

THERMODYNAMIC DESCRIPTION OF THE Cu-Mg-Sn SYSTEM AT THE Cu-Mg SIDE

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ABSTRACT

Thermodynamic description of the Cu-Mg-Sn system at its Cu-Mg side is presented. The thermodynamic parameters of the binary sub-systems, Cu-Mg, Cu-Sn and Mg-Sn, are taken from the earlier CALPHAD-type assessments. The treatment of the Mg-Sn phases was somewhat changed. The adjustable parameters of the Cu-Mg-Sn system are optimized in this work. For this purpose experimental thermodynamic and phase equilibrium data were used and compared to calculated quantities.

Key words: *Thermodynamic description, Cu–Mg–Sn system, Phase diagrams*

INTRODUCTION

This study continues the recently started work for the development of a thermodynamic database for technically important copper alloys [1, 2]. Namely, thermodynamic description is presented for the ternary Cu-Mg-Sn system at its Cu-Mg side. Thermodynamic data are optimized for the

ternary system using the earlier assessed data of Cu-Mg [3], Cu-Sn [4] and Mg-Sn [5] (partially reassessed in this study), and applying the experimental thermodynamic and phase equilibrium data from the literature.

PHASES AND MODELS

In this work the optimizations of Coughanowr et al. [3], Miettinen [4], and Morioka and Hasebe [5] were retained for the Cu-Mg, Cu-Sn and Mg-Sn systems, respectively. The phase diagram Mg-Sn, however, was not represented so well, as the hcp solubility was somewhat too high and the melting point of Mg₂Sn was somewhat too low in regard to the measured values. Therefore, both the hcp and the Mg₂Sn parameters were modified slightly in this work, whereas the liquid state parameters were adopted from [5] as such. In the newly optimized Mg-Sn diagram, the liquid+Mg₂Sn region is worse established than by [5] but the improved agreement with the higher melting point value of Mg₂Sn [6] was preferred as it is so clearly supported by the experimental study on the ternary Cu-Mg-Sn system of Tesluk [7].

The phase equilibria of the Cu-Mg-Sn system have been reviewed by Chang et al. [8]. In the present Cu-Mg-Sn description, the following phases are considered: liquid, fcc, bcc, hcp (A3), gamma (γ), Cu₂Mg (Laves C15), CuMg₂, Cu₄₁Sn₁₁ (δ), Cu₃Sn (ϵ), Mg₂Sn, Cu₄MgSn (T₁) and CuMgSn (T₂). The disordered solution phases, i.e., liquid, fcc, bcc and hcp, and the ordered gamma phase (treated as a disordered solution phase by Miettinen [4, 9]), are described with the substitutional solution model. The fcc and hcp (A3) solid solutions contain mainly copper and magnesium, respectively. The bcc and gamma phases (γ) are copper-rich and originate from the binary Cu-Sn system. The first one (bcc) contains around 15 at. % Sn, while in the second the tin content varies from around 17 to approximately 27 at. % Sn.

The Cu₂Mg phase extending to the ternary system is described with the sublattice model and the rest of the phases, CuMg₂, Cu₄₁Sn₁₁, Cu₃Sn, Mg₂Sn, Cu₄MgSn and CuMgSn, are treated as stoichiometric phases.

The substitutional solution model was applied for the description of the molar Gibbs energy (G_m^ϕ) of the solution phases of the Cu-Mg-Sn system (i.e. liquid, fcc, bcc, hcp). The gamma phase (γ) was treated with this model as well.

The Gibbs energy (${}^oG_i^\phi$) of the pure component i in a phase ϕ is expressed relative to the enthalpy of the component in its stable phase at 298.15 K [10].

L_{ij}^ϕ is a binary parameter describing the interaction between components i and j in phase ϕ , and $L_{Cu,Mg,Sn}^\phi$ is a ternary interaction parameter of phase ϕ . For these parameters, ${}^oG_i^\phi$ is a function of temperature, and L_{ij}^ϕ and $L_{Cu,Mg,Sn}^\phi$ can be functions of temperature and composition.

