J. Chem. Thermodynamics 40 (2008) 1064–1076

Contents lists available at ScienceDirect

J. Chem. Thermodynamics

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

The equilibrium phase diagram of the magnesium–copper–yttrium system

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ARTICLE INFO

Article history:
Received 8 November 2007
Received in revised form 5 March 2008
Accepted 5 March 2008
Available online 15 March 2008

Keywords:
Ternary phase diagram
Thermodynamic modelling
Modified quasichemical model
Mg alloys

ABSTRACT

Thermodynamic modelling of the Mg–Cu–Y system is carried out as a part of thermodynamic database construction for Mg alloys. This system is being modelled for the first time using the modified quasichemical model which considers the presence of short range ordering in the liquid. A self-consistent thermodynamic database for the Mg–Cu–Y system was constructed by combining the thermodynamic descriptions of the constituent binaries, Mg–Cu, Cu–Y, and Mg–Y. All the three binaries have been re-optimized based on the experimental phase equilibrium and thermodynamic data available in the literature. The constructed database is used to calculate and predict thermodynamic properties, the binary phase diagrams and *liquidus* projections of the ternary Mg–Cu–Y system. The current calculation results are in good agreement with the experimental data reported in the literature.

1. Introduction

Magnesium alloys are getting considerable attention for automobile and aerospace applications because they are the lightest among the commercially available structural alloys. They have high specific properties but low corrosion resistance which limited their use. While metallic glass, a new class of wonder material, is attracting attention due to its high mechanical strength and good corrosion resistance [1]. Mg–Cu–Y alloy system is a promising candidate for metallic glass since it has the largest super cooled liquid region among other Mg-alloy systems [2–5].

Despite its importance, this system has not yet been modelled thermodynamically. Also, the available descriptions for the binaries are contradictory to each other and none of the assessment was done considering the presence of short range ordering in the liquid. Hence the main objective of this work is to construct a reliable thermodynamic database of the Mg–Cu–Y system using sound thermodynamic models. The three constituent binary systems Mg–Cu, Cu–Y, and Mg–Y were re-optimized using the modified quasichemical model for the liquid phase. This model has the ability to take into consideration the presence of short range ordering in the liquid.

2. Analytical descriptions of the thermodynamic models employed

The Gibbs free energy function used for the pure elements (Mg, Cu, and Y) are taken from the SGTE (Scientific Group Thermodata Europe) compilation of Dinsdale [6].

The Gibbs free energy of a binary stoichiometric phase is given by

$$G^{\phi} = x_i{}^0G_i^{\phi_1} + x_j{}^0G_j^{\phi_2} + \Delta G_f, \quad (1)$$

where ϕ denotes the phase of interest, x_i and x_j are mole fractions of elements i and j which are given by the stoichiometry of the compound, and are the respective reference states of elements i and j in their standard state and $\Delta G_f = a + b(T/\mathrm{K})$ represents the Gibbs free energy of formation of the stoichiometric compound. The parameters a and b were obtained by optimization using experimental data.

The Gibbs free energy of the terminal solid solutions is described by the following equation:

$$G^{\phi} = x_i{}^0G_i^{\phi} + x_i{}^0G_j^{\phi} + R(T/\mathrm{K})[x_i \ln x_i + x_j \ln x_j] + {}^{ex}G^{\phi}. \quad (2)$$

The excess Gibbs free energy ${}^{ex}G^{\phi}$ is described by the Redlich–Kister polynomial model [7].

The modified quasichemical model [8–10] was chosen to describe the liquid phases of the three constituent binaries. From the literature survey, it was found that all the three binary systems have a very high negative enthalpy of mixing. Also, the calculated entropy of mixing curves of the Cu–Y and Mg–Y systems assume m-shaped characteristics. All these are indications of the presence of short range ordering [8]. The modified quasichemical model has

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doi:10.1016/j.jct.2008.03.004

three distinct characteristics [8–10]: (i) it permits the composition of maximum short range ordering in a binary system to be freely chosen, (ii) it expresses the energy of pair formation as a function of composition which can be expanded as a polynomial in the pair fraction and the coordination numbers are permitted to vary with the composition, and (iii) the model can be extended to multi-component systems. The model has been discussed extensively in the literature [8–10] and will be outlined briefly here. The energy of pair formation can be expressed by the following equation:

$$\Delta g_{AB} = \Delta g^{\circ}_{AB} + \sum_{i\geqslant 1} g^{i\circ}_{AB} X^{i}_{AA} + \sum_{j\geqslant 1} g^{\circ j}_{AB} X^{j}_{BB}, \tag{3}$$

where Δg°_{AB}, $\Delta g^{i\circ}_{AB}$, and $\Delta g^{\circ j}_{AB}$ are the parameters of the model and can be expressed as functions of temperature ($\Delta g^{\circ}_{AB} = a + b(T/\mathrm{K})$). Also, the atom to atom coordination numbers, Z_A and Z_B, can be expressed as a function of composition and can be represented by the following equations:

$$\frac{1}{Z_A} = \frac{1}{Z^{A}_{AA}}\left(\frac{2n_{AA}}{2n_{AA}+n_{AB}}\right) + \frac{1}{Z^{A}_{AB}}\left(\frac{n_{AB}}{2n_{AA}+n_{AB}}\right), \tag{4}$$

$$\frac{1}{Z_B} = \frac{1}{Z^{B}_{BB}}\left(\frac{2n_{BB}}{2n_{BB}+n_{AB}}\right) + \frac{1}{Z^{B}_{BA}}\left(\frac{n_{AB}}{2n_{BB}+n_{AB}}\right), \tag{5}$$

