

THERMODYNAMIC RE-OPTIMIZATION OF THE Cu-Mg-Sn SYSTEM AT THE Cu-Mg SIDE

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Abstract

Thermodynamic description of the ternary 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 SGTE-based assessments (modifying the Mg-Sn description slightly) and those of the Cu-Mg-Si system are optimized in this study using the experimental thermodynamic and phase equilibrium data. The solution phases of the systems are described with the substitutional solution model and the intermetallic Cu₂Mg compound (Laves C15), treated as simple semi-stoichiometric phases of the (A,B)_pC_q type, is described with the two-sublattice model. The present ternary description is valid for tin contents up to 45 wt% ($x_{\text{Sn}} \approx 0.30$).

Keywords: Phase diagrams; Thermodynamic modeling; Ternary systems, Copper-magnesium alloys

1. Introduction

Ternary metal systems continue to be subject of developing new approaches and classical assessments [1]. Especially, fundamental investigations of multicomponent Cu-Mg alloys are under

way in view of a variety of industrial applications [2, 3].

In the present study, thermodynamic description is presented for the ternary Cu-Mg-Sn at its Cu-Mg side. Thermodynamic data are optimized for the system using the earlier assessed data of binaries Cu-Mg [4],

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Cu-Sn [5] and Mg-Sn [6] (partially reassessed in this study), and applying the experimental thermodynamic and phase equilibrium data of the literature. The study continues the recently started work for the development of a thermodynamic database for technically important copper alloys [7]. It is worth noting that the binary Cu-Mg and Cu-Sn systems continue to be the subject of experimental phase diagram and thermochemical studies [8–10].

The assessments of Coughanowr et al. [4] for Cu-Mg and Miettinen [5] for Cu-Sn were retained for the sake of the present database construction by the latter author [7]. In the present description more Cu-Mg-Sn system experimental data of Vicente et al. [11, 12] have been taken into account. In such a way we have improved the tentative optimization of the system, recently made by the same authors [13].

2. Phases and Models

Figs.1a and 1b show calculated phase diagrams for binaries Cu-Mg [4] and Cu-Sn [5]. They agree well with the experimental phase equilibrium data as presented in these studies. The Mg-Sn system was assessed by Morioka and Hasebe [6]. Good agreement was obtained between the calculated and experimental tin activity and mixing enthalpy and entropy data of the liquid phase. The phase diagram, however, was not established so well, as the hcp-phase (i.e. the phase (Mg)) solubility was somewhat too high and the melting point of Mg_2Sn was somewhat too low in regard to the measured values. Therefore, both the hcp and the Mg_2Sn adjustable parameters were modified

slightly in the present study, whereas the liquid state data was adopted from [6] as such. The new and the earlier diagram together with experimental data from Massalski et al. [14] are shown in Fig.1c. In

