Experimental Determination and Thermodynamic Calculation of the Phase Equilibria in the Cu-In-Sn System

X.J. LIU,[1] H.S. LIU,[1] I. OHNUMA,[1] R. KAINUMA,[1] K. ISHIDA,[1] S. ITABASHI,[2] K. KAMEDA,[2] and K. YAMAGUCHI[2]

1.—Tohoku University, Department of Materials Science, Graduate School of Engineering, Sendai 980-8579, Japan. 2—Iwate University, Department of Materials Science and Technology, Faculty of Engineering, Morioka 020-8551, Japan

The phase equilibria of the Cu-In-Sn system were investigated by means of the diffusion couple method, differential scanning calorimetry (DSC) and metallography. The isothermal sections at 110–900°C, as well as vertical sections at 10wt.%Cu-70wt.%Cu were determined. It was found that there are large solubilities of In in the ε(Cu_3Sn), δ($Cu_{41}Sn_{11}$), and η phases in the Cu-Sn system, and large solubilities of Sn in the γ, η, and δ(Cu_7In_3) phases in the Cu-In system. The η phase was found to continuously form from the Cu-In side to the Cu-Sn side, and a ternary compound (Cu_2In_3Sn) was found to exist at 110°C. Thermodynamic assessment of the Cu-In-Sn system was also carried out based on experimental data of activity and phase equilibria using the CALPHAD method, in which the Gibbs energies of the liquid, fcc and bcc phases are described by the subregular solution model and that of compounds, including two ternary compounds, are represented by the sublattice model. The thermodynamic parameters for describing the phase equilibria were optimized, and agreement between the calculated and experimental results was obtained.

Key words: Phase diagram, thermodynamic calculation, Pb-free solders, diffusion couple

INTRODUCTION

The development of Pb-free solders has become an important issue for electronic interconnection materials in the packaging of electronic devices because of the health and environmental safety problem posed by lead usage, despite the favorable properties of conventional Pb-Sn solders, such as good wetting, low melting temperature, attractive price, and well-established technology.[1–3] Numerous studies have indicated multi-component Pb-free solders to be potential substitutes for the Pb-Sn solders, and thus thermodynamic modeling is becoming an increasingly important tool in the design and evaluation of various solder materials since it significantly decreases the amount of required experimental work. Recently, the present authors have developed a thermodynamic database including the elements Ag, Bi, Cu, In, Sn, Sb, Zn and Pb, which is expected to play an important role in the alloy design of solders. [4,5]

The Sn-In base alloys may be the promising candidates because of their good wetting, thermal fatigue, and suitable melting point.[6,7] The phase equilibria of the Cu-In-Sn system are important for developing Sn-In base micro-soldering alloys and understanding the phase formation between the Cu substrate and Sn-In base solders. An investigation of the phase equilibria of the Cu-Sn-In system was performed by Koster et al.,[8] who determined some isothermal and vertical sections by metallography and differential thermal analysis (DTA), but some uncertainties regarding the phase equilibria of this system remain.

The purpose of this study was to experimentally investigate the phase equilibria of the Cu-In-Sn system, with subsequent thermodynamic assessment of the phase equilibria on the basis of the CALPHAD (calculation of phase diagram) method.

EXPERIMENTAL PROCEDURE

Cu-In-Sn ternary alloys were made using pure metals Cu (99.99%), In(99.99%), and Sn (99.99%) in evacuated transparent quartz capsules at 1200°C for 2 h. The specimens with two- or three-phase structures and In-Sn alloys/pure Cu diffusion couples were prepared, and equilibrated at 110–900°C for 24–1000 h. Examination of the microstructure of each specimen was carried out by optical microscopy using an etchant solution ($FeCl:HCl:H_2O$ = 10 g:25 ml:100 ml). Equilibrium compositions in multi-phase specimens were determined by energy dispersive x-ray spectroscopy

(Received February 13, 2001; accepted April 17, 2001)

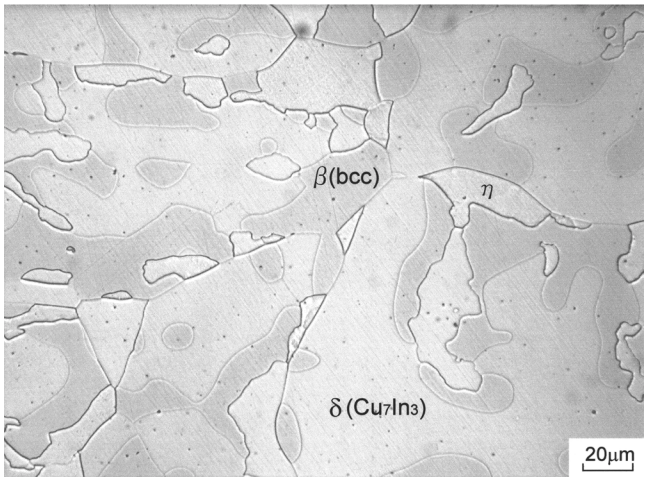

Fig. 1. Microstructure of the alloy $Cu_{60}In_{22}Sn_{18}$ (wt.%) equilibrated at 600°C for 48 hours.

(EDS) using a standard calibration method. The phase boundaries were also determined by the diffusion couple method as described in a previous work.[9]

Transformation temperatures were determined by differential scanning calorimetry (DSC) using the heating curve. The experiments were carried out in flowing argon atmosphere, with heating and cooling at rates of 3°C/min or less using sintered Al_2O_3 as the reference specimen.

THERMODYNAMIC MODELS

The phase constitutions in the Cu-In, Cu-Sn and Sn-In binary systems are listed in Table I. The Gibbs energy of constituent phase is described as follows.

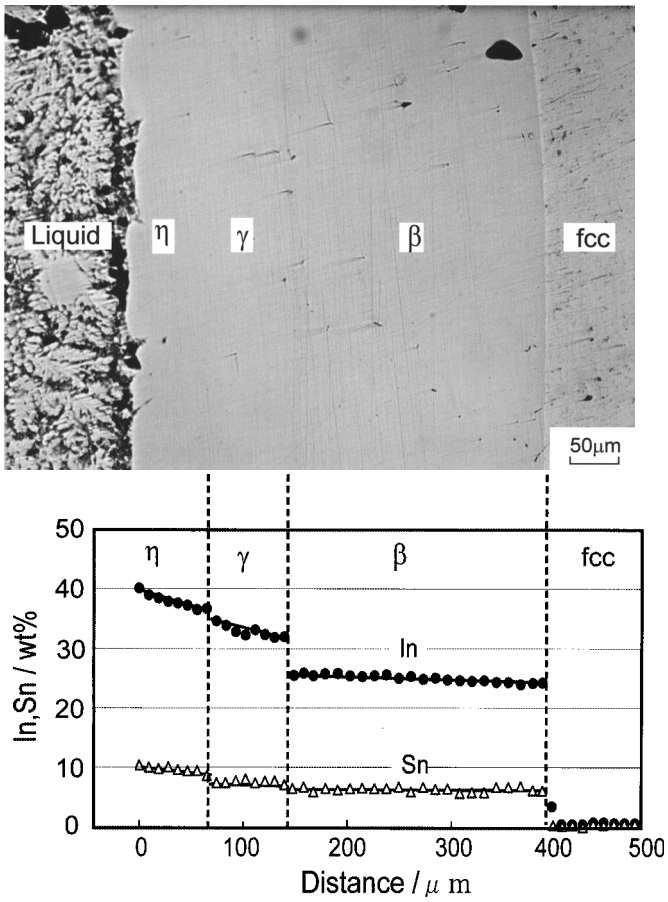

Fig. 2. Microstructure and concentration profile of the diffusion couple Cu/In-20wt.%Sn annealed at 600°C for 4 hours.