where n_{ij} is the number of moles of (i–j) pairs, Z^{A}_{AA} and Z^{A}_{AB} are the coordination numbers when all nearest neighbours of an A atom are A or B atoms, respectively. The composition at maximum short range ordering is determined by the ratio Z^{B}_{BA}/Z^{A}_{AB}. Values of Z^{A}_{AB} and Z^{B}_{BA} are unique to the A – B binary system and should be carefully determined to fit the thermodynamic experimental data (enthalpy of mixing, activity, *etc.*). The value of Z^{A}_{AA} is common for all systems containing A as a component. In this work, the value of Z^{Mg}_{MgMg}, Z^{Cu}_{CuCu} and Z^{Y}_{YY} was chosen to be 6 because it gave the best possible fit for many binary systems and is recommended by Dr. Pelton's group [8–10]. The values of Z^{Mg}_{MgCu}, Z^{Y}_{CuMg}, Z^{Mg}_{MgY}, Z^{Y}_{YMg}, Z^{Y}_{CuY}, and Z^{Y}_{YCu} are chosen to permit the composition at maximum short range ordering in the binary system to be consistent with the composition that corresponds to the minimum enthalpy of mixing. These values are given in table 1. The tendency to maximum short range ordering near the composition 40 atomic per cent (at.%) Mg in the Mg–Cu system was obtained by setting $Z^{Mg}_{MgCu} = 4$ and $Z^{Y}_{CuMg} = 2$. For the Cu–Y system, maximum short range ordering near 30 at.% Y was obtained by setting $Z^{Y}_{CuY} = 3$ and $Z^{Y}_{YCu} = 6$. Similarly for the Mg–Y system, the tendency to maximum short range ordering near the composition 30 at.% Y was obtained by setting $Z^{Mg}_{MgY} = 2$ and $Z^{Y}_{YMg} = 4$.

The Gibbs free energy of intermediate solid solutions is described by the compound energy formalism as shown in the following equations:

$$G = G^{ref} + G^{ideal} + G^{excess}, \tag{6}$$

$$G^{ref} = \sum y^{l}_{i} y^{m}_{j} \ldots y^{q}_{k} {}^{0}G_{(i:j:\ldots:k)}, \tag{7}$$

$$G^{ideal} = R(T/\mathrm{K}) \sum_{l} f_l \sum_{i} y^{l}_{i} \ln y^{l}_{i}, \tag{8}$$

$$G^{excess} = \sum y^{l}_{i} y^{l}_{j} y^{m}_{k} \sum_{\gamma=0} {}^{\gamma}L_{(i,j):k} \times (y^{l}_{i} - y^{l}_{j})^{\gamma}, \tag{9}$$

where $i,j,\ldots k$ represent components or vacancy, l, m and q represent sub-lattices, y^{l}_{i} is the site fraction of component i on sub-lattice l, f_l is the fraction of sub-lattice l relative to the total lattice sites, ${}^{0}G_{(i:j:\ldots k)}$ represents a real or a hypothetical compound (end member) energy, and ${}^{\gamma}L_{(i,j)}$ represent the interaction parameters which describe the interaction within the sub-lattice.

Modelling of the intermetallic solid solution phases requires information regarding the crystal structure of the phases and their homogeneity range. From the crystallographic data summarized in table 2, the following model is applied to represent the $MgCu_2$ phase:

$$(\mathrm{Mg}\%, \mathrm{Cu})_8 : (\mathrm{Cu}\%, \mathrm{Mg})_{16}.$$

Here, the '%' denotes the major constituent of the sub-lattice. This model covers the $0 \leqslant X_{Mg} \leqslant 1$ composition range and, of course, includes the homogeneity range of $0.31 \leqslant X_{Mg} \leqslant 0.353$ which was reported by Bagnoud and Feschotte [11].

The crystal structure data of the Cu_6Y intermediate solid solution was obtained by Buschow and Goot [12] and are listed in table 3.

According to Buschow and Goot [12] some of the Yttrium atomic sites are occupied by a pair of Cu atoms, which can be described by the following model with two sub-lattices:

$$(\mathrm{Y}\%, \mathrm{Cu}_2)(\mathrm{Cu})_5$$

This is actually a Wagner–Schottky type model [13]. The same model was used by Fries *et al.* [14] to represent Cu_6Y in their assessment of the Cu–Y system. This type of model can be used only for intermediate phases with a narrow homogeneity range [15]. This model covers $0.83 \leqslant X_{Cu} \leqslant 1$ composition range. This range includes homogeneity $0.84 \leqslant X_{Cu} \leqslant 0.87$ which was reported by Fries *et al.* [14]. The optimized model parameters are listed in table 4.

TABLE 1
Atom–atom "coordination numbers" of the liquid

A	B	Z^{A}_{AB}	Z^{B}_{AB}
Mg	Mg	6	6
Cu	Cu	6	6
Y	Y	6	6
Mg	Cu	4	2
Cu	Y	3	6
Mg	Y	2	4

3. Experimental data evaluation

According to the CALPHAD method, the first step of the thermodynamic optimization is to extract and categorize the available

TABLE 2
Crystal structure and lattice parameters of $MgCu_2$ phase

Phase	Crystal data		Atom	WP[a]	CN[b]	Atomic position			Reference
						X	*Y*	*Z*	
$MgCu_2$	Prototype	$MgCu_2$	Cu	16d	12	0.625	0.625	0.625	[68]
	Pearson symbol	cF24	Mg	8a	16	0	0	0	
	Space group	$Fd\bar{3}m$							
	Space group No.	227							
	Lattice parameter/nm	$a = 0.7035$							[11]
	Angles: $\alpha = 90°$, $\beta = 90°$, $\gamma = 90°$								

[a] WP, Wyckoff Position.
[b] CN, coordination number.