The Cu_2Mg having ternary solubility is described as a semi-stoichiometric phase as $(Cu, Sn)_2Mg$ using the sublattice model. The Gibbs energy (per mol of formula unit) of that phase becomes

$$G_m^\phi = y_{Cu}^\phi {}^oG_{Cu:Mg}^\phi + y_{Sn}^\phi {}^oG_{Sn:Mg}^\phi + 2RT(y_{Cu}^\phi \ln y_{Cu}^\phi + y_{Sn}^\phi \ln y_{Sn}^\phi) + y_{Cu}^\phi y_{Sn}^\phi L_{Cu,Sn:Mg}^\phi \quad (1)$$

where ${}^oG_{Me:Mg}^\phi$ is the Gibbs energy of pure Me_2Mg ($Me=Cu,Sn$), y_{Me}^ϕ is the site fraction of Me atoms occupying the first sublattice, and $L_{Cu,Sn:Mg}^\phi$ is a parameter describing the interaction between Cu and Sn atoms in that sublattice. For copper and tin, the site fractions are expressed with mole fractions x_i as $y_i^\phi = x_i^\phi / (x_{Cu}^\phi + x_{Sn}^\phi)$, whereas for magnesium, $y_{Mg}^\phi = 3x_{Mg}^\phi = 1$.

The binary $CuMg_2$, $Cu_{41}Sn_{11}$, Cu_3Sn , Mg_2Sn phases and the ternary Cu_4MgSn and $CuMgSn$ phases are treated as stoichiometric phases. The Gibbs energy of formation of the binary compounds is expressed as

$${}^oG_{A:B}^\phi = a {}^oG_A^\alpha + b {}^oG_B^\beta + A + BT \quad (2)$$

where a and b are stoichiometric coefficients and ${}^oG_i^\phi$ is the Gibbs energy of the pure component i in its stable phase at 298.15K [10]. Similarly, for the ternary compounds, Cu_4MgSn and $CuMgSn$, the Gibbs energy of formation becomes.

$${}^oG_{Cu:Mg:Sn}^\phi = a {}^oG_{Cu}^{fcc} + b {}^oG_{Mg}^{hcp} + c {}^oG_{Sn}^{bct} + A + BT \quad (3)$$

RESULTS AND DISCUSSION

Chang et al. [8] have reviewed the experimental studies on the $Cu-Mg-Sn$ systems before 1979. Later studies seem not be available. Table 1 shows the experimental information [7, 8, 11–14] selected in the present optimization.

The thermodynamic description of the Cu-Mg-Sn system is presented in Table 2. The parameters marked with a reference code [2 – 5, 15 – 17] were adopted from the earlier SGTE assessments and those marked with *O or *E were optimized or estimated in the present study. By *O, the parameter was optimized using the experimental data of literature (Table 2) and by *E, the parameter was estimated arbitrarily, by applying no experimental data (since not available). The thermodynamic data for the pure components are given by [10] except for the gamma phase (see Table 2).

Table 1. *Experimental information applied in the optimization process*

Experimental information type	Ref.
Primary surfaces	
Three isopleths, at sections Cu-MgSn, Cu ₂ Mg-Mg ₂ Sn and CuMg ₂ -Mg ₂ Sn	[8]
Three isopleths, at Mg:Sn= 3.70, Mg:Sn= 0.41, 4% Sn (composition in weight pct)	[6]
Two isotherms, at 670 and 400°C	[11, 12]
	[13, 14]

In the following, calculated results are compared with the original experimental data to demonstrate the successfulness of the optimization. All calculations were carried out with the ThermoCalc software [18].

Calculated monovariant curves of primary solidification are presented in Fig. 1. They agree reasonably well with the curves assessed tentatively by Chang et al. [8].

