemistry 55 (2016) 77–87

Contents lists available at ScienceDirect

CALPHAD: Computer Coupling of Phase Diagrams and Thermochemistry

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

‘Thermodynamic assessment of the Ag-Zr and Cu-Zr binary systems

Hsien-Ming Hsiao [a,b], Song-Mao Liang [c], Rainer Schmid-Fetzer [c], Yee-wen Yen [a,*]

[a] Department of Materials Science and Engineering, National Taiwan University of Science and Technology, Taipei, Taiwan, ROC
[b] Chemical Engineering Division, Institute of Nuclear Energy Research, Longtan, Taiwan, ROC
[c] Institute of Metallurgy, Clausthal University of Technology, Robert-Koch-Str. 42, d-38678 Clausthal-Zellerfeld, Germany

ARTICLE INFO

Article history:
Received 16 March 2016
Received in revised form
2 August 2016
Accepted 8 August 2016
Available online 17 August 2016

Keywords:
CALPHAD method
Thermodynamic assessment
Ag-Zr system
Cu-Zr system

ABSTRACT

The Ag-Zr and Cu-Zr binary systems are thermodynamically reassessed in this study. Not only phase diagrams, but also thermodynamic properties, such as enthalpy of formation for solids, activity for liquid, and enthalpy of mixing for liquid, are all calculated and compared with available experimental data to assure the accuracy of the assessment. Cu_2Zr and $Cu_{24}Zr_{13}$ phases are considered as meta-stable phases, which would not exist in the Cu-Zr equilibrium phase diagram. The artifact of liquid miscibility gap at high temperature is avoided in the presently calculated phase diagrams.

1. Introduction

The Cu-Zr-based alloys are of great interest because of their easy formation of amorphous metallic glasses, in other words, high glass-forming ability (GFA) in this system [1,2]. With the addition of Ag element, the stability of supercooled liquid and GFA would be increased; also, the mechanical properties were improved [3]. Hence, the understanding of Ag-Cu-Zr system is important for industrial application. Furthermore, by using the thermodynamic dataset, the formation region of bulk metallic glasses (BMGs) could be predicted and later verified by experimental methods, such as copper mold or roller melt-spinning methods [4–6]. The experimental number of samples could be reduced in a large amount due to thermodynamic prediction based on reliable and consistent thermodynamic description of Ag-Cu-Zr ternary system, which first requires reliable modeling of binary Ag-Zr and Cu-Zr sub-systems. The Ag-Cu system was assessed several times [7–11] and not discussed in this work.

The phase diagram of Ag-Zr system was reviewed and established by Karakaya and Thompson [12]. There were two intermetallic phases, AgZr and $AgZr_2$, existing in this system after assessment and calculation. The Ag-Zr system was optimized by Karakaya et al. [12], He et al. [13], and Kang et al. [14]. But in Ref. [12], the experimental data from Zhang et al. [15] were not considered. Thermodynamic description of Ref. [13] resulted in a liquid miscibility gap at high temperature. Kang et al. [14] used Modified Quasichemical Model and FactSage to assess the system in 2010. However, the quasichemical model can be only applied in FactSage and is not compatible with Pandat and ThermoCalc.

The Cu-Zr system, on the other hand, was thermodynamically assessed by several authors [14,16–21]. There were several contradictions in the results of these thermodynamic descriptions. The first question was whether the copper-rich intermetallic compound has Cu_9Zr_2 or Cu_5Zr stoichiometry. The second one was whether Cu_5Zr_8, Cu_2Zr, and $Cu_{24}Zr_{13}$ phases claimed by Kneller et al. [22] and Braga et al. [23] are stable or not. In this work, we thermodynamically reassess the Ag-Zr and Cu-Zr binary systems taking into account all the available experimental data.