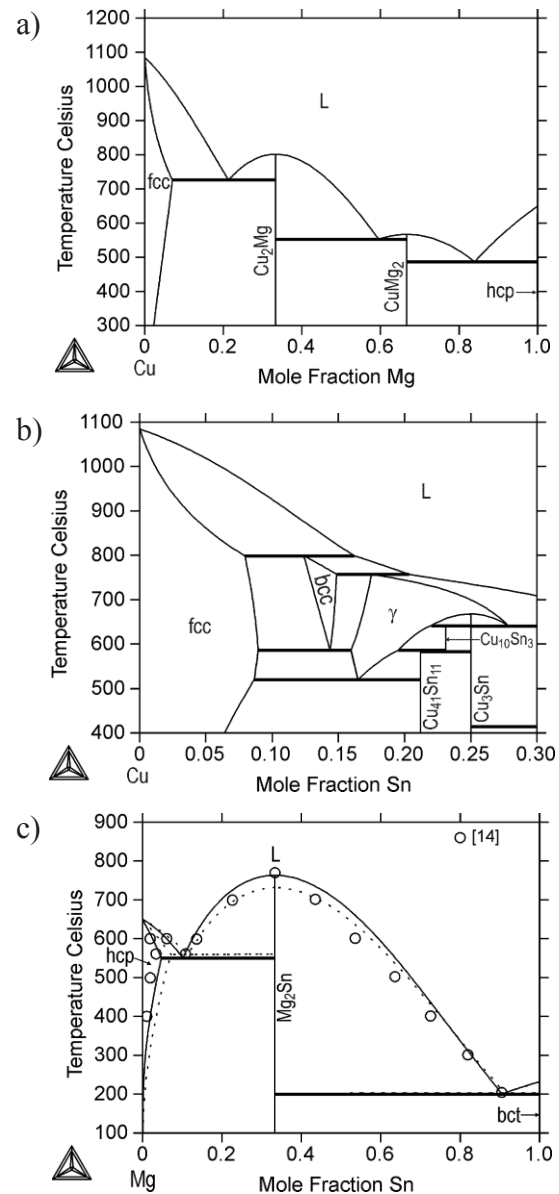


Fig. 1. Calculated phase diagrams of binaries Cu-Mg (a), Cu-Sn (b) and Mg-Sn (c). In figure c, the broken lines refer to the calculations by [6] and the experimental points are from [14].

the new diagram, the region (liquid+Mg₂Sn) is worse established than by [6] but the improved agreement with the higher melting point value of Mg₂Sn [14] was preferred as it is so clearly supported by the experimental study on the ternary Cu-Mg-Sn system of Tesluk [15].

The phase equilibria of the Cu-Mg-Sn system have been reviewed by Chang et al. [16]. In the present Cu-Mg-Sn description, the following phases are considered: liquid, fcc, bcc, hcp (A3), gamma (g), Cu₂Mg (Laves C15), CuMg₂, Cu₄₁Sn₁₁ (d), Cu₃Sn (e), 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 [5, 17]), are described with the substitutional solution model. 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.

By applying the substitutional solution model to the solution phases of the Cu-Mg-Sn system, the molar Gibbs energy of these phases becomes

$$\begin{aligned} G_m^\phi = & x_{Cu}^\phi {}^\circ G_{Cu}^\phi + x_{Mg}^\phi {}^\circ G_{Mg}^\phi + x_{Sn}^\phi {}^\circ G_{Sn}^\phi \\ & + RT(x_{Cu}^\phi \ln x_{Cu}^\phi + x_{Mg}^\phi \ln x_{Mg}^\phi + x_{Sn}^\phi \ln x_{Sn}^\phi) \\ & + x_{Cu}^\phi x_{Mg}^\phi L_{Cu,Mg}^\phi + x_{Cu}^\phi x_{Sn}^\phi L_{Cu,Sn}^\phi + x_{Mg}^\phi x_{Sn}^\phi L_{Mg,Sn}^\phi \\ & + x_{Cu}^\phi x_{Mg}^\phi x_{Sn}^\phi L_{Cu,Mg,Sn}^\phi \end{aligned} \quad (1)$$

where R is the gas constant (8.3145 J/Kmol), T is the absolute temperature, x_i is the mole fraction of component i, ${}^\circ G_i^\phi$ is the Gibbs energy of pure component i in phase ϕ

expressed relative to the enthalpy of the component in its stable phase at 298.15 K [18], $L_{i,j}^\phi$ 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, ${}^\circ G_i^\phi$ is a function of temperature, and $L_{i,j}^\phi$ and $L_{Cu,Mg,Sn}^\phi$ can be functions of temperature and composition.

The Cu₂Mg 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

$$\begin{aligned} G_m^\phi = & y_{Cu}^\phi {}^\circ G_{Cu:Mg}^\phi + y_{Sn}^\phi {}^\circ G_{Sn:Mg}^\phi \\ & + 2RT(y_{Cu}^\phi \ln y_{Cu}^\phi + y_{Sn}^\phi \ln y_{Sn}^\phi) \\ & + y_{Cu}^\phi y_{Sn}^\phi L_{Cu,Sn:Mg}^\phi \end{aligned} \quad (2)$$

where ${}^\circ G_{Me:Mg}^\phi$ is the Gibbs energy of pure Me₂Mg (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, $y_{Mg}^\phi = 3x_{Mg}^\phi$.

