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Journal of Alloys and Compounds 452 (2008) 304–306

Journal of ALLOYS AND COMPOUNDS

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Thermodynamic assessment of the Ag–Yb system

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Received 25 September 2006; received in revised form 2 November 2006; accepted 6 November 2006

Abstract

The Ag–Yb binary system has been thermodynamically assessed with CALPHAD approach. The solution phases including liquid, bcc and fcc were treated as substitutional solution phases, of which the excess Gibbs energies were formulated with Redlich–Kister polynomial functions. The binary intermetallic compounds were treated as stoichiometric phases. A set of self-consistent thermodynamic parameters for describing various phases in this system has been obtained, which can well reproduce the corresponding experimental data.

Keywords: Ag–Yb system; Thermodynamic calculation; Phase diagram

1. Introduction

Cu-based alloys with high strength and high electronic-conductivity have found wide application in high-speed train and electronic industry. However, high strength is usually incompatible with high electric conductivity in materials science and engineering. Addition of alloying elements into copper matrix and adoption of proper heat-treatment may help to achieve high strength while maintain high conductivity. Ag is one of the best alloying elements to improve the properties of Cu-based alloys. Some reports [1–4] show that addition of Ag will increase the strength of Cu alloys and not greatly reduce the conductivity of Cu alloys. Meanwhile, Rare earth elements can also greatly improve the properties of Cu-based alloys, e.g. strength and conductivity [5,6]. Some investigations show that Yb also can highly improve electric properties of Cu-based alloys [7,8]. In order to investigate the alloying of Yb in the Cu–Ag alloys, the phase relations of Cu–Ag–Yb system is very important and necessary. As a part of studies on the phase diagram in this ternary system, thermodynamic assessment of the Ag–Yb system is carried out in this work.

2. Evaluation of experiment information

Gschneidner et al. [9] had determined the solid solubility of Yb in Ag, the eutectic temperature of Ag with the Ag-rich compound, and the composition of Ag-rich compound. It was found the Ag-rich compound is Ag_5Yb, which had the same structure as the high-temperature form of Ag_5La and the phase Ag_5Pr. The temperature of eutectic between Ag and Ag_5Yb was 685 °C. The maximum solubility of Yb in Ag was reported to be 1.92 at.%.

McMasters et al. [10] also observed Ag_5Yb phase, but he did not study the details of the structure.

Palenzona [11] investigated the phase diagram of Ag–Yb system by DTA method. Six intermediate phases: Ag_3Yb_5, Ag_2Yb_3, AgYb, Ag_2Yb, Ag_7Yb_2 and Ag_9Yb_2 had been reported in his work [11]. Structure analysis of the last phase was not completed, but the formula Ag_9Yb_2 was assigned to it based only on the DTA data. The AgYb compound transform from orthorhombic β-type Fe structure at room temperature to cubic CsCl-type structure at 456 °C. No structure change has been reported for the Ag_2Yb in his work [11]. It was also reported [11] that about 2 at.% Yb dissolved in Ag, which agrees well with the value 1.92 at.% reported by Gschneidner et al. [9]. No appreciable solid solubility of Ag in terminal phase β Yb was observed.

Most information about phase equilibria of this system is in agreement with each other, except the formula "Ag_5Yb" and the structure of Ag_2Yb. Gschneidner et al. [9] thought the Ag-rich compound is Ag_5Yb. However, later in Palenzona' work [11], this compound was suggested as Ag_9Yb_2, which was adopted by Gschneidner and Calderwood [12] when assessing the Ag–Yb system. In this work, the formula Ag_9Yb_2 for this compound is accepted. Contradiction also exists in the structure of Ag_2Yb

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doi:10.1016/j.jallcom.2006.11.022

phase. Moriarty et al. [14] reported a tetragonal $MoSi_2$-type structure for Ag_2Yb, but later Iandelli and Palenzona [13] did not find either $MoSi_2$-type for Ag_2Yb, or give an indication of a polymorphic transformation when they investigated this phase. Palenzona [11] and Gschneidner and Calderwood [12] also thought this Ag_2Yb phase had just one structure $CeCu_2$-type. It seems doubtfully that the $MoSi_2$-type structure exists as an equilibrium phase for Ag_2Yb. In this work the structure of Ag_2Yb is just accepted as $CeCu_2$-type, and its polymorphic transformation is not considered.

As for the thermodynamic properties, only heats of mixing of liquid Ag-rich Ag–Yb alloys were measured using isoperibolic calorimetry by Ivanov and Witusiewicz [15]. Besides, no other thermodynamic property of this system was reported.