2. Critical review of experimental literature data

2.1. Ag-Zr binary system

2.1.1. Solid phases

The AgZr intermetallic phase in the Ag-Zr system was confirmed through X-ray analysis by Raub et al. [24] and Karlsson [25]. Later, the $AgZr_2$ phase was identified as the BCT structure with lattice parameter c = 398 pm by Betterton and Easton [26], which is different from the results of Nevitt and Downey [27] who proposed c = 1200.37 pm. Karlsson [25] reported that $AgZr_3$ phase existed in the composition range of 70–80 at% Zr. This intermetallic phase was not taken into consideration in this study, mainly based on other experimental results which indicated existence of $AgZr_2$ phase [15,26–28]. Raub et al. [24] first reported that AgZr had a small homogeneity range. In Ref. [25] the homogeneity range of

* Corresponding author.
E-mail address: ywyen@mail.ntust.edu.tw (Y.-w. Yen).

http://dx.doi.org/10.1016/j.calphad.2016.08.001
0364-5916/

Table 1
Solid phases in the Ag-Zr and Cu-Zr systems.

Phase name / Temperature range (°C)	Pearson symbol /*Space group*/ Prototype	Lattice parameters (pm)	Reference
(Ag) ≤ 961.93	cF4 *Fm-3m* Cu	a = 408.61	[63] (1981 King)
(Cu) ≤ 1084.87	cF4 *Fm-3m* Cu	a = 361.46	[63] (1981 King)
(βZr) 1855–863	cI2 *Im-3 m* W	a = 360.90	[64] (1982 King) [65] (1973 Metals)
(αZr) ≤ 863	hP2 $P6_3/mmc$ Mg	a = 323.17 c = 514.76	[64] (1982 King) [65] (1973 Metals)
AgZr ≤468	tP4 *P4/nmm* γ-CuTi	a = 346.8–347.6 c = 660.3–662.9	[25] (1952 Karlssen)
$AgZr_2$ ≤ 834	tI6 *I4/mmm* $MoSi_2$	a^* = 325 c^*= 398 or a† = 324.64 c†=1200.37	*[26] (1958 Betterton), BCT structure †[27] (1962 Nevitt)
Cu_9Zr_2	F-43 m	a = 685.6	[35] (1985 Glimois)
≤1012		c = 688.2	[37] (2001 Saitoh)
$Cu_{51}Zr_{14}$	hP65	a =1124.44	[66] (1975 Gabathuler)
≤ 1115	*P6/m* $Ag_{51}Gd_{14}$	c = 828.15	[67] (1975 Bsenko)
Cu_8Zr_3	oP44 *Pnma* Cu_8Hf_3	a = 786.93 b = 815.47 c = 998.48	[67] (1975 Bsenko)
$Cu_{10}Zr_7$	oC68 *C2ca* $Ni_{10}Zr_7$	a = 1267.29 b = 931.63 c = 934.66	[67] (1975 Bsenko)
CuZr 960–725**	cP2 *Pm-3 m* CsCl	a = 325.87	[50] (1980 Carvalho) **[23] (1998 Braga)
$CuZr_2$	tI6	a = 322.04	[27] (1962 Nevitt)
1025–950***	*I4/mmm* $MoSi_2$	c = 1118.32	***[22] (1986 Kneller) and [23] (1998 Braga)

Table 2
Experimental and calculated standard enthalpy of formation of the Cu-Zr compounds, $\Delta_f H°$, at 298 K. Reference state of calculated values is fcc-(Cu) and hcp-(αZr).