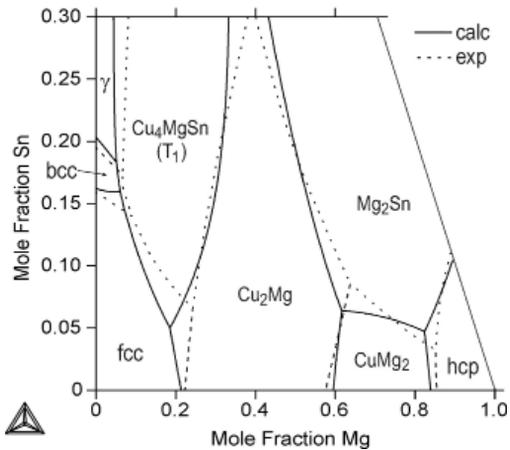


Figure 1. *Calculated primary (i.e. liquidus) surfaces (solid lines) at the Cu-Mg side of the Cu-Mg-Sn system, together with experimentally determined regions [8] (dashed)*

Fig. 2 shows a calculated isopleth, at a sections Cu-MgSn with ratio Mg:Sn=3.70 and Mg:Sn=0.41, and at a constant tin content of 4 wt%. The agreement with the experimental data [11, 12, 7] can be considered very satisfying. Finally, Fig. 3 shows a calculated isothermal section of the system, at temperatures of 670 °C. The results agree reasonably well with the observations of [14]. At 670 °C, the calculated fcc solubility at low tin contents was higher than indicated by the experimental data (see the three black triangles located in the fcc region in Fig. 3). When treating Cu_4MgSn (T_1) as a stoichiometric phase, one can improve the agreement only by introducing a strong composition dependent ternary interaction parameter for the fcc phase. Such a treatment, however, is not justified with the present tiny amount of experimental data.

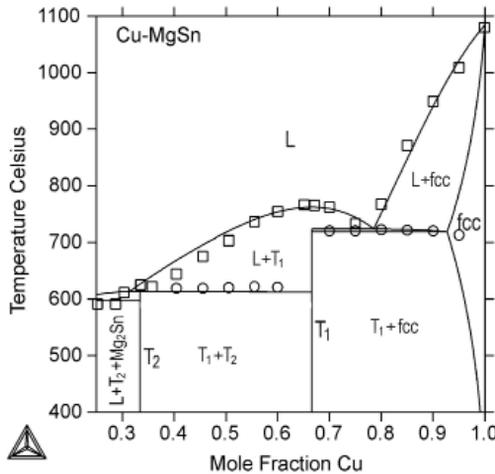


Figure 2. Calculated isopleth at the Cu-MgSn section together with experimental data [7]. The compounds Cu_4MgSn and CuMgSn are denoted as T_1 and T_2 , respectively. The symbol (□) stays for an experimental liquidus point and the symbol (o) – for a thermal arrest.

No experimental thermodynamic data were available for the ternary system except for the enthalpy of formation of two ternary samples containing 33.33 at% Mg with 8.4 and 12.1 at% Sn. For these alloys, Predel and Ruge [19] gave values – 10.3 and – 13.5 kJ/mol, which are lower (less negative) than the calculated values, – 14.2 and – 15.2 kJ/mol.

Figure 3. Calculated isothermal section in the copper-rich part of the Cu-Mg-Sn system at 670° C, together with experimental data from Phillips and Ainsworth [14].

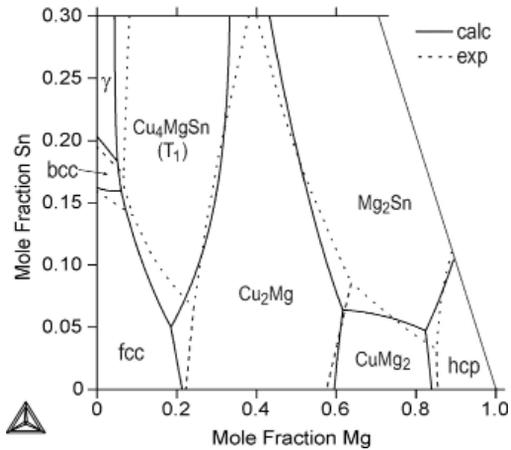


Table 2. Thermodynamic adjustable parameters for the Cu-Mg-Sn system obtained from the literature (reference code) and optimized (*O) or estimated (*E) in this study. All values are in J/mol. T is the absolute temperature (K). The thermodynamic data of the pure components are taken from Dinsdale [10] unless a parameter expression is shown in the Table.