The binary CuMg₂, Cu₄₁Sn₁₁, Cu₃Sn, Mg₂Sn phases and the ternary Cu₄MgSn and CuMgSn phases are treated as stoichiometric phases. The Gibbs energy of formation of the binary compounds is expressed as

$${}^\circ G_{A:B}^\phi = a {}^\circ G_A^\alpha + b {}^\circ G_B^\beta + A + BT \quad (3)$$

where a and b are stoichiometric coefficients and ${}^\circ G_i^\theta$ is the Gibbs energy of pure component i in its stable phase at 298.15 K [18]. Similarly, for ternary

compounds, Cu_4MgSn and CuMgSn , the Gibbs energy of formation of the phase becomes

$${}^oG_{\text{Cu:Mg:Sn}}^{\phi} = a {}^oG_{\text{Cu}}^{\text{fcc}} + b {}^oG_{\text{Mg}}^{\text{hcp}} + c {}^oG_{\text{Sn}}^{\text{bct}} + A + BT \quad (4)$$

3. Experimental and Thermodynamic Data

Chang *et al.* [16] have reviewed the experimental studies on the Cu-Mg-Si systems before 1979. Later studies of

Vicente *et al* [11, 12] have been used as well. Table 1 shows the experimental information 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 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 literature experimental data (Table 1) and by *E, the parameter was estimated

Table 1. Experimental information applied in the optimization process.

Experimental information type	Ref.
Primary surfaces	[16, 11, 12]
Three vertical sections, Cu-MgSn, $\text{Cu}_2\text{Mg-Mg}_2\text{Sn}$ and $\text{CuMg}_2\text{-Mg}_2\text{Sn}$	[15]
Three vertical sections, at Mg:Sn=3.70, Mg:Sn=0.41 and 4%Sn (composition in weight pct)	[19, 20]
Two isotherms, at 670 and 400°C	[21, 22]

Table 2. Thermodynamic data for the Cu-Mg-Sn system obtained from the literature (reference code) and optimized (*O) or estimated (*E) in this study. All parameter values are in J/mol. The thermodynamic data of the pure components are taken from [18] unless a parameter expression is shown in the Table.

liquid (1 sublattice, sites: 1, constituents: Cu,Mg,Sn)	Ref.
$L_{\text{Cu,Mg}}^{\text{L}} = (-35430+4.227T) + (-7454)(x_{\text{Cu}}-x_{\text{Mg}})$	[4]
$L_{\text{Cu,Sn}}^{\text{L}} = (-8124-6.553T) + (-23970+7.037T)(x_{\text{Cu}}-x_{\text{Sn}})$	
$+ (-25124+13.566T)(x_{\text{Cu}}-x_{\text{Sn}})^2 + (-10213+10.042T)(x_{\text{Cu}}-x_{\text{Sn}})^3$	[5]
$L_{\text{Mg,Sn}}^{\text{L}} = (-49353+14.835T) + (-17571+7.906T)(x_{\text{Mg}}-x_{\text{Sn}})$	[6]
$L_{\text{Cu,Mg,Sn}}^{\text{L}} = (-10000+20T)x_{\text{Cu}} + (-20000+20T)x_{\text{Mg}} + (-60000+30T)x_{\text{Sn}}$	*O
fcc (1 sublattice, sites: 1, constituents: Cu,Mg,Sn)	Ref.
$L_{\text{Cu,Mg}}^{\text{fcc}} = -23487+8.26T$	[4]
$L_{\text{Cu,Sn}}^{\text{fcc}} = (-10672-1.484T) + (-15331+6.954T)(x_{\text{Cu}}-x_{\text{Sn}})$	[23]
$L_{\text{Mg,Sn}}^{\text{fcc}} = L_{\text{Mg,Sn}}^{\text{hcp}}$ (fcc not stable in binary Mg-Sn)	*E

