A Thermodynamic Description for the Al-Cu-Zn System

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A thermodynamic description of the Al-Cu-Zn system is obtained by thermodynamic modeling of the Gibbs energies of all the phases in the system. The model parameters are optimized based on the established descriptions of the constituent binaries and ternary experimental phase equilibrium and thermodynamic data available in the literature. The agreement obtained between calculated phase equilibria and thermodynamic properties and experimental data suggest that the current description of this system is reasonable. The calculated phase equilibria close to the Al-Zn side are believed to be reliable for research in related fields such as solidification and phase transformation and for practical applications, while those near the Cu-rich region are topologically correct but need to be confirmed by future experimental investigations.

1. Introduction

Because the Al-Cu-Mg-Zn system is the basis for many high-strength Al alloys such as alloy 7075, development of a thermodynamic description for this quaternary is of great importance. Such a description is important not only for basic materials research in related areas, such as solidification and solid-state phase transformation, but also for alloy design and processing development/improvement. However, in order to obtain a thermodynamic description for the Al-Cu-Mg-Zn quaternary, it is necessary to develop descriptions for its con-

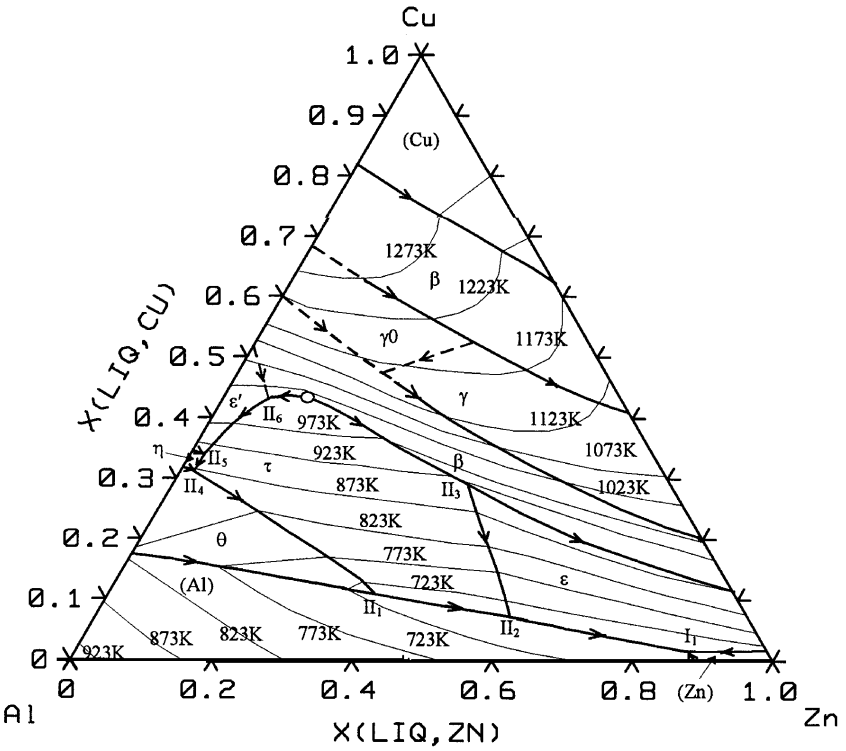

Fig. 1 Assessed liquidus projection based on experimental data.