Phase	Reference
liquid (1 sublattice, sites: 1, constituents: Cu,Mg,Sn) $L_{Cu,Mg}^L = (-35430+4.227T) + (-7454)(x_{Cu}-x_{Mg})$ $L_{Cu,Sn}^L = (-8124-6.553T) + (-23970+7.037T)(x_{Cu}-x_{Sn})$ $+ (-25124+13.566T)(x_{Cu}-x_{Sn})^2 + (-10213+10.042T)(x_{Cu}-x_{Sn})^3$ $L_{Mg,Sn}^L = (-49353+14.835T) + (-17571+7.906T)(x_{Mg}-x_{Sn})$ $L_{Cu,Mg,Sn}^L = (-10000+20T)x_{Cu} + (-10000+20T)x_{Mg}$ $+ (-50000+20T)x_{Sn}$	[3] [4] [5] *O
fcc (1 sublattice, sites: 1, constituents: Cu,Mg,Sn) $L_{Cu,Mg}^{fcc} = -23487+8.26T$ $L_{Cu,Sn}^{fcc} = (-10672-1.484T) + (-15331+6.954T)(x_{Cu}-x_{Sn})$ $L_{Mg,Sn}^{fcc} = L_{Mg,Sn}^{hcp}$ (fcc not stable in binary Mg-Sn)	[3] [15] *E
bcc (1 sublattice, sites: 1, constituents: Cu,Mg,Sn) $L_{Cu,Mg}^{bcc} = -6500$ (bcc not stable in binary Cu-Mg) $L_{Cu,Sn}^{bcc} = (-44822+51.216T) + (-6877-56.427T)(x_{Cu}-x_{Sn})$ $L_{Mg,Sn}^{bcc} = L_{Mg,Sn}^{hcp}$ (bcc not stable in binary Mg-Sn)	[16] [15] *E