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bcc (1 sublattice, sites: 1, constituents: Cu,Mg,Sn)	Ref.
$L_{\text{Cu,Mg}}^{\text{bcc}} = -6500$ (bcc not stable in binary Cu-Mg)	[24]
$L_{\text{Cu,Sn}}^{\text{bcc}} = (-44822+51.216T) + (-6877-56.427T)(x_{\text{Cu}}-x_{\text{Sn}})$	[23]
$L_{\text{Mg,Sn}}^{\text{bcc}} = L_{\text{Mg,Sn}}^{\text{hcp}}$ (bcc not stable in binary Mg-Sn)	*E
hcp (A3) (1 sublattice, sites: 1, constituents: Cu,Mg,Sn)	Ref.
$L_{\text{Cu,Mg}}^{\text{hcp}} = 10000$	[25]
$L_{\text{Cu,Sn}}^{\text{hcp}} = (-26799-0.732T) + (-28065-0.029T)(x_{\text{Cu}}-x_{\text{Sn}})$	[23]
$L_{\text{Mg,Sn}}^{\text{hcp}} = (-22000) + (-20000)(x_{\text{Mg}}-x_{\text{Sn}})$	*O
gamma (γ) (1 sublattice, sites: 1, constituents: Cu,Mg,Sn)	Ref.
${}^{\circ}G_{\text{Cu}}^{\gamma} = {}^{\circ}G_{\text{Cu}}^{\text{fcc}} + 10$	[5]
${}^{\circ}G_{\text{Mg}}^{\gamma} = {}^{\circ}G_{\text{Mg}}^{\text{hcp}} + 10$	[25]
${}^{\circ}G_{\text{Sn}}^{\gamma} = {}^{\circ}G_{\text{Sn}}^{\text{bct}} + 10$	[5]
$L_{\text{Cu,Mg}}^{\gamma} = 50000$	[25]
$L_{\text{Cu,Sn}}^{\gamma} = (40039-32.912T) + (-232532+135.367)(x_{\text{Cu}}-x_{\text{Sn}}) + (210180-129.043T)(x_{\text{Cu}}-x_{\text{Sn}})^2$	[5]
$L_{\text{Mg,Sn}}^{\gamma} = 50000$ (gamma not stable in binary Mg-Sn)	*E
$L_{\text{Cu,Mg,Sn}}^{\gamma} = -60000$	*O
Cu₂Mg (C15) (2 sublattices, sites: 0.6667:0.3333, constituents: Cu,Sn:Mg)	Ref.
${}^{\circ}G_{\text{Cu:Mg}}^{\text{C15}} = 0.6667{}^{\circ}G_{\text{Cu}}^{\text{fcc}} + 0.3333{}^{\circ}G_{\text{Mg}}^{\text{hcp}} + (-9270-42.588T+6.6537T\ln T-0.005732T^2)$	[25]
${}^{\circ}G_{\text{Sn:Mg}}^{\text{C15}} = 0.6667{}^{\circ}G_{\text{Sn}}^{\text{bct}} + 0.3333{}^{\circ}G_{\text{Mg}}^{\text{hcp}} + (0)$	*O
$L_{\text{Cu,Sn:Mg}}^{\text{C15}} = -42000+14T$	*O
CuMg₂ (2 sublattices, sites: 0.3333:0.6667, constituents: Cu:Mg)	Ref.
${}^{\circ}G_{\text{Cu:Mg}}^{\text{CuMg}_2} = 0.3333{}^{\circ}G_{\text{Cu}}^{\text{fcc}} + 0.6667{}^{\circ}G_{\text{Mg}}^{\text{hcp}} + (-9540+0.862T)$	[4]
Cu₄₁Sn₁₁ (δ) (2 sublattices, sites: 0.788:0.212, constituents: Cu:Sn)	Ref.
${}^{\circ}G_{\text{Cu:Sn}}^{\delta} = 0.788{}^{\circ}G_{\text{Cu}}^{\text{fcc}} + 0.212{}^{\circ}G_{\text{Sn}}^{\text{bct}} + (-6323.5-1.2808T)$	[23]
Cu₃Sn (ϵ) (2 sublattices, sites: 0.75:0.25, constituents: Cu:Sn)	Ref.
${}^{\circ}G_{\text{Cu:Sn}}^{\epsilon} = 0.75{}^{\circ}G_{\text{Cu}}^{\text{fcc}} + 0.25{}^{\circ}G_{\text{Sn}}^{\text{bct}} + (-8218-0.18T)$	[26]
Mg₂Sn (2 sublattices, sites: 0.6667:0.3333, constituents: Mg:Sn)	Ref.
${}^{\circ}G_{\text{Mg:Sn}}^{\text{Mg}_2\text{Sn}} = 0.6667{}^{\circ}G_{\text{Mg}}^{\text{hcp}} + 0.3333{}^{\circ}G_{\text{Sn}}^{\text{bct}} + (-26200+9T)$	*O
Cu₄MgSn (T₁) (3 sublattices, sites: 0.666:0.167:0.167, constituents: Cu:Mg:Sn)	Ref.
${}^{\circ}G_{\text{Cu:Mg:Sn}}^{\text{T}_1} = 0.666{}^{\circ}G_{\text{Cu}}^{\text{fcc}} + 0.167{}^{\circ}G_{\text{Mg}}^{\text{hcp}} + 0.167{}^{\circ}G_{\text{Sn}}^{\text{bct}} + (-19600+5T)$	*O
CuMgSn (T₂) (3 sublattices, sites: 0.334:0.333:0.333, constituents: Cu:Mg:Sn)	Ref.
${}^{\circ}G_{\text{Cu:Mg:Sn}}^{\text{T}_2} = 0.334{}^{\circ}G_{\text{Cu}}^{\text{fcc}} + 0.333{}^{\circ}G_{\text{Mg}}^{\text{hcp}} + 0.333{}^{\circ}G_{\text{Sn}}^{\text{bct}} + (-26500+10T)$	*O