Table I. Solid Phases in the Cu-In, Cu-Sn and In-Sn Binary Systems

System	Phase	Composition	Strukturbericht designation	Prototype	Modeling
Cu-In	(Cu)	0-10.9 at%In	A1	Cu	(Cu,In)
	β	18.05-24.5 at%In	A2	W	(Cu,In)
	γ	27.7-31.3 at%In	—	$InMn_3$	$Cu_{0.654}(Cu,In)_{0.115}In_{0.231}$
	δ	29.05-30.6 at%In	—	Cu_7In_3	$Cu_{0.7}In_{0.3}$
	η	32.9-37.8 at%In	$B8_1$	NiAs	$Cu_{0.545}(Cu,In)_{0.112}In_{0.333}$
	η′	—	$B8_2$	Ni_2In	$Cu_{0.545}(Cu,In)_{0.112}In_{0.333}$
	$Cu_{11}In_9$	44 at%In	—	AlCu	$Cu_{0.55}In_{0.45}$
	(In)	100	A6	In	(In)
Cu-Sn	(Cu)	0-9.1 at%Sn	A1	Cu	(Cu,Sn)
	β	13.1-16.5 at%Sn	A2, B2, D03	W	(Cu,Sn)
	δ	20-21 at.%Sn	—	$Cu_{41}Sn_{11}$	$Cu_{0.788}Sn_{0.212}$
	ζ	20.3-22.5 at%Sn	—	$Cu_{10}Sn_3$	$Cu_{0.769}Sn_{0.231}$
	ε	24.5-25.9 at%Sn		Cu_3Sn	$Cu_{0.75}Sn_{0.25}$
	η	43.5-44.5 at%Sn	$B8_1$	NiAs	$Cu_{0.545}(Cu, Sn)_{0.122}Sn_{0.455}$
	η′	45 at%Sn	—	—	$Cu_{0.545}Sn_{0.455}$
	(βSn)	100 at%Sn	A5	βSn	(Cu,Sn)
In-Sn	(In)	0-11at%Sn	A6	In	(In,Sn)
	β	12-44 at%Sn	A6	In	(In,Sn)
	γ	72-? at%Sn	—	—	(In,Sn)
	(βSn)	100 at%Sn	A5	βSn	(In,Sn)

Solution Phases

The subregular solution model is used to describe the Gibbs energies of the liquid, bcc and fcc phases with the Redlich-Kister formula,[10] as follows:

$$G_m^\phi = \sum_{i=Cu,In,Sn} {}^0G_i^\phi x_i^\phi + RT \sum_{i=Cu,In,Sn} x_i^\phi \ln x_i^\phi + x_{Cu}^\phi x_{In}^\phi L_{Cu,In}^\phi + x_{Cu}^\phi x_{Sn}^\phi L_{Cu,Sn}^\phi + x_{In}^\phi x_{Sn}^\phi L_{In,Sn}^\phi + \Delta^{ex}G^{tern} \quad (1)$$

where ${}^0G_i^\phi$ is the molar Gibbs energy of the pure component i with ϕ phase, and x_i is the mole fraction of component i. $L_{i,j}^\phi$ is the interaction parameter between i and j atoms in i-j binary system, and $\Delta^{ex}G^{tern}$ is the excess term of the interaction between atoms in ternary system, which can be expressed in the following forms, respectively:

$$L_{i,j}^\phi = \sum_{m=0}^{n} {}^mL_{i,j}^\phi (x_i - x_j)^m$$

$$\Delta^{ex}G^{tern} = x_{Cu}^\phi x_{In}^\phi x_{Sn}^\phi (x_{Cu}^\phi {}^0L_{CuInSn}^\phi + x_{In}^\phi {}^1L_{CuInSn}^\phi + x_{Sn}^\phi {}^2L_{CuInSn}^\phi)$$

where the coefficient ${}^mL_{i,j}^\phi$ is the parameters in the sub-binary system, and ${}^nL_{CuInSn}^\phi$ may be temperature dependent, and is optimized in the present calculation.

INTERMETALLIC COMPOUNDS

By considering the solubility of the third element in some binary compounds, the Gibbs energies of these compounds are expressed using the sublattice model as follows:[11]

(a) The compounds of the $\varepsilon(Cu_3Sn)$, and $\delta(Cu_{41}Sn_{11})$ in the Cu-Sn system and $\delta(Cu_7In_3)$ in the Cu-In system are described by the formula $Cu_p(In,Sn)_q$, and their Gibbs energies are represented as

$$G = y_{In}^{II}\,{}^0G_{Cu:In} + y_{Sn}^{II}\,{}^0G_{Cu:Sn} + qRT(y_{In}^{II}\ln y_{In}^{II} + y_{Sn}^{II}\ln y_{Sn}^{II}) + y_{In}^{II}y_{Sn}^{II}L_{Cu:In:Sn} \quad (2)$$

where y_i^{II} is the fraction of element i in sublattice II, and ${}^0G_{i:j}$ is the Gibbs energy of formation of the compound ij. $L_{Cu:In:Sn}$ is the interaction parameter between In and Sn in sublattice II.

(b) The γ phase is described by three sublattices, i.e. $Cu_{0.654}(Cu,In)_{0.115}(In,Sn)_{0.231}$, and the Gibbs energy is expressed by

$$\begin{aligned} G = {} & y_{Cu}^{II}y_{In}^{III}\,{}^0G_{Cu:Cu:In} + y_{Cu}^{II}y_{Sn}^{III}\,{}^0G_{Cu:Cu:Sn} \\ & + y_{In}^{II}y_{In}^{III}\,{}^0G_{Cu:In:In} + y_{In}^{II}y_{Sn}^{III}\,{}^0G_{Cu:In:Sn} \\ & + 0.115RT(y_{Cu}^{II}\ln y_{Cu}^{II} + y_{In}^{II}\ln y_{In}^{II}) \\ & + 0.231RT(y_{In}^{III}\ln y_{In}^{III} + y_{Sn}^{III}\ln y_{Sn}^{III}) \\ & + y_{Cu}^{II}y_{In}^{II}L_{Cu:Cu,In:In} + y_{Cu}^{II}y_{In}^{II}L_{Cu:Cu,In:Sn} \\ & + y_{In}^{III}y_{Sn}^{III}L_{Cu:Cu:In,Sn} + y_{In}^{III}y_{Sn}^{III}L_{Cu:In:In,Sn} \end{aligned} \quad (3)$$

where y_i^{II} and y_i^{III} are the fractions of element i in sublattices II and III, respectively, and ${}^0G_{i:j:k}$ is the Gibbs energy of formation of the compound ijk. The four L terms are the interaction parameters between Cu and In in sublattice II, and between In and Sn in sublattice III, respectively.