3. Thermodynamic model

The lattice stabilities for element Ag and Yb are referred to Dinsdale [16]. An ordinary substitutional solution model is employed to describe liquid, bcc and fcc terminal solution. The mole Gibbs energy of a solution phase Φ (Φ = liqiud, fcc, bcc) can be represented as a sum of the weighted Gibbs energy for the pure components, the ideal entropy term describing a random mixing of the components, and the excess Gibbs energy describing the degree of deviation from ideal mixing, i.e.:

$$G_m^{\Phi} = \sum x_i^0 G_i^{\Phi} + RT \sum x_i \ \ln(x_i) + {}^{E}G_m^{\Phi} \qquad (1)$$

where G_m^{Φ} is the molar Gibbs energy of a solution phase Φ, ${}^0G_i^{\Phi}$ the Gibbs energy of pure element i, x_i the mole fraction of component i (i = Ag, Yb), R the gas constant, T the temperature, ${}^{E}G_m^{\Phi}$ is the excess Gibbs energy. For ordinary substitutional solution, the excess Gibbs energy of phase Φ can be written in the form of a Redlich–Kister polynomial as follows:

$$^{E}G_m^{\Phi} = x_{Ag}x_{Yb}\sum_{j=0}^{n}{}^{(j)}L_{Ag,Yb}^{\Phi}(x_{Ag} - x_{Yb})^j \qquad (2)$$

${}^{(j)}L_{Ag,Yb}^{\Phi}$ an interaction parameter and can be expressed as temperature dependent as follows:

$${}^{(j)}L_{Ag,Yb}^{\Phi} = A_j + B_jT \qquad (3)$$

where A_j and B_j are the model parameters to be optimized.

All the intermetallic phases were treated as stoichiometric phases, which were described as Ag_pYb_q. Due to lack of heat capacity C_p, according to Neumann–Kopp rule, the Gibbs energy of the phase Ag_pYb_q was formulated as

$$G_{Ag_pYb_q} = \frac{p}{p+q}{}^0G_{Ag}^{fcc} + \frac{q}{p+q}{}^0G_{Yb}^{fcc} + A + BT \qquad (4)$$

A and B are the adjusted parameters being optimized in the present work.

Table 1
Thermodynamic parameters of the Ag–Yb system

Phase	Thermodynamic parameters
Liquid	${}^0L_{Ag,Yb} = -77285.337 + 24.999T$ ${}^1L_{Ag,Yb} = -10774.088 + 2.205T$
fcc	${}^0L_{Ag,Yb}^{fcc} = 0$ ${}^1L_{Ag,Yb}^{fcc} = -29495.384$
Ag_9Yb_2	$G^{Ag_9Yb_2} = 0.8182^0G_{Ag}^{fcc} + 0.1818^0G_{Yb}^{fcc} - 13035.539 + 2.404T$
Ag_7Yb_2	$G^{Ag_7Yb_2} = 0.7778^0G_{Ag}^{fcc} + 0.2222^0G_{Yb}^{fcc} - 13365.526 + 0.709T$
Ag_2Yb	$G^{Ag_2Yb} = 0.6667^0G_{Ag}^{fcc} + 0.3333^0G_{Yb}^{fcc} - 14729.956 - 0.500T$
AgYb_H	$G^{AgYb\_H} = 0.5^0G_{Ag}^{fcc} + 0.5^0G_{Yb}^{fcc} - 16252.257 - 1.116T$
AgYb_L	$G^{AgYb\_L} = 0.5^0G_{Ag}^{fcc} + 0.5^0G_{Yb}^{fcc} - 16628.481 - 0.600T$
Ag_2Yb_3	$G^{Ag_2Yb_3} = 0.4^0G_{Ag}^{fcc} + 0.6^0G_{Yb}^{fcc} - 18497.088 + 3.219T$
Ag_3Yb_5	$G^{Ag_3Yb_5} = 0.375^0G_{Ag}^{fcc} + 0.625^0G_{Yb}^{fcc} - 18993.989 + 4.713T$

Note: Gibbs energies are expressed in J/mol. Lattice stabilities of elements Ag and Yb are referred to Dinsdale [16].

4. Results and discussion

On the basis of lattice stabilities cited from Dinsdale [16], the optimization of the Ag–Yb system is carried out using the Parrot modules in the Thermo_Calc program developed by Sundman et al. [17]. The phase diagram and thermochemical data were used as input to the program for the optimization. Each piece of selected information was given a certain weight by personal judgment, and verified by trial and error method during the assessment, until most of the selected experimental information was reproduced within the selected uncertainty limits.

The parameters for the liquid phase were first optimized using the mixing enthalpy of liquid. The thermodynamic parameters of the congruent intermetallic compounds were investigated next by using phase diagram data. The other compounds were optimized consequently. The parameters of terminal solution phases were obtained at last based on the solid solubility of the second

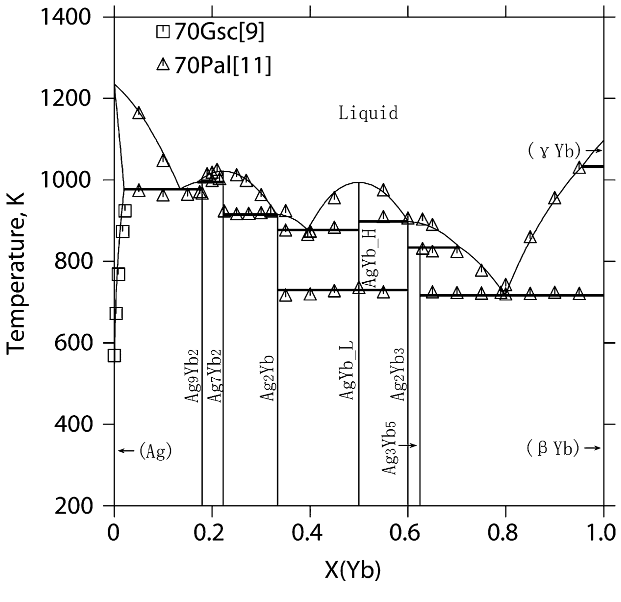

Fig. 1. The calculated Ag–Yb phase diagram with experimental data [9,11].