arbitrarily, by applying no experimental data (since not available). The thermodynamic data for the pure components are given by [18] except for the gamma phase (see Table 2).

4. Results and discussion

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 [27].

According to Chang et al. [16], the available information in 1979 was insufficient to give details concerning the liquidus valleys and the four-phase equilibria of the Cu-Mg-Sn system. Some estimation, however, was made by them [16]. Since 1979, two four-phase equilibria have been measured by Vicente et al. [11, 12]. These equilibria and those estimated by [16] are shown in Table 3. It summarizes the calculated and the experimental four-phase

equilibria of the Cu-Mg-Sn system up to $x_{\text{Sn}}=0.3$. The agreement between calculations and measurements/estimations is quite reasonable.

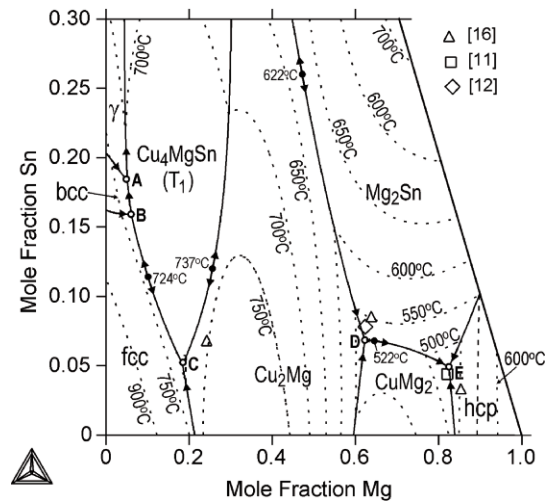


Fig. 2. Calculated liquidus projection (solid lines) and liquidus isotherms (dotted lines) at the Cu-Mg side of the Cu-Mg-Sn system, together with experimentally determined four-phase equilibria [11, 12, 16]. Indexes A to E refer to the four-phase equilibria of Table 3.

Table 3. Calculated four-phase equilibria of the Cu-Mg-Sn system up to tin content of $x_{\text{Sn}}=0.3$, together with experimental data [11, 12, 16]. T – Temperature, x_i^L – mole fraction of component i in the liquid phase

Equilibrium	Code	T °C	x_{Mg}^L	x_{Sn}^L	Reference
$L + \text{bcc} = \gamma + T_1$	A	706	0.051	0.183	calc.
$L + \text{fcc} = \text{bcc} + T_1$	B	712	0.06	0.16	calc.
$L = \text{fcc} + T_1 + \text{Cu}_2\text{Mg}$	C	689	0.184	0.051	calc.
		-	0.242	0.067	[16]
$L = \text{Cu}_2\text{Mg} + \text{CuMg}_2 + \text{Mg}_2\text{Sn}$	D	519	0.623	0.068	calc.
		520	0.624	0.078	[12]
		520	0.638	0.084	[16]
$L = \text{CuMg}_2 + \text{Mg}_2\text{Sn} + \text{hcp}$	E	465	0.825	0.049	calc.
		467	0.821	0.044	[11]
		-	0.854	0.032	[16]

Calculated monovariant curves of primary solidification and some liquidus isotherms are presented in Fig.2. The figure also shows the calculated and the experimental four-phase equilibria of Table 3.