(c) Since the η phase exists in both the Cu-In and

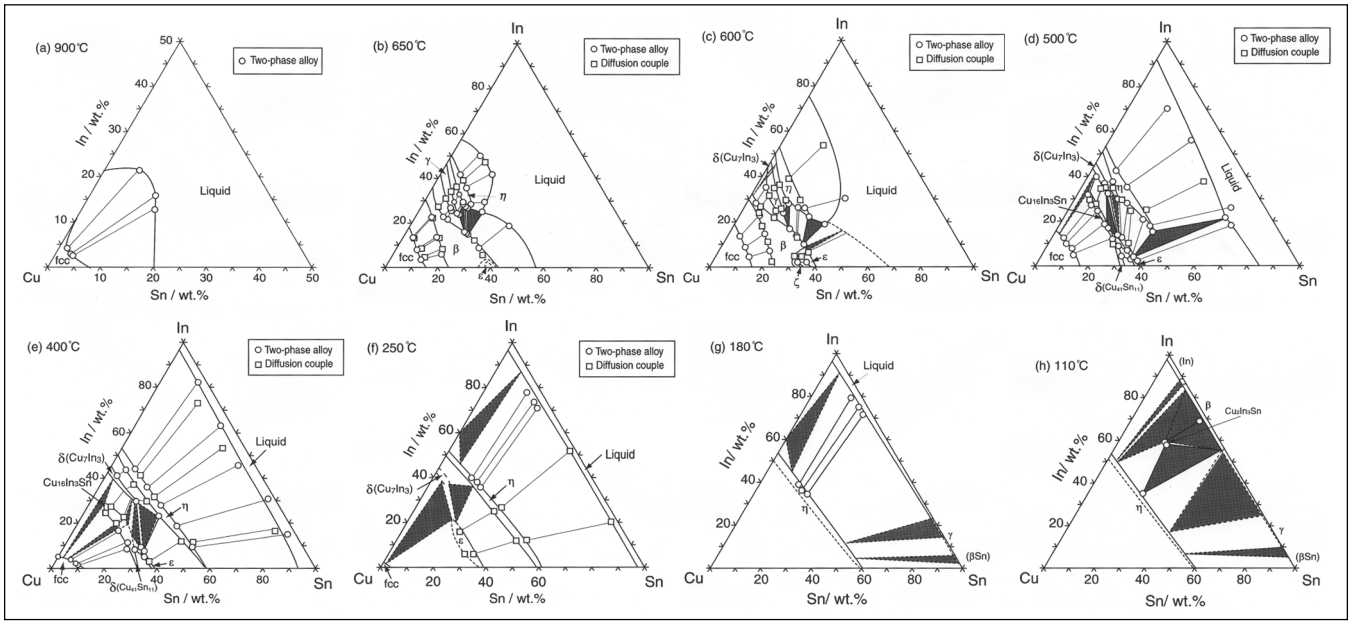

Fig. 3. Isothermal sections determined by present work.

Table II. Phase Equilibrium Compositions of the Cu-Sn-In System Determined by the Present Work

Temp. (°C)	Equilibria	Composition (wt.%) Phase 1 In	Phase 1 Sn	Phase 2 In	Phase 2 Sn	Phase 3 In	Phase 3 Sn
900	fcc/liquid	4.1	1.6	21.6	6.7	—	—
		2.5	3.7	12.4	13.8	—	—
		2.7	3.1	15.4	12.7	—	—
650	β(bcc)/liquid	11.8	27.4	—	—	—	—
		5.4	33.7	—	—	—	—
		8.2	31.4	19.8	38.0	—	—
	η/liquid	40.2	8.4	50.2	11.6	—	—
		34.7	13.4	41.5	20.4	—	—
		37.4	10.3	46.4	14.4	—	—
		28.2	18.8	28.5	23.5	—	—
	β(bcc)/η/liquid	14.3	24.6	25.8	19.1	23.9	25.4
	fcc/β(bcc)	13.0	4.0	22.3	6.4	—	—
		8.4	9.2	13.0	13.8	—	—
		4.7	12.4	8.1	17.3	—	—
		12.8	4.4	21.9	6.7	—	—
		7.7	8.4	13.3	13.0	—	—
		3.5	11.8	5.8	18.5	—	—
	β(bcc)/γ	22.2	10.9	25.7	11.9	—	—
		27.6	8.2	31.3	7.4	—	—
		21.0	13.4	24.9	12.6	—	—
	γ/η	30.6	10.5	33.8	10.6	—	—
		24.3	15.3	28.7	15.2	—	—
		33.4	8.3	35.8	8.9	—	—
	β(bcc)/η	15.4	23.0	26.8	17.6	—	—
	γ/η/ β(bcc)	22.7	16.5	27.2	16.6	16.3	21.8
600	η/lquid	39.4	10.8	53.5	16.4	—	—
		29.6	19.4	—	—	—	—
		26.5	22.1	31.1	36.9	—	—
	β(bcc)/η	11.8	27.0	24.9	21.5	—	—
		12.3	26.5	25.2	20.5	—	—
	β(bcc)/η /liquid	9.0	30.6	21.5	26.3	19.4	33.8
	ε/liquid	7.0	34.2	—	—	—	—
	fcc/β(bcc)	12.8	4.6	21.8	7.3	—	—
		8.1	8.6	13.6	13.4	—	—
		4.1	12.4	6.5	19.0	—	—
		—	—	23.3	6.4	—	—
		—	—	17.4	10.4	—	—
		—	—	10.2	16.0	—	—
		—	—	2.1	22.6	—	—
	β(bcc)/γ	25.4	6.4	31.1	7.3	—	—
		21.0	14.0	24.1	13.2	—	—
		28.4	3.3	36.4	3.9	—	—
	γ/η	33.8	7.6	35.4	8.9	—	—
		24.4	14.8	29.1	14.8	—	—
	β(bcc)/γ/η	16.3	21.7	22.6	16.4	27.9	16.2
	β(bcc)/ζ	4.0	29.7	3.5	32.8	—	—
	ζ/ε	1.9	32.1	1.5	35.6	—	—
500	η/liquid	23.3	29.7	37.9	45.4	—	—
		41.8	9.7	70.8	15.8	—	—
		34.1	17.5	55.8	32.6	—	—
		18.2	34.6	25.2	62.6	—	—
500	ε/liquid	1.6	36.0	18.5	65.1	—	—
	ε/η	—	—	29.8	17.8	—	—

Temp. (°C)	Equilibria	Composition (wt.%) Phase 1 In	Phase 1 Sn	Phase 2 In	Phase 2 Sn	Phase 3 In	Phase 3 Sn
		7.6	30.6	23.8	24.3	—	—
		11.4	26.6	29.3	16.4	—	—
		11.5	27.0	26.8	21.1	—	—
		3.3	34.5	20.0	30.7	—	—
	η/ε/ liquid	15.9	37.0	2.2	35.4	20.3	63.5
	fcc/$Cu_{16}In_3Sn$	—	—	27.9	6.1	—	—
		6.8	9.5	17.8	16.9	—	—
		11.3	4.2	27.2	7.9	—	—
		9.5	6.4	23.4	11.6	—	—
		9.3	6.4	23.6	11.7	—	—
	fcc/δ($Cu_{41}Sn_{11}$)	—	—	9.7	23.6	—	—
		4.6	11.2	11.3	22.7	—	—
	δ(Cu_7In_3)/η	34.4	8.7	34.6	11.3	—	—
		37.2	7.6	37.8	9.8	—	—
	δ(Cu_7In_3)/ε	31.2	12.4	12.6	25.5	—	—
	δ($Cu_{41}Sn_{11}$)/ε/δ(Cu_7In_3)	15.9	19.1	12.5	24.3	31.5	11.0
	$Cu_{16}In_3Sn$/δ(Cu_7In_3)	27.0	7.9	33.6	8.1	—	—
		31.7	4.4	39.7	2.9	—	—
400	η/liquid	40.7	13.7	71.8	19.9	—	—
		11.4	46.9	17.3	76.7	—	—
		31.5	23.2	53.3	39.5	—	—
		42.8	10.1	80.3	15.2	—	—
		34.9	18.8	61.7	33.4	—	—
		27.2	27.9	46.8	47.8	—	—
		18.5	38.1	30.0	67.2	—	—
		9.3	48.7	14.7	82.4	—	—
	ε/η	2.6	35.1	12.3	43.4	—	—
		7.4	31.1	22.5	29.5	—	—
	δ(Cu_7In_3)/ε	8.9	12.9	29.0	17.4	—	—
		8.8	29.3	29.1	17.5	—	—
	fcc/$Cu_{16}In_3Sn$	—	—	26.5	8.5	—	—
		—	—	21.8	14.8	—	—
	fcc/δ($Cu_{41}Sn_{11}$)	2.3	8.0	11.4	23.1	—	—
		3.9	5.1	16.4	17.3	—	—
		1.6	9.3	8.5	24.2	—	—
	δ(Cu_7In_3)/η	40.5	4.9	42.6	6.5	—	—
		—	—	36.9	12.9		
		—	—	29.9	21.5		
		26.9	9.3	—	—	—	—
		23.2	16.8	—	—	—	—
250	η/liquid	25.6	32.1	50.8	46.9	—	—
		10.8	48.6	19.2	79.3	—	—
		37.0	17.4	74.4	22.6	—	—
		40.6	14.4	78.3	17.5	—	—
		37.6	17.9	73.6	22.4	—	—
	ε/η	15.7	20.4	24.6	32.0	—	—
		6.4	30.3	10.7	47.6	—	—
	fcc/ε	—	—	6.4	28.4	—	—
180	η/liquid	36.8	18.3	75.4	21.9	—	—
		39.4	16.2	80.6	16.6	—	—
		34.4	21.5	72.2	25.2	—	—
110	Cu_2In_3Sn/liquid	58.8	18.8	69.2	28.5	—	—
	η/Cu_2In_3Sn	33.9	22.8	57.3	19.9	—	—