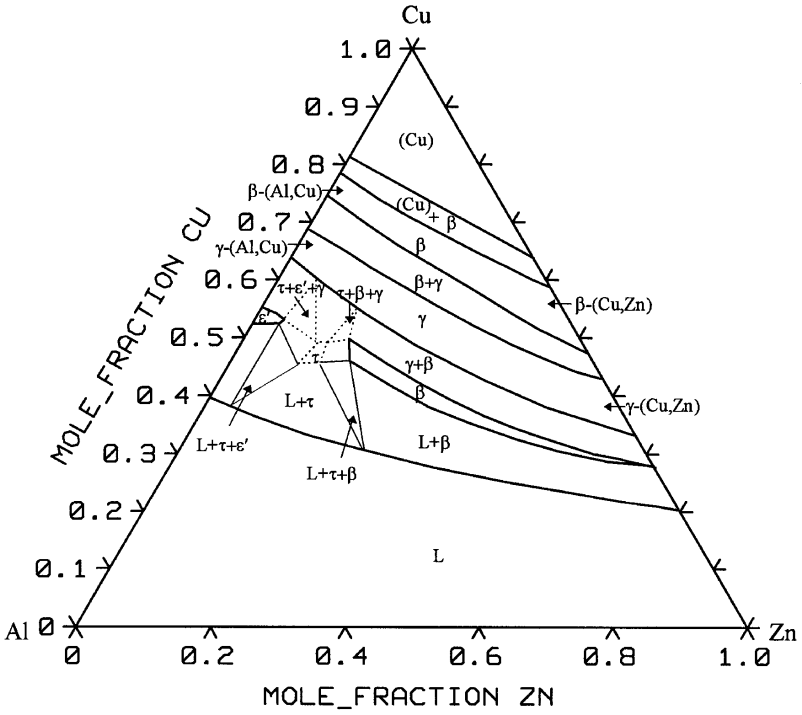

Fig. 2 Assessed experimental isotherm at 700 °C.

stituent ternaries first. In previous articles, the authors have reported their descriptions on two constituent ternaries: Al-Mg-Cu [97Che] and Al-Mg-Zn [97Lia]. This study reports a description for the Al-Cu-Zn ternary. The description is developed based on the ternary experimental phase equilibrium and thermodynamic data available in the literature and on the established descriptions of the constituent binaries: Al-Cu [93Sau], Al-Zn [93Che], and Cu-Zn [93Kow], using the CALPHAD method [70Kau]. The following presents first a review of the experimental data, then thermodynamic models, next optimization of model parameters, and finally calculated results and a discussion of them.

2. Review of Experimental Data

Because of their technical importance, the phase equilibria of the Al-Cu-Zn system have been investigated in numerous studies [11Lev, 12Car, 12Lev, 19Jar, 19Sch, 20Ros, 21Hau, 25Han, 26Nis, 27Nis, 28Bra, 28Ham, 32Bau1, 32Bau2, 32Bau3, 34Fus, 36Bur, 40Geb, 40Loe, 41Geb1, 41Geb2, 41Kos1, 41Kos2, 41Kos3, 42Geb, 42Kos, 42Wei, 43Mon, 48Ray, 48Str, 49Geb, 52Han, 57Wat, 60Arn1, 60Arn2, 61Phi, 67Coo, 69Cia, 69Gue, 70Fle, 72Kan1, 72Kan2, 73Ash, 73Wil, 74Ash, 75Mur, 76Mon, 77Rap, 78Sin, 79Cha, 80Ahl, 80Mur, 84Man, 85Seb, 86Ahl, 86Myk, 86Sug, 86Yan, 88Gra, 88Kis, 92Gho]. Reviews of the experimental results have been reported by a number of researchers [34Fus, 43Mon, 52Han, 61Phi, 69Gue, 73Wil, 76Mon, 79Cha, 92Gho] with that of [92Gho] being the most recent. Figures 1 to 3 show the assessed liquidus projection and two isothermal sections at 700 and 500 °C, which are almost the same as those accepted by most reviewers except for some modifications on the liquidus projection made in this study. These modifications are to be discussed later. As shown in these diagrams, there is only one ternary intermetallic compound $\tau Al_3Cu_5Zn_2$ in this system. The homogeneity range of the τ phase is highly temperature dependent and not well determined. In fact, it was found that the τ phase appears as two separate phases, τ and its structurally related phase τ', below about 250 °C [41Kos1]. However, neither the compositional stability of the τ' nor its temperature ranges have been determined. The τ' phase is thus ignored in this study. Among the binary intermetallic phases in this system, both the β-brass and γ-brass phases form continuous solid solutions as shown in Fig. 2 and 3. The two ordered bcc phases ε_1(Al,Cu) and δ(Cu,Zn) were reported to be completely soluble [41Kos3, 60Arn2]. Because they were modeled as β phases in the respective binaries [93Sau, 93Kow], in the present study they are taken to form a solid solution in ternary Al-Cu-Zn. The ε(Cu,Zn) phase has a large range of homogeneity in the ternary that strongly depends on temperature. The ternary solubility of the other binary intermetallic phases, such as $\theta(Al_2Cu)$, η(Al,Cu), and so forth, are relatively small and not well established. To facilitate reading, the symbols used to represent all the phases in this system are summarized in Table 1.