Figs. 3 through 8 show six calculated

vertical sections, at sections Cu-MgSn, Cu_2Mg - Mg_2Sn and CuMg_2 - Mg_2Sn , at ratios $\text{Mg}:\text{Sn}=3.70$ and $\text{Mg}:\text{Sn}=0.41$, and at a constant tin content of 4 wt%. The agreement with the experimental data [15, 19, 20] can be considered very satisfying. Note that the

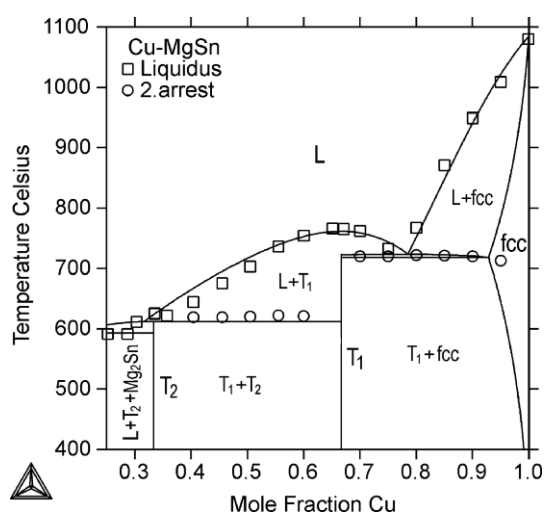


Fig. 3 Calculated vertical section of Cu-MgSn in the Cu-Mg-Sn system, together with experimental data points [15].

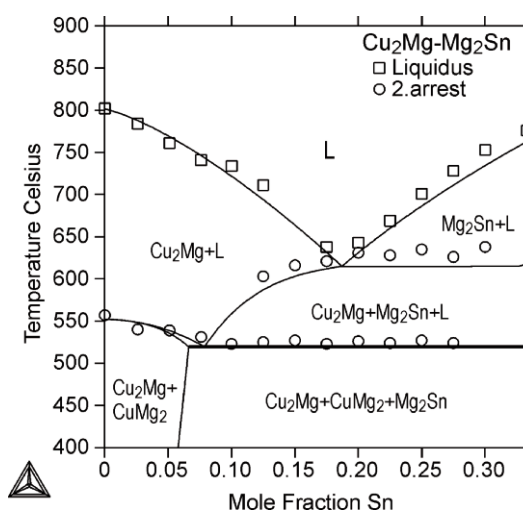


Fig. 4 Calculated vertical section of Cu_2Mg - Mg_2Sn in the Cu-Mg-Sn system, together with experimental data points [15].

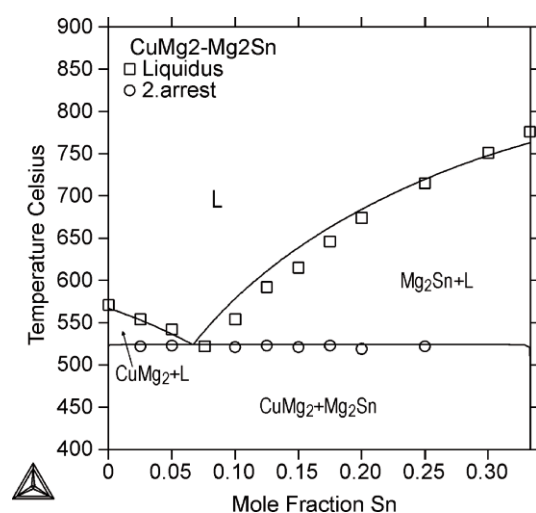


Fig. 5 Calculated vertical section of CuMg_2 - Mg_2Sn ($x_{\text{Mg}}=0.6666$) in the Cu-Mg-Sn system, together with experimental data points [15].

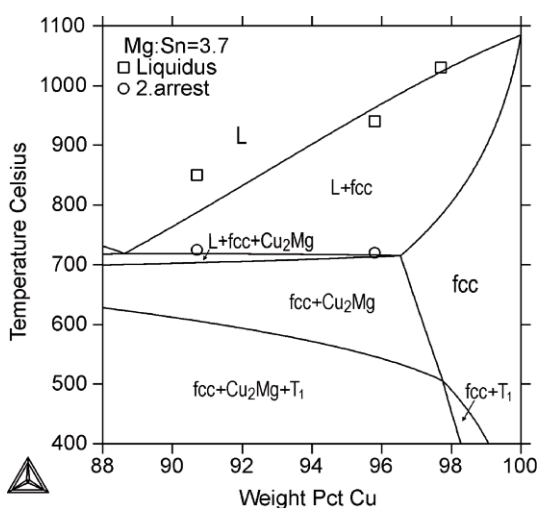


Fig. 6 Calculated vertical section at ratio $\text{wt}\%\text{Mg}:\text{wt}\%\text{Sn}=3.7$ in the Cu-Mg-Sn system, together with experimental data points [19].

pseudo-binary eutectic reaction $L = \text{CuMg}_2 + \text{Mg}_2\text{Sn}$ (Fig.5) was suggested to occur at 522 °C and $x_{\text{Sn}} = 0.077$ [15, 11], which are quite close to the calculated values of 524 °C and $x_{\text{Sn}} = 0.067$.