Table III. Transformation Temperatures Determined by DSC

(Alloy composition (wt.%) In	Sn	Liquidus (°C)	Other transformation temperature(°C)
10	80	457.2	192.8, 215.9
20	70	455.5	117.6, 198.1
30	60	475.1	117.6, 169.7
40	50	473.9	118.3, 141.6
50	40	503.9	102.5, 118.6
60	30	513.5	126.7
70	20	516.5	131.0, 150.6
80	10	525.5	143.0, 175.8
10	70	551.1	191.9, 276.9, 446.4
20	60	527.9	127.3, 201.6
30	50	535.1	122.2, 162.8
40	40	560.6	128.6
50	30	558.7	99.0, 127.4
60	20	571.2	—
70	10	578.9	145.5, 174.8, 274.3
10	60	585.8	186.9, 450.5, 525.0, 527.2
30	40	575.9	122.6, 150.1
50	20	605.9	130.7, 157.9, 580.7
10	50	620.3	199.2, 454.5
30	30	613.8	121.9
50	10	642.1	134.9, 166.4
40	10	657.0	137.6, 174.5
30	20	650.3	—
20	30	661.0	567.4, 588.1, 625.9
10	40	603.0	472.6, 558.0
30	10	694.0	525.4
20	20	699.4	516.1, 557.9, 659.5, 679.2
10	30	716.0	585.6, 607.7
20	10	751.0	563.2, 569.7, 718.7
10	20	761.7	540.7, 563.0, 722.4
10	10	905.3	549.8, 575.0, 748.9

Cu-Sn systems, it is described by three sublattices, i.e. $Cu_{0.545}(Cu,In,Sn)_{0.122}(In, Sn)_{0.333}$, and the Gibbs energy is expressed by

$$\begin{aligned} G = {} & y^{II}_{Cu}y^{III^0}_{In}G_{Cu:Cu:In} + y^{II}_{Cu}y^{III^0}_{Sn}G_{Cu:Cu:Sn} \\ & + y^{II}_{In}y^{III^0}_{In}G_{Cu:In:In} + y^{II}_{In}y^{III^0}_{Sn}G_{Cu:In:Sn} \\ & + y^{II}_{Sn}y^{III^0}_{In}G_{Cu:Sn:In} + y^{II}_{Sn}y^{III^0}_{Sn}G_{Cu:Sn:Sn} \\ & + 0.122RT(y^{II}_{Cu}\ln y^{II}_{Cu} + y^{II}_{In}\ln y^{II}_{In} + y^{II}_{Sn}\ln y^{II}_{Sn}) \\ & + 0.333RT(y^{III}_{In}\ln y^{III}_{In} + y^{III}_{Sn}\ln y^{III}_{Sn}) \\ & + y^{II}_{Cu}y^{II}_{In}L_{Cu:Cu,In:In} + y^{II}_{Cu}y^{II}_{In}L_{Cu:Cu,In:Sn} \\ & + y^{II}_{Cu}y^{II}_{Sn}L_{Cu:Cu,Sn:In} + y^{II}_{Cu}y^{II}_{Sn}L_{Cu:Cu,Sn:Sn} \\ & + y^{II}_{In}y^{II}_{Sn}L_{Cu:In,Sn:In} + y^{II}_{In}y^{II}_{Sn}L_{Cu:In,Sn:Sn} \\ & + y^{III}_{In}y^{III}_{Sn}L_{Cu:Cu:In,Sn} + y^{III}_{In}y^{III}_{Sn}L_{Cu:In:In,Sn} \\ & + y^{III}_{In}y^{III}_{Sn}L_{Cu:Sn:In,Sn} \end{aligned} \quad (4)$$

(d) Two ternary compounds are taken into account in the present work and are described as $Cu_{0.77}(In,Sn)_{0.23,}$ reported by Koster et al.[8] and Cu_2In_3Sn, respectively. The Gibbs energies of two compounds can be written as

$$\begin{aligned} G^{Cu_{0.77}(In,Sn)_{0.23}} = {} & y^{II}_{In}{}^0G_{Cu:In} + y^{II}_{Sn}{}^0G_{Cu:Sn} \\ & + 0.23RT(y^{II}_{In}\ln y^{II}_{In} + y^{II}_{Sn}\ln y^{II}_{Sn} \\ & + y^{II}_{In}y^{II}_{Sn}L_{Cu:In,Sn} \end{aligned} \quad (5)$$

$$\begin{aligned} & {}^0G^{Cu_2In_3Sn} - 0.3333{}^0F^{fcc}_{Cu} - 0.5{}^0G^{tetra}_{In} \\ & -0.6667{}^0G^{\beta Sn}_{Sn} = A + BT \end{aligned} \quad (6)$$

where the new parameters α and β are optimized based on the experimental data.

The unary data for the pure elements are taken from Dinsdale.[12]

EXPERIMENTAL RESULTS

A typical microstructure of the $Cu_{60}In_{22}Sn_{18}$ (wt.%) alloy equilibrated at 600°C for 48 h is shown in Fig. 1, in which three phases of the β(bcc), η, and δ(Cu_7In_3) can be distinguished and the equilibrium compositions of these phases can be determined by EDS.

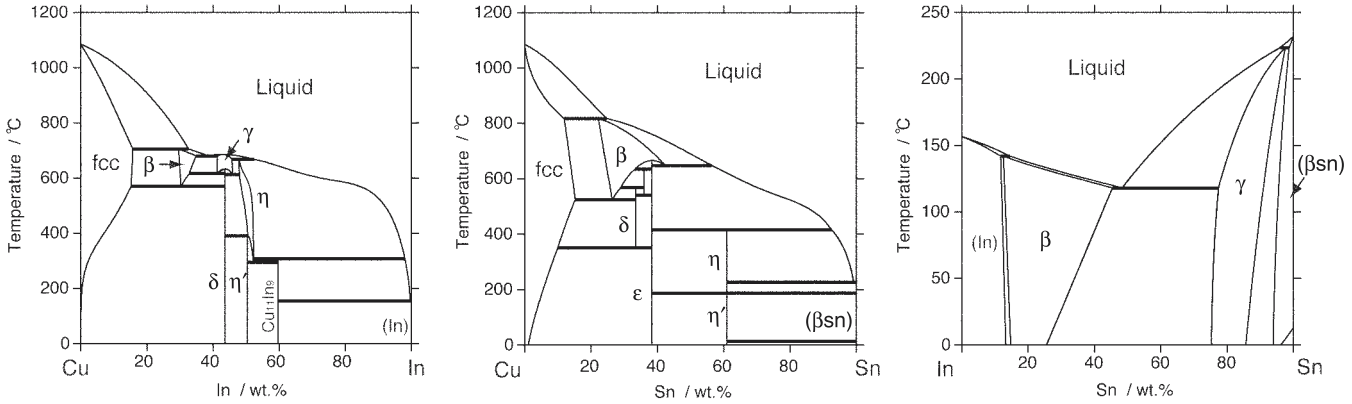

Fig. 4. Calculated Cu-In,[12] Cu-Sn, and Sn-In[18] binary phase diagrams.