The assessed liquidus projection shown in Fig. 1 is mainly based on the work of [41Kos3] and [60Arn2], following the nomenclature of [56Rhi] and the format of [79Cha]. The dashed lines are the modifications made in this study. These

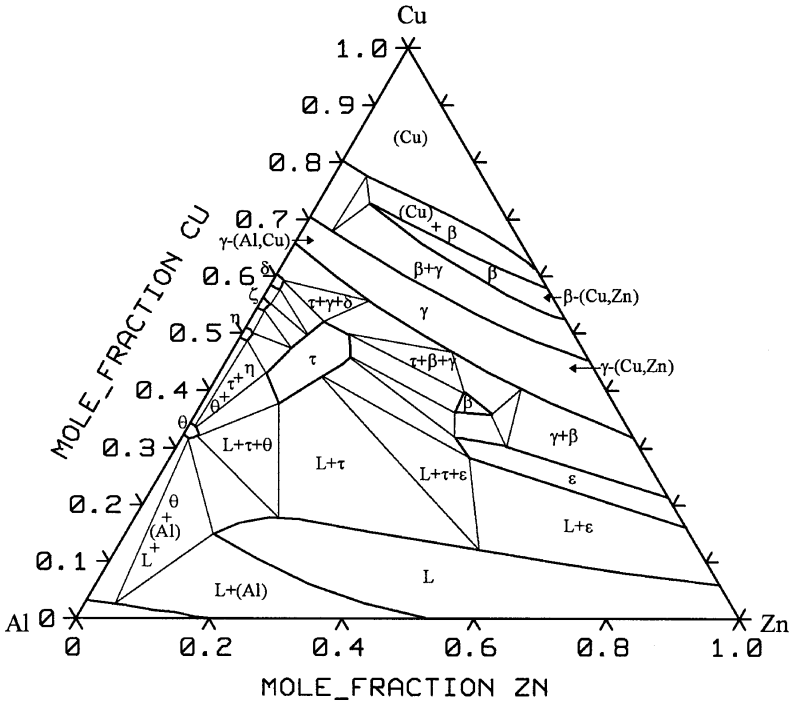

Fig. 3 Assessed experimental isotherm at 500 °C.

modifications are made so that the ternary phase equilibria are consistent with the currently accepted binary equilibria. These dashed lines are topologically correct, but should be considered tentative owing to the absence of experimental confirmation. The liquidus projection reported in earlier works [11Lev, 12Lev, 12Car, 19Jar, 20Ros, 21Hau, 25Han, 26Nis, 27Nis, 28Ham] agree only qualitatively with the investigations by [41Kos3] and [60Arn2]. The results of [41Kos2] and [60Arn2] have been widely accepted now. The 700 and 500 °C isotherms shown in Fig. 2 and 3 are also mainly based on the work of [41Kos2] and [60Arn2] with the Cu-rich region derived from the work by [32Bau1], [32Bau2], and [32Bau3] and the Al-rich and Zn-rich corners from some other studies [40Geb, 41Geb1, 42Geb, 49Geb].

In general, the phase equilibria of the Al-Cu-Zn system are not well established over the entire composition range. Only the invariant equilibria near the Al-Zn side have been determined [41Kos3] such as the invariant reactions II_1, II_2, and I_1 as shown in Fig. 1. The earlier results of [19Jar] differ appreciably from those of [41Kos3]. The phase equilibria near the Cu-rich region, especially those close to the Al-Cu binary, are not well established due to insufficient experimental data. In comparison, the isothermal curves shown in Fig. 1 and the corresponding solidus, determined by a series of investigations [41Kos1, 41Kos2, 41Kos3, 60Arn1, 60Arn2], are believed to be more reliable. The assessed data for the invariant reactions shown in Table 2 are mainly based on the studies of [41Kos3], [60Arn2], and [49Geb].