Finally, Figs. 9 through 12 show four calculated isothermal sections of the system, at temperatures of 700, 670, 570 and 400 °C,

respectively. No experimental data were available for isotherms 700 and 570 °C but at 670 and 400 °C, the results agree reasonably well with the observations of [22] and [21], in that order. At 670 °C, the calculated fcc-phase solubility at low tin contents was higher than indicated by the experimental

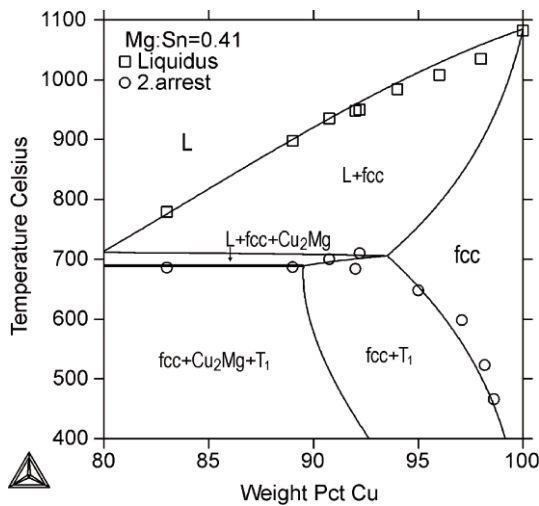


Fig. 7 Calculated vertical section at ratio $\text{wt}\%\text{Mg}:\text{wt}\%\text{Sn}=0.41$ in the Cu-Mg-Sn system, together with experimental data points [19, 20].

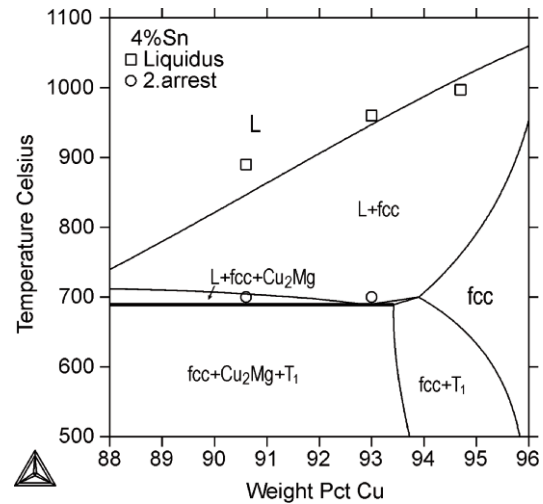


Fig. 8 Calculated vertical section at 4 wt% Sn in the Cu-Mg-Sn system, together with experimental data points [19].

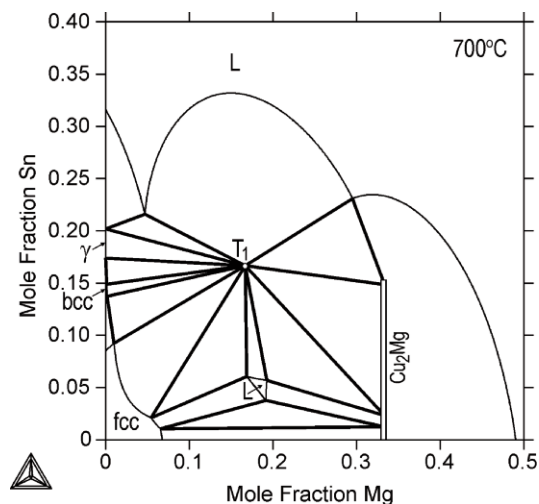


Fig. 9. Calculated isothermal section of the Cu-Mg-Sn system at 700 °C.