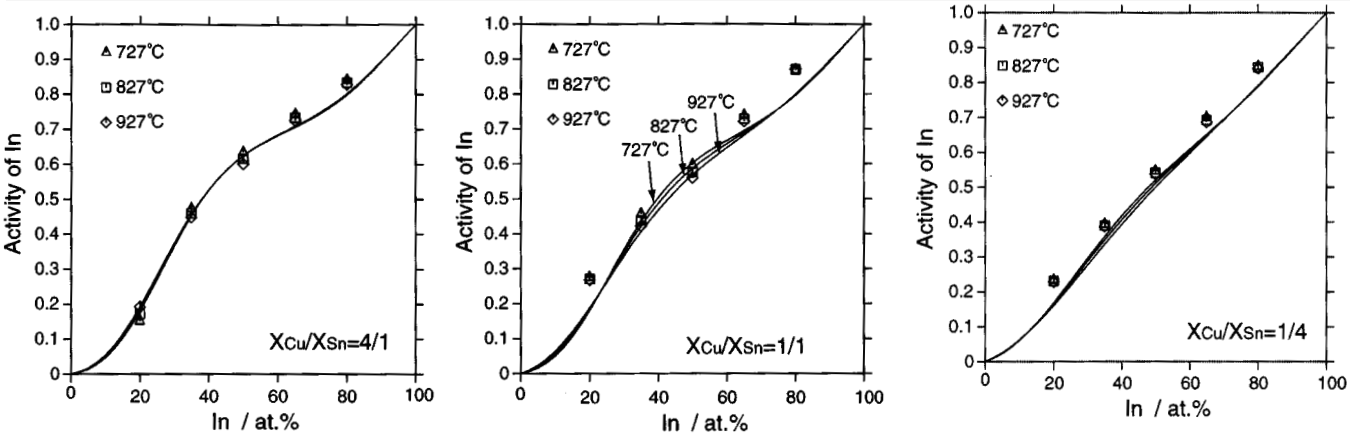

Fig. 5. A comparison of the activity of In in the liquid phase between the measured[19] and calculated results.

Figure 2 shows the microstructure and concentration profile of the Cu/In-20wt.%Sn diffusion couple annealed at 600°C for 4 h, where four Cu/β(bcc)/δ(Cu_7In_3)/η/liquid interphase boundaries can be observed, and where there are the composition gaps corresponding to these interfaces. Equilibrium compositions determined by extrapolation of the composition curves to the interphase boundaries are listed in Table II and are plotted in Fig. 3, in which eight isothermal sections at 900, 650, 600, 500, 400, 250, 180, and 110°C are presented. The main feature of the phase equilibria in this system is that there are large solubilities of In in the ε(Cu_3Sn), δ($Cu_{41}Sn_{11}$), and η phases in the Cu-Sn system, and large solubilities of Sn in the γ, η, and δ(Cu_7In_3) phases in the Cu-In system, and continuous formation of the η phase from the Cu-In side to the Cu-Sn side.

By comparing the present results with the data reported by Koster et al.,[6] it is seen that the main difference in the isothermal sections at 650°C and 600°C is due to the disappearance of the β(bcc)/γ(D03) phase equilibria in the present results. Their results indicate that there is large solubility of In in the β and γ phases and that the γ(D03)+β+γ(CuIn) three-phase equilibrium exists. However, the present authors have confirmed the existence of second ordering reaction of the bcc phase, rather than the β(bcc)+γ(D03) two-phase equilibrium in the Cu-Sn binary system.[13]

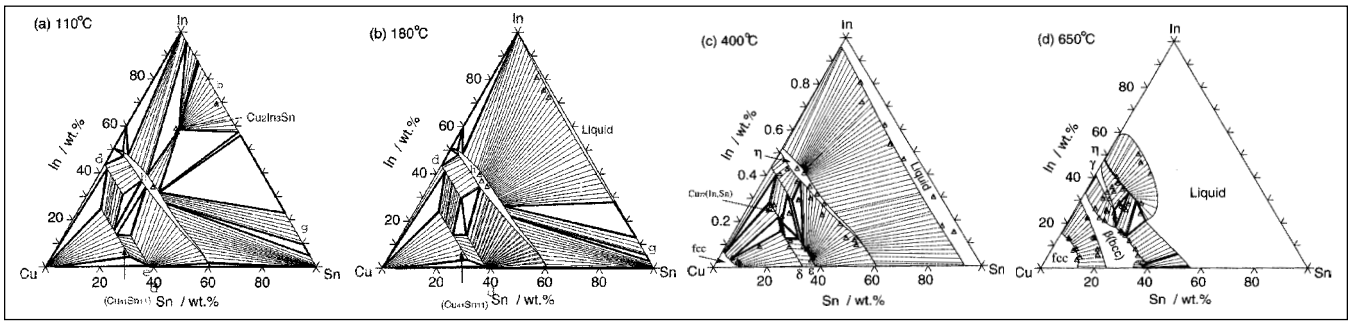

Fig. 6. Calculated isothermal sections at (a) 110°C, (b) 180°C, (c) 400°C, and (d) 650°C compared with the present experimental data.

Table IV. Thermodynamic Parameters of the Cu-Sn-In System Used in This Work (J/mol)

Liquid Phase (Cu,Sn,In)

$${}^{0}L^{Liq}_{Cu,In} = -41564.79 + 238.616\times T - 29.827\times T\times Ln(T)$$
$${}^{1}L^{Liq}_{Cu,In} = -76057.785 + 371.306\times T - 44.944\times T\times Ln(T)$$
$${}^{2}L^{Liq}_{Cu,In} = -42076.516 + 192.395\times T - 23.281\times T\times Ln(T)$$
$${}^{0}L^{Liq}_{Cu,Sn} = -9002.8 - 5.8381\times T$$
$${}^{1}L^{Liq}_{Cu,Sn} = -20100.4 + 3.6366\times T$$
$${}^{2}L^{Liq}_{Cu,Sn} = -10528.4$$
$${}^{0}L^{Liq}_{In,Sn} = -711 - 1.6934\times T$$
$${}^{1}L^{Liq}_{In,Sn} = -64 - 1.3592\times T$$
$${}^{0}L^{Liq}_{Cu,In,Sn} = 308713.7 - 283.755\times T$$
$${}^{1}L^{Liq}_{Cu,In,Sn} = -138024.654 + 150.6387\times T$$
$${}^{2}L^{Liq}_{Cu,In,Sn} = 22783.4854 - 69.65\times T$$

Fcc Phase (Cu,In,Sn)

$${}^{0}L^{Fcc}_{Cu,In} = -6475.911 + 21.83\times T$$
$${}^{1}L^{Fcc}_{Cu,In} = -29935.183 - 5.672\times T$$
$${}^{2}L^{Fcc}_{Cu,In} = 47350.167 - 40.21\times T$$
$${}^{0}L^{Fcc}_{Cu,Sn} = -10672.0 - 1.4837\times T$$
$${}^{1}L^{Fcc}_{Cu,Sn} = -15331 + 6.9539\times T$$
$${}^{0}L^{Fcc}_{In,Sn} = 25000$$
$${}^{0}L^{Fcc}_{Cu,In,Sn} = -55000$$
$${}^{1}L^{Fcc}_{Cu,In,Sn} = -55000$$
$${}^{2}L^{Fcc}_{Cu,In,Sn} = -55000$$