<p>hcp (A3) (1 sublattice, sites: 1, constituents: Cu,Mg,Sn) $L_{Cu,Mg}^{hcp} = 10000$ [2] $L_{Cu,Sn}^{hcp} = (-26799-0.732T) + (-28065-0.029T)(x_{Cu}-x_{Sn})$ [15] $L_{Mg,Sn}^{hcp} = (-24000) + (-20000)(x_{Mg}-x_{Sn})$ *O</p>	
<p>Cu₃Sn (ε) (2 sublattices, sites: 0.75:0.25, constituents: Cu:Sn) ${}^{\circ}G_{Cu,Sn}^{\epsilon} = 0.75{}^{\circ}G_{Cu}^{fcc} + 0.25{}^{\circ}G_{Sn}^{bet} + (-8218-0.18T)$ [17]</p>	
<p>gamma (γ) (1 sublattice, sites: 1, constituents: Cu, Mg, Sn) ${}^{\circ}G_{Cu}^{\gamma} = {}^{\circ}G_{Cu}^{fcc} + 10$ [4] ${}^{\circ}G_{Mg}^{\gamma} = {}^{\circ}G_{Mg}^{hcp} + 10$ [2] ${}^{\circ}G_{Sn}^{\gamma} = {}^{\circ}G_{Sn}^{bet} + 10$ [4] $L_{Cu,Mg}^{\gamma} = 50000$ [2] $L_{Cu,Sn}^{\gamma} = (40039-32.912T) + (-232532+135.367T)(x_{Cu}-x_{Sn})$ $+ (210180-129.043T)(x_{Cu}-x_{Sn})^2$ [4] $L_{Mg,Sn}^{\gamma} = 50000$ (gamma not stable in binary Mg-Sn) *E $L_{Cu,Mg,Sn}^{\gamma} = -60000$ *O</p>	
<p>Cu₂Mg (C15) (2 sublattices, sites: 0.6667:0.3333, constituents: Cu,Sn:Mg) ${}^{\circ}G_{Cu,Mg}^{C15} = 0.6667{}^{\circ}G_{Cu}^{fcc} + 0.3333{}^{\circ}G_{Mg}^{hcp}$ $+ (-9270-42.588T+6.6537T \ln T-0.005732T^2)$ [2] ${}^{\circ}G_{Sn,Mg}^{C15} = 0.6667{}^{\circ}G_{Sn}^{bet} + 0.3333{}^{\circ}G_{Mg}^{hcp} + (0)$ *O $L_{Cu,Sn,Mg}^{C15} = -43500+18T$ *O</p>	
<p>CuMg₂ (2 sublattices, sites: 0.3333:0.6667, constituents: Cu:Mg) ${}^{\circ}G_{Cu,Mg}^{CuMg2} = 0.3333{}^{\circ}G_{Cu}^{fcc} + 0.6667{}^{\circ}G_{Mg}^{hcp} + (-9540+0.862T)$ [3]</p>	
<p>Cu₄₁Sn₁₁ (δ) (2 sublattices, sites: 0.788:0.212, constituents: Cu:Sn) ${}^{\circ}G_{Cu,Sn}^{\delta} = 0.788{}^{\circ}G_{Cu}^{fcc} + 0.212{}^{\circ}G_{Sn}^{bet} + (-6323.5-1.2808T)$ [15]</p>	
<p>Mg₂Sn (2 sublattices, sites: 0.6667:0.3333, constituents: Mg:Sn) ${}^{\circ}G_{Mg,Sn}^{Mg2Sn} = 0.6667{}^{\circ}G_{Mg}^{hcp} + 0.3333{}^{\circ}G_{Sn}^{bet} + (-26200+9T)$ *O</p>	
<p>Cu₄MgSn (T₁) (3 sublattices, sites: 0.666:0.167:0.167, constituents: Cu:Mg:Sn) ${}^{\circ}G_{Cu,Mg,Sn}^{T1} = 0.666{}^{\circ}G_{Cu}^{fcc} + 0.167{}^{\circ}G_{Mg}^{hcp} + 0.167{}^{\circ}G_{Sn}^{bet}$ $+ (-19600+5T)$ *O</p>	
<p>CuMgSn (T₂) (3 sublattices, sites: 0.334:0.333:0.333, constituents: Cu:Mg:Sn) ${}^{\circ}G_{Cu,Mg,Sn}^{T2} = 0.334{}^{\circ}G_{Cu}^{fcc} + 0.333{}^{\circ}G_{Mg}^{hcp} + 0.333{}^{\circ}G_{Sn}^{bet}$ $+ (-26400+10T)$ *O</p>	

On the other hand, the enthalpy of formation value of [19] for the binary Cu_2Mg is also quite low, i.e., -8.1 kJ/mol, whereas two other studies [20, 21] suggest values between -11 and -12 kJ/mol, which agree better with the calculated value of -10.8 kJ/mol. Consequently, the measurements of [19] may suffer from a systematic error. Shifting the dataset of [19] with the measurements of [20, 21] would improve the agreement clearly.

CONCLUSIONS

A thermodynamic description was optimized for the ternary Cu-Mg-Sn system applying the experimental phase equilibrium data of the literature. In this description, twelve phases, i.e., liquid, fcc, bcc, hcp, gamma, Cu_2Mg (Laves C15), CuMg_2 , $\text{Cu}_{41}\text{Sn}_{11}$ (δ), Cu_3Sn (ϵ), Mg_2Sn , Cu_4MgSn (T_1) and CuMgSn (T_2), were considered. The disordered solution phases, i.e., liquid, fcc, bcc and hcp, and the ordered gamma phase were described with the substitutional solution model, while the semi-stoichiometric Cu_2Mg phase was described with the sublattice model. The rest of the phases, the near-stoichiometric compounds, were treated as stoichiometric phases. In the optimization, the unary and binary thermodynamic data of the systems were taken from previous binary descriptions. Good or at least reasonable correlation was obtained between the calculated and the experimental thermodynamic and phase equilibrium data.

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