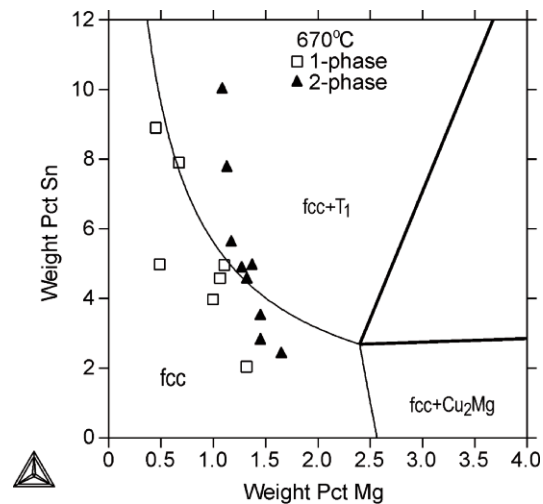


Fig. 10. Calculated isothermal section in the copper-rich part of the Cu-Mg-Sn system at 670 °C, together with experimental data [22].

data (see the three black triangles located in the fcc region in Fig.10). 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.

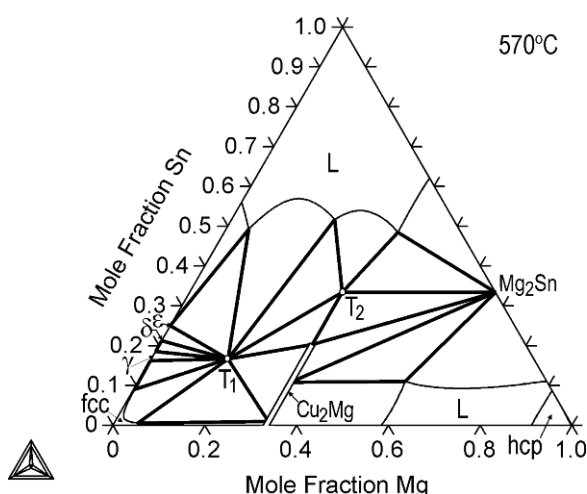


Fig. 11. Calculated isothermal section of the Cu-Mg-Sn system at 570 °C.

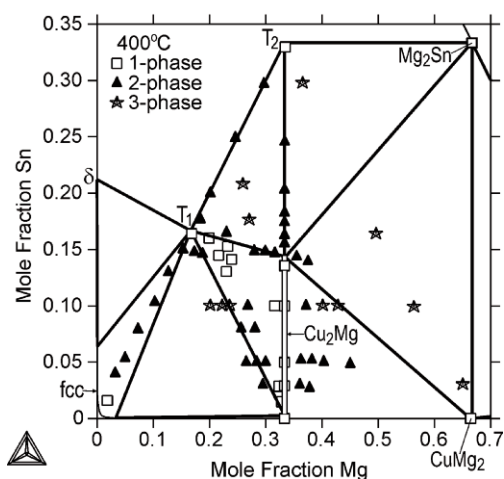


Fig. 12. Calculated isothermal section in the copper-rich part of the Cu-Mg-Sn system at 400 °C, together with experimental data points [21].

No experimental thermodynamic data were available for the ternary system except for the enthalpy of formation of two ternary alloys containing 33.33 at% Mg with 8.4 and 12.1 at% Sn. For these alloys, [28] gave values -10.3 and -13.5 kJ/mol, which are lower (less negative) than the calculated values, -14.0 and -15.0 kJ/mol. On the other hand, also the value of [28] for the binary Cu_2Mg is quite low, i.e., -8.1 kJ/mol, whereas two other studies [29, 30] suggest values between -11 and -12 kJ/mol, which agree better with the calculated value of -10.7 kJ/mol. Consequently, the measurements of [28] may suffer from a systematic error. Shifting the dataset of [28] with the measurements of [29, 30] would improve the agreement clearly.

5. Conclusions

A thermodynamic description was optimized for the ternary Cu-Mg-Sn system applying the experimental phase equilibrium data of the literature. In these descriptions, twelve phases, i.e., liquid, fcc, bcc, hcp, gamma, Cu_2Mg (Laves C15), CuMg_2 , $\text{Cu}_{41}\text{Sn}_{11}$ (d), Cu_3Sn (e), 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, and 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 the recently assessed

descriptions. Good or at least reasonable correlation was obtained between the calculated and the experimental thermodynamic and phase equilibrium data.

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