Very few thermodynamic data on this system are available in the literature. The activities of Al in Zn-rich liquid alloys were measured by [85Seb] at 700, 750, and 800 °C using the electromotive force (emf) method. The authors also evaluated their data to yield the activity coefficients and the partial Gibbs energies. Their results show positive derivation from ideal behavior for Al in Zn-rich alloys [85Seb]. Using an isopiestic method, [86Sug] measured the activities of Zn in Cu-rich liquid alloys at 1100 and 1150 °C. Their data show positive deviation for Zn in Cu-rich liquid alloys. These results are believed to be reliable.

Table 1 Phase Nomenclature in the Al-Cu-Zn System

Symbols	Phases	Crystal structures
L	Liquid	…
fcc	(Al),(Cu)	fcc
cph	(Zn)	cph
b	β(Al,Cu)	bcc
	β(Cu,Zn)	bcc
	ε_1(Al,Cu)	Ordered bcc
	δ(Cu,Zn)	Ordered bcc
q	Al_2Cu	bct
d	Al_2Cu_3	Unknown
eé	ε_2-AlCu	Unknown
z	$Al_{45}Cu_{55}$	Hex
h	(Al,Cu)Cu	Ortho
g	γ-Al_4Cu_9(r)	Ordered bcc
	γ-Cu_5Zn_8	Ordered bcc
g^0	γ-Al_4Cu_9	Unknown
e	ε(Cu,Zn)	cph

Table 2 Assessed Experimental Invariant Equilibria

Reaction	Class	Temperature (*T*), K		*X*(Al)	*X*(Cu)	*X*(Zn)	Reference
L + θ → (Al) + τ	II_1	695	L	0.445	0.113	0.442	[41Kos3]
			θ	0.668	0.320	0.012	
			(Al)	0.544	0.014	0.442	
			τ	0.521	0.390	0.089	
L + τ → (Al) + ε	II_2	680	L	0.307	0.088	0.605	[41Kos3]
			τ	0.510	0.393	0.097	
			(Al)	0.462	0.014	0.524	
			ε	0.110	0.216	0.674	
L → (Al) + (Zn) + ε	I_1	653	L	0.154	0.037	0.809	[40Geb]
			(Al)	0.370	0.014	0.616	
			(Zn)	0.031	0.029	0.940	
			ε	0.033	0.153	0.814	
L + β + τ → ε	III	898	L	0.297	0.269	0.434	[41Kos3]
			β	0.263	0.454	0.283	
			ε	0.279	0.441	0.280	
			τ	0.335	0.467	0.198	
L + η → τ + θ	II_4	853	L	0.659	0.316	0.025	[60Arn2]
			η	0.294	0.481	0.225	
			τ	0.300	0.460	0.240	
			θ	0.470	0.325	0.205	
L + ε′ → τ + η	II_5	893	L	0.626	0.352	0.002	[60Arn2]
			ε′	0.220	0.530	0.250	
			τ	0.240	0.510	0.250	
			η	0.255	0.514	0.231	
b → τ + ε + γ	I_2	753	β	0.191	0.480	0.377	[41Kos3]
			τ	0.262	0.402	0.258	
			ε	0.172	0.444	0.426	
			γ	0.152	0.113	0.404	