Bcc Phase (Cu,In,Sn)

$${}^{0}L^{Bcc}_{Cu,In} = -20532.763 + 12.724\times T$$
$${}^{1}L^{Bcc}_{Cu,In} = -13379.27 - 12.358\times T$$
$${}^{0}L^{Bcc}_{Cu,Sn} = -32656.8 + 25.015776\times T$$
$${}^{1}L^{Bcc}_{Cu,Sn} = -13862.5 - 32.0218\times T$$
$${}^{2}L^{Bcc}_{Cu,Sn} = -4175.47 + 5.0083\times T$$
$${}^{0}L^{Bcc}_{In,Sn} = 25000$$
$${}^{0}L^{Bcc}_{Cu,In,Sn} = 18052.7$$
$${}^{1}L^{Bcc}_{Cu,In,Sn} = -9000$$
$${}^{2}L^{Bcc}_{Cu,In,Sn} = 25000$$

ε(Cu_3Sn) Compound $(Cu)_{0.75}(In,Sn)_{0.25}$

$${}^{0}G^{Cu_3Sn}_{Cu:Sn} - 0.75\times{}^{0}G^{fcc}_{Cu} - 0.25\times{}^{0}G^{bct}_{Sn} = -8194.2 - 0.2043\times T$$
$${}^{0}G^{Cu_3Sn}_{Cu:In} - 0.75\times{}^{0}G^{fcc}_{Cu} - 0.25\times{}^{0}G^{tetr}_{In} = -7900 + 4\times T$$
$${}^{0}L^{Cu_3Sn}_{Cu:In,Sn} = -5800 + 3\times T$$

δ ($Cu_{41}Sn_{11}$) Compound

$Cu_{0.788}(In,Sn)_{0.212}$

$${}^{0}G^{Cu_{41}Sn_{11}}_{Cu:Sn} - 0.788\times{}^{0}G^{fcc}_{Cu} - 0.212\times{}^{0}G^{bct}_{Sn} = -6323.5 - 1.2808\times T$$
$${}^{0}G^{Cu_{41}Sn_{11}}_{Cu:In} - 0.788\times{}^{0}G^{fcc}_{Cu} - 0.212\times{}^{0}G^{tetr}_{In} = -5350 + 1.5\times T$$
$${}^{0}L^{Cu_{41}Sn_{11}}_{Cu:In,Sn} = -13000 + 14.77\times T$$

η Compound $(Cu)_{0.545}(Cu,In,Sn)_{0.122}(In,Sn)_{0.333}$

$${}^{0}G^{\eta}_{Cu:Cu:In} - 0.667\times{}^{0}G^{fcc}_{Cu} - 0.333\times{}^{0}G^{tetra}_{In} = -6301.497 - 0.9396\times T$$
$${}^{0}G^{\eta}_{Cu:In:In} - 0.545\times{}^{0}G^{fcc}_{Cu} - 0.455\times{}^{0}G^{tetra}_{In} = -156.679 - 7.0297\times T$$
$${}^{0}G^{\eta}_{Cu:Sn:In} - 0.545{}^{0}G^{fcc}_{Cu} - 0.122\times{}^{0}G^{bct}_{Sn} - 0.333\times{}^{0}G^{tetra}_{In} = 16000$$
$${}^{0}G^{\eta}_{Cu:Cu:Sn} - 0.667\times{}^{0}G^{fcc}_{Cu} - 0.333\times{}^{0}G^{bct}_{Sn} = 3200 + 2\times T$$
$${}^{0}G^{\eta}_{Cu:In:Sn} - 0.667\times{}^{0}G^{fcc}_{Cu} - 0.122\times{}^{0}G^{tetra}_{In} - 0.333\times{}^{0}G^{bct}_{Sn} = -2492 + 4\times T$$
$${}^{0}G^{\eta}_{Cu:Sn:Sn} - 0.545\times{}^{0}G^{fcc}_{Cu} - 0.455\times{}^{0}G^{bct}_{Sn} = -6869.5 - 0.1589\times T$$
$${}^{0}L^{\eta}_{Cu:Cu,In:In} = -14526.546 + 18.02\times T$$
$${}^{0}L^{\eta}_{Cu:Cu,Sn:In} = -37093.16 + 18.52\times T$$
$${}^{0}L^{\eta}_{Cu:Cu,Sn:Sn} = -8300$$
$${}^{0}L^{\eta}_{Cu:In,Sn:In} = -8300$$
$${}^{0}L^{\eta}_{Cu:In,Sn:Sn} = -8300$$
$${}^{0}L^{\eta}_{Cu:Cu,In:Sn} = -14526.546 + 18.02\times T$$
$${}^{0}L^{\eta}_{Cu:Cu:In,Sn} = -19650.8 - 0.4\times T$$
$${}^{0}L^{\eta}_{Cu:In:In,Sn} = -44570.8 + 39.6\times T$$
$${}^{0}L^{\eta}_{Cu:Sn:In,Sn} = -30000 + T$$

η′(CuIn) Compound $(Cu)_{0.64}(In)_{0.36}$

$${}^{0}G^{\eta'} - 0.64\times{}^{0}G^{fcc}_{Cu} - 0.36\times{}^{0}G^{tetra}_{In} = -8173.8 + 1.38\times T$$

$Cu1In_9$ Compound $(Cu)_{0.55}(In)_{0.45}$

$${}^{0}G^{Cu_{11}In_9} - 0.55\times{}^{0}G^{fcc}_{Cu} - 0.45\times{}^{0}G^{tetra}_{In} = -7525.6 + 1.703\times T$$

δ Compound $(Cu)_{0.769}(Sn)_{0.231}$

$${}^{0}G^{\delta} - 0.769\times{}^{0}G^{fcc}_{Cu} - 0.231\times{}^{0}G^{fcc}_{Sn} = -6655.1 - 1.485\times T$$

η′(CuSn) compund $(Cu)_{0.545}(Sn)_{0.455}$

$${}^{0}G^{\eta} - 0.545\times{}^{0}G^{fcc}_{Cu} - 0.455\times{}^{0}G^{fcc}_{Sn} = -7129.7 + 0.4059\times T$$

δ(Cu_7In_3) Compound $(Cu)_{0.7}(In,Sn)_{0.3}$

$${}^0G^{\delta}_{Cu:In} - 0.7\times{}^0G^{fcc}_{Cu} - 0.3\times{}^0G^{tetra}_{In} = -7991.308 + 1.1703\times T$$
$${}^0G^{\delta}_{Cu:Sn} - 0.7\times{}^0G^{fcc}_{Cu} - 0.3\times{}^0G^{bct}_{Sn} = -5200 + 0.5\times T$$
$${}^0L^{\delta}_{Cu:In,Sn} = -13800 + 10.5\times T$$

$Cu_{77}(In,Sn)_{23}$ Ternary Compound $(Cu)_{0.77}(In,Sn)_{0.23}$

$${}^0G^{Cu_{77}(In,Sn)_{23}}_{Cu:In} - 0.77\times{}^0G^{fcc}_{Cu} - 0.23\times{}^0G^{tetra}_{In} = -6250$$
$${}^0G^{Cu_{77}(In,Sn)_{23}}_{Cu:Sn} - 0.77\times{}^0G^{fcc}_{Cu} - 0.23\times{}^0G^{bct}_{Sn} = -7000 + T$$
$${}^0L^{Cu_{77}(In,Sn)_{23}}_{Cu:In,Sn} = -4600$$

Cu_2In_3Sn Ternary Compound $(Cu)_{0.333}(In)_{0.5}(Sn)_{0.167}$

$${}^0G^{Cu_2In_3Sn}_{Cu:In:Sn} - 0.333\times{}^0G^{fcc}_{Cu} - 0.5\times{}^0G^{tetra}_{In} - 0.167\times{}^0G^{bct}_{Sn} = -9315 + 5\times T$$