Table 2
Invariant reactions in the Ag–Yb system

Reaction	Composition of liquid (at.% Yb)	*T* (K)	Reaction type	Source
L ⇔ fcc + Ag_9Yb_2	13.5	977	Eutectic	This work
	13.0	968	Eutectic	[9]
	13.0	958	Eutectic	[11]
L + Ag_7Yb_2 ⇔ Ag_9Yb_2	17.2	997	Peritectic	This work
	17.0	1000	Peritectic	[11]
L ⇔ Ag_7Yb_2	–	1022	Congruent	This work
		1022	Congruent	[11]
L ⇔ Ag_7Yb_2 + Ag_2Yb	33.1	916	Eutectic	This work
	32.5	919	Eutectic	[11]
L ⇔ Ag_2Yb + AgYb_H	39.5	877	Eutectic	This work
	39.5	865	Eutectic	[11]
L ⇔ AgYb_H	–	994	Congruent	This work
		997	Congruent	[11]
AgYb_H ⇔ AgYb_L	–	729	Allotropic	This Work
		729	Allotropic	[11]
L + AgYb_H ⇔ Ag_2Yb_3	60.1	897	Peritectic	This work
	60.5	905	Peritectic	[11]
L + Ag_2Yb_3 ⇔ Ag_3Yb_5	70.6	834	Peritectic	This work
	69.5	825	Peritectic	[11]
L ⇔ Ag_3Yb_5 + fcc	79.9	716	Eutectic	This work
	79.0	719	Eutectic	[11]

component. All the parameters were finally evaluated together to give a reasonable description of this system. All the evaluated parameters are listed in Table 1.

Fig. 1 shows the calculated phase diagram of Ag–Yb system compared with experimental data, While Table 2 lists the invariant reactions in the Ag–Yb system. An agreement within 9 K between the calculated and experimentally determined temperatures for these invariant reactions has been obtained except for the congruent melting temperature of Ag_2Yb phase, where the disagreement is 18 K. This congruent melting temperature cannot be reproduced well thermodynamically despite great care taken in optimization. The precisely determination of such a temperature is very difficult, because Yb are very active, and, in some case, it was carried out several years ago. For these reasons, we think it was unnecessary to introduce more complex thermodynamic functions in order to match closely such experimental data. As such the liquidus of Ag_2Yb phase requires further study. The assessed maximum terminal solubility of Yb in Ag is 2.0 at.% Ag, which agrees well with experimental data (1.92 at.% Ag) [9,11]. As shown in Fig. 2, the calculated mixing enthalpy is reasonably agreement with the experiment data. It is demonstrated that the experimental data of thermodynamically properties can be well described by the present calculation within the experimental errors.

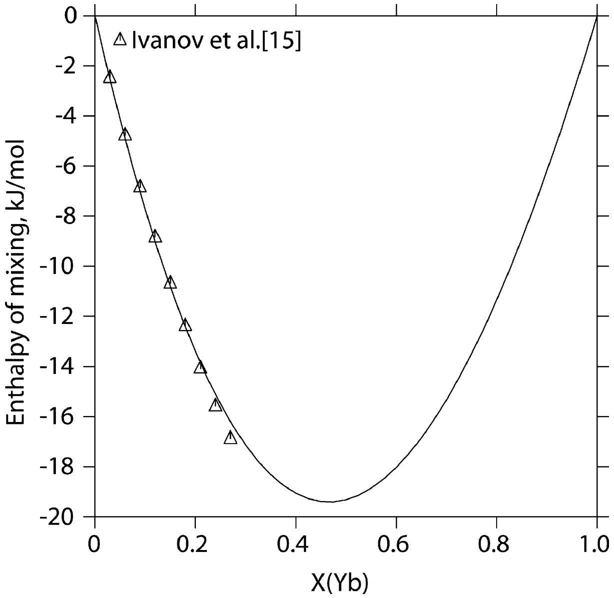

Fig. 2. The calculated enthalpy of mixing of liquid at 1463 K in Ag–Yb system with the experimental data [15]. Reference states: liquid Ag and liquid Yb.

5. Conclusions

The Ag–Yb binary systems have been assessed thermodynamically based on reported experimental data of phase diagrams and thermodynamic properties. Reasonable agreement between calculated and experimental data has been reached and thermodynamic parameters for various phases in this binary system have been obtained.

Acknowledgments

This work was financially supported by National Science Foundation of China (Grant No. 50401011). One of the authors, H.S. Liu, would like to thank for the Program for New Century Excellent Talents in Universities, P.R. China.

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