Phases	Method	$\Delta_f H^0$, kJ/mol-atoms	Reference
Cu_9Zr_2	Measured	−8.7 ± 1.9[a]	[43] (1989Sommer)
		−10.389 ± 0.077	[40] (2003Zaitsev)
		−23.8	[19] (2008Yamaguchi)
		−9.0597	[14] (2010Kang)
	Calphad	−9.93153	This work
$Cu_{51}Zr_{14}$	Measured	−14.07 ± 1.24[b]	[41] (1982Kleppa)
		−14.3 ± 0.3	[45] (1996Weihs)
		−11.241 ± 0.076	[40] (2003Zaitsev)
		−24.3 ± 2.2	[68] (2003Meschel)
		−25.2	[19] (2008Yamaguchi)
	Calphad	−12.97558	[16] (1994Zeng)
		−12.601	[18] (2008Turchanin)
		−20.252	[20] (2010Zhou)
		−9.6663	[14] (2010Kang)
		−12.2164	This work
Cu_8Zr_3	Measured	−13.129 ± 0.083	[40] (2003Zaitsev)
		−16.2	[19] (2008Yamaguchi)
	Calphad	−13.46029	[16] (1994Zeng)
		−14.788	[18] (2008Turchanin)
		−18.55966	[20] (2010Zhou)
		−11.135	[14] (2010Kang)
		−13.1058	This work
$Cu_{10}Zr_7$	Measured	−12.31 ± 0.24[b]	[41] (1982Kleppa)
		−22.004 ± 0.259	[40] (2003Zaitsev)
		−22.9	[19] (2008Yamaguchi)
	Calphad	−14.22059	[16] (1994Zeng)
		−20.466	[18] (2008Turchanin)
		−16.133	[20] (2010Zhou)
		−18.994	[14] (2010Kang)
		−15.353	This work
CuZr	Measured	−9.05 ± 1.18	[41] (1982Kleppa)
		−24.4 ± 0.96	[42] (1982Ansara)
		−24 ± 2	[44] (1989Sidoro)
		−17.9 ± 2.8	[47] (1996Turchanin)
		−17.282 ± 0.309	[40] (2003Zaitsev)
	Calphad	−10.05212	[16] (1994Zeng)
		−17.014	[18] (2008Turchanin)
		−12.44168	[20] (2010Zhou)
		−13.626	[14] (2010Kang)
		−9.38877	This work
$CuZr_2$	Measured	−10.95 ± 0.69	[41] (1982Kleppa)
		−17.3 ± 0.84	[42] (1982Ansara)
		−19.797 ± 0.357	[40] (2003Zaitsev)
		−16.6	[19] (2008Yamaguchi)
	Calphad	−14.63467	[16] (1994Zeng)
		−23.635	[18] (2008Turchanin)
		−13.84	[20] (2010Zhou)
		−14.923	[14] (2010Kang)
		-12.4512	This work

[a] In [43] (1989Sommer), Cu_9Zr_2 was designated as Cu_4Zr.
[b] In [41] (1982Kleppa), $Cu_{51}Zr_{14}$ and $Cu_{10}Zr_7$ were designated as Cu_3Zr and Cu_3Zr_2, respectively.

AgZr is given to be less than 3 at%. Zhang et al. [15] observed that the AgZr and $AgZr_2$ phases at 900 °C were homogeneous in the range from 47.5 to 51.0 at% Ag and from 31.3 to 34.0 at% Ag, respectively. For simplicity, this work set AgZr and $AgZr_2$ phases as stoichiometric compounds.

2.1.2. Thermodynamic data

Only Fitzner and Kleppa [29] reported values of enthalpy of formation of intermetallic AgZr and $AgZr_2$ phases at 298 K. These values were obtained from observed heats of reaction at 1473 K, and then they transferred the measured heat effect to standard enthalpy of formation at 298 K. Hence, the values presented in Ref. [29] are not reliable; even the authors marked that these values were uncertain. There is no experimental measurement of heat capacities and entropies of AgZr and $AgZr_2$ phases.

2.1.3. Phase equilibrium data

The experimental data for the Ag-Zr phase equilibria were mainly from Karakaya et al. [12]. For the Ag-Zr system, Raub and Engel [24] measured the liquidus and solidus temperatures for a composition range from 4 to 51 at% Zr and found the eutectic reaction L ↔ (Ag)+ AgZr at 955 °C. Betterton et al. [26] investigated the Zr-rich part (up to 36 at% Ag) of the Ag-Zr system and determined the formation of AgZr and $AgZr_2$ intermetallic phases. The eutectoid reaction, in which the (βZr) solid solution decomposed into (αZr) and $AgZr_2$ phases, was determined. They also found that the solubility of Ag in (βZr) at peritectic temperature of 1190 °C was about 20 at%. The solubility of Ag in (αZr) was found to be about 0.1 at% at the eutectoid temperature 823 °C [26]. Later, Loboda et al. [28] used DTA for analysis of Ag-Zr alloys in a composition range from 30 to 70 at% Zr and obtained peritectic reactions of formation of AgZr at 1135 °C and $AgZr_2$ at 1170 °C. The melting temperatures were chosen from onset