3 Thermodynamic Models

The thermodynamic description of the ternary is developed on the basis of the established descriptions of its constituent binaries. The descriptions of the binaries accepted in this study are Al-Cu by [93Sau], Al-Zn by [93Che], and Cu-Zn by [93Kow], which are believed to be the best descriptions available for these systems. Most of the phases with large ternary solubility in the Al-Cu-Zn system are described as disordered solutions, such as the liquid, fcc(Al)/(Cu), β(Al,Cu,Zn), γ(Al,Cu,Zn), ε(Cu,Zn), and (Zn); the exception is the ternary compound τ and the γ^0 phase. The remodeling work that was involved with describing the binary γ phases is discussed in detail in section 4. The τ phase is modeled in this study as a semistoichiometric phase $(Al,Cu)_1Al_4Cu_4Zn_1$, a pseudobinary solid solution of two hypothetical stoichiometric compounds, $Al_5Cu_4Zn_1$ and $Al_4Cu_5Zn_1$. Such a model is chosen mainly for simplicity; however, it does describe the τ phase with composition close to its actual homogeneity range. In fact, this is a good approximation considering that large uncertainty still exists with respect to the compositional stability of the τ phase. Its structure-related low-temperature τ′ phase is ignored in this study as stated in section 2. All the other binary intermetallic phases except the γ^0 are treated as phases without ternary solubility because their ternary solubilities are either negligible or unknown. The ternary solubility of the γ^0 phase, which in fact is still unknown, is modeled in this study in order to fit its stable temperature range as shown in the liquidus projection in Fig. 1. Considering the uncertainties of the data for the intermetallic phases in this system, these treatments are reasonable. The analytical expressions of the models used in this study are presented in the following section.

3.1 Disordered Solutions

The Gibbs energies of the disordered solutions in this ternary, such as the liquid, β and γ phases, are described by:

$$G_m^\Phi = X_{Al}\,{}^0G_{Al}^\Phi + X_{Cu}\,{}^0G_{Cu}^\Phi + X_{Zn}\,{}^0G_{Zn}^\Phi + RT(X_{Al}\ln X_{Al} + X_{Cu}\ln X_{Cu} + X_{Zn}\ln X_{Zn}) + X_{Al}X_{Cu}\Sigma\,{}^nL_{Al,Cu}^\Phi (X_{Al}-X_{Cu})^n + X_{Al}X_{Zn}\Sigma\,{}^nL_{Al,Zn}^\Phi (X_{Al}-X_{Zn})^n + X_{Cu}X_{Zn}\Sigma\,{}^nL_{Cu,Zn}^\Phi (X_{Cu}-X_{Zn})^n + X_{Al}X_{Cu}X_{Zn}({}^0L_{Al,Cu,Zn}^\Phi X_{Al} + {}^1L_{Al,Cu,Zn}^\Phi X_{Cu} + {}^2L_{Al,Cu,Zn}^\Phi X_{Zn}) \quad \text{(Eq 1)}$$

Table 3 The Model Parameters for All Phases in the Al-Cu-Zn

Liquid: disordered solution

$L^{0,L}_{Al,Cu} = -66\,622 + 8.1T$
$L^{1,L}_{Al,Cu} = +46\,800 - 90.8T + 10T \ln T$
$L^{2,L}_{Al,Cu} = -2812$
$L^{0,L}_{Al,Zn} = +10\,288 - 3.035T$
$L^{1,L}_{Al,Zn} = -810 + 0.471T$
$L^{0,L}_{Cu,Zn} = -40\,695.54 + 12.6527T$
$L^{1,L}_{Cu,Zn} = +4402.72 - 6.55425T$
$L^{2,L}_{Cu,Zn} = +7818.1 - 3.25416T$
$L^{0,L}_{Al,Cu,Zn} = +5475$(a)
$L^{1,L}_{Al,Cu,Zn} = +11\,615$(a)
$L^{2,L}_{Al,Cu,Zn} = +43\,600$(a)

fcc-(Al),(Cu): disordered solution

$L^{0,fcc}_{Al,Cu} = -53\,520 + 2T$
$L^{1,fcc}_{Al,Cu} = +38\,590 - 2T$
$L^{2,fcc}_{Al,Cu} = -1170$
$L^{0,fcc}_{Al,Zn} = +6656 + 1.615T$
$L^{1,fcc}_{Al,Zn} = +6793 - 4.982T$
$L^{2,fcc}_{Al,Zn} = -5352 + 7.261T$
$L^{0,fcc}_{Cu,Zn} = -42\,803.75 + 10.0226T$
$L^{1,fcc}_{Cu,Zn} = +2936.39 - 3.053T$
$L^{2,fcc}_{Cu,Zn} = +9034.2 - 5.393T$
$L^{0,fcc}_{Al,Cu,Zn} = 70\,000$(a)
$L^{1,fcc}_{Al,Cu,Zn} = 10\,000$(a)
$L^{2,fcc}_{Al,Cu,Zn} = 70\,000$(a)