γ(CuIn) Phase $Cu_{0.654}(Cu,In)_{0.115}(In,Sn)_{0.231}$

$${}^0G^{\gamma}_{Cu:Cu:In} - 0.769\times{}^0G^{fcc}_{Cu} - 0.231\times{}^0G^{tetra}_{In} = -2204.82 - 3.446\times T$$
$${}^0G^{\gamma}_{Cu:In:In} - 0.654\times{}^0G^{fcc}_{Cu} - 0.346\times{}^0G^{tetra}_{In} = -7131.647 + 0.11183\times T$$
$${}^0G^{\gamma}_{Cu:Cu:Sn} - 0.769\times{}^0G^{fcc}_{Cu} - 0.231\times{}^0G^{bct}_{Sn} = -7900 + 5.43113\times T$$
$${}^0G^{\gamma}_{Cu:In:Sn} - 0.654\times{}^0G^{fcc}_{Cu} - 0.115\times{}^0G^{fcc}_{In} - 0.231\times{}^0G^{bct}_{Sn} = 3144.8 - 2.4\times T$$
$${}^0L^{\gamma}_{Cu:Cu,In:In} = 0.0$$
$${}^0L^{\gamma}_{Cu:Cu,In:Sn} = -2000$$
$${}^0L^{\gamma}_{Cu:Cu:In,Sn} = -2000$$
$${}^0L^{\gamma}_{Cu:In:In,Sn} = -5200$$

γ(InSn) Phase (In,Sn)

$${}^0L^{\gamma}_{In,Sn} = -15715.5 + 19.3402\times T$$

β(InSn) Phase (In,Sn)

$${}^0L^{\beta}_{In,Sn} = -235 - 3.6954\times T$$

Bct (βSn) Phase (Cu,In,Sn)

$${}^0L^{Bct}_{Cu,Sn} = 0.0$$
$${}^0L^{Bct}_{Cu,In} = 0.0$$
$${}^0L^{Bct}_{In,Sn} = -239 + 2.8509\times T$$

Tetragonal (In) (In,Sn)

$${}^0L^{Tetra}_{In,Sn} = 743 - 3.3139\times T$$
$${}^1L^{Tetra}_{In,Sn} = -1487$$

In the present experiment, the first order reaction of the β(bcc)+γ(D03) two-phase equilibrium in the ternary Cu-In-Sn system was also not found in the Cu-In alloys/Cu diffusion couple.

Based on Koster's results,[8] the phase equilibria of this system were summarized by Villars et al.,[14] who pointed out that there might be three ternary compounds above 400°C in this system. However, considering the present results and Koster's original data only a ternary compound, $Cu_{16}In_3Sn$, exists although the crystal structure of the phase was not studied in the present investigation, whereas the other two ternary compounds compiled by Villars et al.[14] can be considered to be binary compounds with large solubilities. From the section in the portion of the In-Sn side at 110°C, it is seen that there is a new compound with a Cu_2In_3Sn composition ratio, which has not been previously reported. By comparing the sections at 110°C and 180°C, it is indicated that this compound phase is stable below 180°C.

Eight vertical sections at 10, 20, 30, 40, 50, 60, 70 and 80 wt.%Cu were also determined by DSC. These

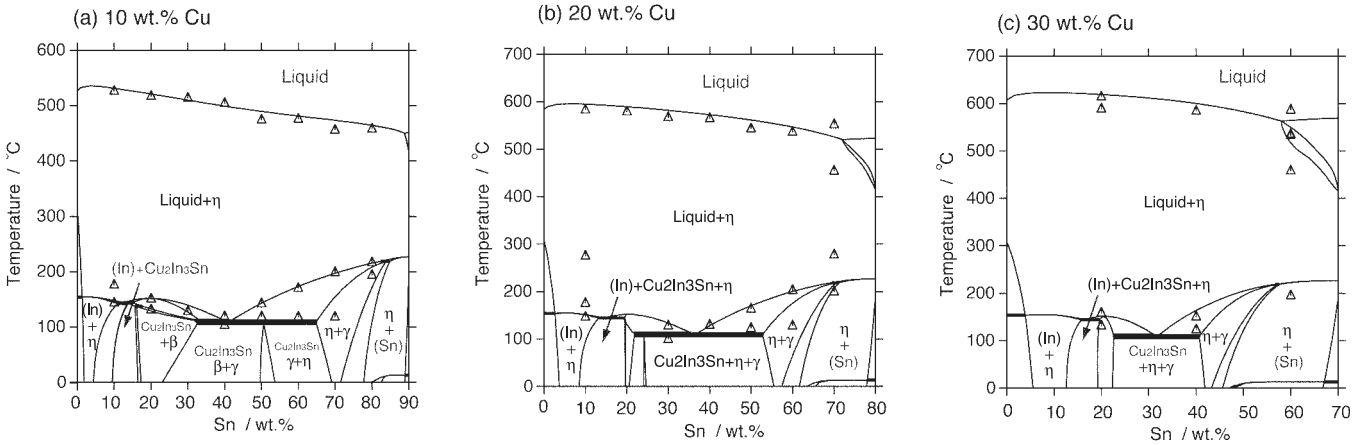

Fig. 7. Calculated vertical sections at (a) 10wt.%Cu, (b) 20wt.%Cu, and (c) 30wt.%Cu compared with the present experimental data.

Table V1. Calculated Invariant Reactions of the Cu-In-Sn System

Reaction	Temp. (°C)	Phase	Composition wt.% (at.%) In	Composition wt.% (at.%) Sn
$L+Cu_3Sn \Leftrightarrow \beta(bcc)+\eta$ (P1)	612.4	L	17.11 (12.88)	40.51 (29.49)
		Cu3Sn	4.04 (2.72)	34.25 (22.28)
		β	9.23 (6.36)	33.40 (22.25)
		η	24.77 (17.98)	27.37 (19.22)
$L+\gamma \Leftrightarrow \beta(bcc)+\eta$ (P2)	651.6	L	24.92 (17.71)	23.67 (16.27)
		γ	25.95 (17.66)	15.26 (10.05)
		β	18.17 (12.23)	20.80 (13.54)
		η	33.13 (23.63)	16.38 (11.30)
$L+(In) \Leftrightarrow \beta(InSn)+\eta$ (P3)	136.8	L	83.62 (83.68)	15.83 (15.32)
		β(InSn)	87.36 (87.72)	12.64 (12.28)
		η	37.00 (27.68)	20.40 (14.76)
		(In)	88.19 (88.53)	11.81 (11.47)
$L+Cu_{11}In_9 \Leftrightarrow \eta+(In)$ (P4)	154.1	L	99.68 (99.43)	1.5×10^{-3} (1.4×10^{-3})
		Cu11In9	59.65 (45.0)	0.0 (0.0)
		η	48.07(35.13)	6.02 (4.26)
		(In)	99.999(99.999)	0.001 (0.001)
$L \Leftrightarrow \gamma(InSn)+\beta(InSn)+\eta$ (E1)	111.2	L	53.27 (53.78)	46.02 (44.94)
		γ(InSn)	22.85 (23.44)	77.15 (76.56)
		β(InSn)	55.73 (56.55)	44.27 (43.45)
		η	31.68 (23.81)	26.26 (19.09)
$L+(Sn) \Leftrightarrow \gamma(InSn)+\eta$ (P5)	218.5	L	4.95(5.08)	94.41 (93.74)
		γ(InSn)	2.83 (2.93)	97.17 (97.07)
		η	16.42 (12.47)	42.67 (31.36)
		(Sn)	1.53 (1.56)	98.47 (98.42)

results are shown in Fig. 6 for comparison with the calculated results.