cph-(Zn): disordered solution

$L^{0,cph}_{Al,Zn} = +14\,620$
$L^{0,cph}_{Cu,Zn} = -14\,432.17 - 10.7814T$

β(Al,Cu,Zn): disordered solution

$L^{0,\beta}_{Al:Cu} = -73\,554 + 4.0T$
$L^{1,\beta}_{Al:Cu} = +51\,500 - 11.84T$
$L^{0,\beta}_{Al,Zn} = +20\,000$(a)
$L^{0,\beta}_{Cu,Zn} = -51\,595.87 + 13.06392T$
$L^{1,\beta}_{Cu,Zn} = +7562.13 - 6.45432T$
$L^{2,\beta}_{Cu,Zn} = +30\,743.74 - 29.91503T$
$L^{0,\beta}_{Al,Cu,Zn} = -10\,000$(a)
$L^{1,\beta}_{Al,Cu,Zn} = -30\,000 + 20T$(a)
$L^{2,\beta}_{Al,Cu,Zn} = -10\,000$(a)

γ(Al,Cu,Zn): disordered solution

$G^{0,\gamma}_{Al} = G^{0,fcc}_{Al} + 10$
$G^{0,\gamma}_{Cu} = G^{0,fcc}_{Cu} + 10$
$G^{0,\gamma}_{Zn} = G^{0,cph}_{Zn} + 10$
$L^{0,\gamma}_{Al:Cu} = -48\,025.3 + 14.55872T$
$L^{1,\gamma}_{Al:Cu} = +187\,178.0 + 3.02112T$
$L^{2,\gamma}_{Al:Cu} = +254\,993.9 - 8.16271T$
$L^{0,\gamma}_{Al,Zn} = +75\,000$(a)
$L^{0,\gamma}_{Cu,Zn} = -39\,470.1 + 9.43583T$
$L^{1,\gamma}_{Cu,Zn} = +36\,675.1 - 5.19593T$
$L^{2,\gamma}_{Cu,Zn} = +90\,162.6 - 32.61986T$
$L^{0,\gamma}_{Al,Cu,Zn} = +250\,000$(a)
$L^{1,\gamma}_{Al,Cu,Zn} = -443\,000 - 25T$(a)
$L^{2,\gamma}_{Al,Cu,Zn} = +20\,000$(a)

γ^0(Al,Cu,Zn): $(Al,Zn)_{0.3077}(Al,Cu,Zn)_{0.0769}(Cu)_{0.6154}$

$G^{0,\gamma 0}_{Al:Al:Cu} - 0.3846\,G^{0,fcc}_{Al} - 0.6154\,G^{0,fcc}_{Cu} = -16\,866 - 3.5T$
$G^{0,\gamma 0}_{Al:Cu:Cu} - 0.3077\,G^{0,fcc}_{Al} - 0.6923\,G^{0,fcc}_{Cu} = -15\,420 - 4.5T$
$G^{0,\gamma 0}_{Zn:Cu:Cu} - 0.3077\,G^{0,cph}_{Zn} - 0.6923\,G^{0,fcc}_{Cu} = -6000 - 5T$(a)
$G^{0,\gamma 0}_{Zn:Zn:Cu} - 0.3846\,G^{0,cph}_{Zn} - 0.6154\,G^{0,fcc}_{Cu} = -7000 - 5T$(a)
$G^{0,\gamma 0}_{Al:Zn:Cu} - 0.3077\,G^{0,fcc}_{Al} - 0.6154\,G^{0,fcc}_{Cu} - 0.0769\,G^{0,cph}_{Zn} = -9500 - 10T$(a)
$G^{0,\gamma 0}_{Zn:Al:Cu} - 0.0769\,G^{0,fcc}_{Al} - 0.6154\,G^{0,fcc}_{Cu} - 0.3077\,G^{0,cph}_{Zn} = -1538.5 - 10T$(a)