CALCULATION OF PHASE EQUILIBRIA

Evaluation of Three Binary Systems

The phase diagram of the Cu-In binary system was first assessed by Kao et al.,[15] who gave a good description of the liquid and fcc phases based on experimental data including phase equilibria and thermodynamic properties. However, some phases and compounds with smaller solubility were not carefully considered; in particular, the β and γ phases were not included in their assessment. More recently, the present authors[16] reassessed the phase diagram of this system by taking into account three solution phases and five compounds.

Shim et al.[17] thermodynamically assessed the Cu-Sn binary system on the basis of experimental results of the thermodynamic properties and phase equilibria. However, the present authors have recently confirmed that there is a two-stage ordering reaction A2-B2-D03 in the bcc phase region, rather than a γ(D03)/β(A2) two-phase equilibrium as previously reported.[13] A new thermodynamic assessment of the phase diagram in this system was made by taking into account the A2/B2 ordering reaction by the present authors.[13] In the present paper a simplified description of the Gibbs energy of the bcc phase is made where the ordering reaction of the bcc phase is not considered.

Thermodynamic assessment of the In-Sn system was carried out by Lee et al.,[18] and their parameters are used in the present work.

The calculated phase diagrams of the Cu-In, Cu-Sn, and In-Sn binary systems used in the present assessment are shown in Fig. 4.

Calculation of Ternary System

The activities of In in the liquid phase of the Cu-In-Sn system measured by Itabashi et al. [19] are used to optimize the parameters of the liquid phase. Figure 5 shows a comparison of the measured[19] and calculated activity in the liquid phase of the Cu-In-Sn ternary system at 727°C, 827°C, and 927°C, which indicates that good agreement is obtained between the experiment and calculation. The parameters for other phases are assessed based on the present experimental data on the phase equilibria. The optimized thermodynamic parameters for describing the phase equilibria of the Cu-In-Sn system are listed in Table IV. Comparisons between calculated and experimental results are made in Figs. 6 and 7.

The calculated isothermal sections are in basic agreement with the experimental data. Four examples of the calculated isothermal sections at 110, 180, 400, and 650°C with the experimental data are shown in Fig. 6. Based on the parameters evaluated in the present work, the phase equilibria in the Cu-rich portion at 110°C and 180°C are predicted because

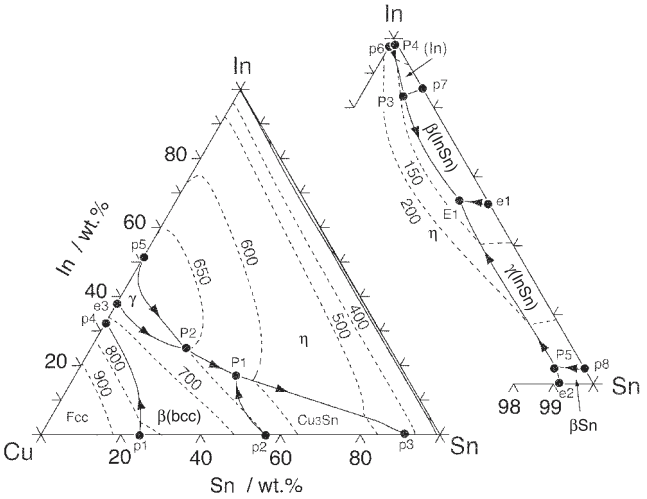

Fig. 8. Calculated liquidus projection in the Cu-In-Sn system.

there are no experimental data in this portion. It is indicated that the ternary compound ($Cu_{77}(In,Sn)_{23}$) disappears, but the δ compound in the binary Cu-Sn system is stable at the lower temperature. The parameter of another ternary compound (Cu_2In_3Sn) was only optimized based on the limited data of phase equilibria because no information on the phase stability of this compound is available. From the calculated results it is estimated that this compound exists below 156°C. A satisfactory agreement was also obtained for the comparison between the calculated vertical section and the experimental data, as shown in Fig. 7. Based on the optimized thermodynamic parameters, the calculated liquidus projection of this system is shown in Fig. 8, in which there are five peritectic reactions and a eutectic reaction on the In-Sn side. The types of reactions are listed in Table V.

CONCLUSIONS

(1) The phase equilibria of the Cu-In-Sn system, including eight isothermal sections at 110–900°C, as well as seven vertical sections at 10wt.%Cu- 70wt.%Cu were determined. The results indicate that there are large solubilities of In in the ε(Cu_3Sn) and δ($Cu_{41}Sn_{11}$) compounds in the Cu-Sn system, and large solubilities of Sn in the γ and δ(Cu_7In_3) phases in the Cu-In system. It was also found that the η phase continuously exists from the Cu-In to the Cu-Sn system and that a new ternary compound designated as Cu_2In_3Sn exist at 110°C.

(2) Thermodynamic assessment of the Cu-In-Sn system was carried out based on the experimental data. The thermodynamic parameters for describing the phase equilibria were optimized, resulting in good agreement between calculated and observed phase equilibria and thermodynamic properties.

ACKNOWLEDGEMENT

The authors wish to thank Mr. Y. Nakayama and Y. Inohana for their help with the experimental work. Support from The Mitsubishi Foundation is also acknowledged. One of the authors (HSL) acknowledges the support from Marubun Research Promotion Foundation.

REFERENCES

1. P.T. Vianco and D.R. Frear, *JOM* 45, 14 (1993).
2. J. Glazer, *Int. Mater. Rev.* 40, 65 (1995).
3. M. Abtew and G. Selvaduray, *Mater. Sci. Eng. R* 27, 95 (2000).
4. I. Ohnuma, X.J. Liu, H. Ohtani, and K. Ishida, *J. Electron. Mater.* 28, 1164 (1999).
5. I. Ohnuma, X.J. Liu, H. Ohtani, and K. Ishida, *Functional Materials,* ed. K. Grassie et al. (Weinheim, Germany: Wiley-VCH, 2000), p. 69.
6. J.W. Morris, J.L.F. Goldstein, and Z. Mei, *JOM* 45, 25 (1993).
7. K. Shimizu, T. Nakanishi, K. Karasawa, K. Hashimoto, and K. Niwa, *J. Electron. Mater.* 24, 39 (1995).
8. W. Koster, T. Godecke, and D. Heine, *Z. Metallkde.* 63, 802 (1972).
9. H. Enoki, K. Ishida, and T. Nishizawa, *J. Less-Common Met.* 160, 153 (1990).
10. O. Redlich and A.T. Kister, *Ind. Eng. Chem.* 24, 345 (1948).
11. M. Hillert and L.I. Staffansson, *Acta Chem. Scand.* 24, 3618 (1970).
12. A.T. Dinsdale, *CALPHAD* 15, 317 (1991).
13. X.J. Liu, C.P. Wang, I. Ohnuma, R. Kainuma, and K. Ishida, to be submitted to *Mater. Trans. A.*
14. P. Villars, A. Prince, and H. Okamoto, *Ternary Alloy Phase Diagram,* Vol. 7 (Materials Park, OH: ASM Int., 1995), p. 9605.
15. C.R. Kao, A. Bolcavage, S.-L. Chen, S.W. Chen, and Y.A. Chang, *J. Phase Equilibria* 14, 22 (1993).
16. H.S. Liu, X.J. Liu, Y. Cui, C.P. Wang, I. Ohnuma, and K. Ishida, to be submitted to *J. Phase Equilibria*.
17. J.H. Shim, C.S. Oh, B.J. Lee, and D.N. Lee, *Z. Metallkde.* 87, 205 (1996).
18. B.J. Lee, C.S. Oh, and J.H. Shim, *J. Electron. Mater.* 25, 983 (1994).
19. S. Itabashi, K. Kameda, and K. Yamaguchi, Abstracts of the 128th Japan Institute of Metals Annual Meetings in Spring, JIM, Narashino, Japan (2001).