ε(Al,Cu,Zn): disordered solution

$G^{0,\varepsilon}_{Al} = G^{0,cph}_{Al}$
$G^{0,\varepsilon}_{Cu} = G^{0,fcc}_{Cu} + 10$
$G^{0,\varepsilon}_{Zn} = G^{0,fcc}_{Zn}$
$L^{0,\varepsilon}_{Al:Cu} = -50\,000$(a)
$L^{0,\varepsilon}_{Al:Zn} = +10\,000$(a)
$L^{0,\varepsilon}_{Cu,Zn} = -35\,433.3 + 5.24516T$
$L^{1,\varepsilon}_{Cu,Zn} = +25\,276.81 - 9.96989T$
$L^{0,\varepsilon}_{Al,Cu,Zn} = +62\,500$(a)
$L^{1,\varepsilon}_{Al,Cu,Zn} = -218\,000$(a)
$L^{2,\varepsilon}_{Al,Cu,Zn} = +38\,500$(a)

τ-$Al_3Cu_5Zn_2$: $(Al,Cu)_{0.1}Al_{0.4}Cu_{0.4}Zn_{0.1}$

$G^{0,\tau}_{Al:Al:Cu:Zn} - 0.5G^{0,L}_{Al} - 0.4G^{0,L}_{Cu} - 0.1G^{0,L}_{Zn} = -36\,831.74 + 23T$(a)
$G^{0,\tau}_{Cu:Al:Cu:Zn} - 0.4G^{0,L}_{Al} - 0.5G^{0,L}_{Cu} - 0.1G^{0,L}_{Zn} = -32\,571.32 + 11.8T$(a)
$G^{0,\tau}_{Al,Cu:Al:Cu:Zn} = 21\,228.02 - 30T$(a)

θ_{AlCu}: $(Al)_{0.667}(Al,Cu)_{0.333}$

$G^{0,\theta}_{Al:Al} = G^{0,bcc}_{Al}$
$G^{0,\theta}_{Al:Cu} - 0.667G^{0,fcc}_{Al} - 0.333G^{0,fcc}_{Cu} = -15\,802 + 2.25T$
$L^{0,\theta}_{Al:Al,Cu} = 737$

η_{AlCu}: $(Al,Cu)_{0.5}(Cu)_{0.5}$

$G^{0,\varepsilon}_{Al:Cu} - 0.5G^{0,fcc}_{Al} - 0.5G^{0,fcc}_{Cu} = -20\,280 + 1.57T$
$G^{0,\delta}_{Cu:Cu} = G^{0,bcc}_{Cu}$
$L^{0,\varepsilon}_{Al,Cu:Cu} = -12\,870 - 10T$

ζ_{AlCu}: $(Al)_{0.45}(Cu)_{0.55}$

$G^{0,\zeta}_{Al:Cu} - 0.45G^{0,fcc}_{Al} - 0.55G^{0,fcc}_{Cu} = -21\,000 + 0.9T$

δAlCu: $(Al)0.4(Cu)_{0.6}$

$G^{0,\delta}_{Al:Cu} - 0.4G^{0,fcc}_{Al} - 0.6G^{0,fcc}_{Cu} = -21\,340 + 0.6T$

ε_{AlCu}: $(Al,Cu)_{0.5}(Cu)_{0.5}$

$G^{0,\varepsilon}_{Al:Cu} - 0.5G^{0,fcc}_{Al} - 0.5G^{0,fcc}_{Cu} = -18\,488 + 0.6T$
$G^{0,\delta}_{Cu:Cu} = G^{0,bcc}_{Cu}$
$L^{0,\varepsilon}_{Al,Cu:Cu} = 3800 - 12T$
$L^{1,\varepsilon}_{Al,Cu:Cu} = -36\,000$

(continued next column)

(a) The parameters are obtained in this study.

Table 4 Calculated Temperatures and Compositions of the Liquid at the Invariant Equilibria

Reaction	Class	Temperature (*T*), K	*X*(Al)	Liquid *X*(Cu)	*X*(Zn)
$L + \theta \rightarrow (Al) + \tau$	II_1	698	0.409	0.086	0.505
		(695)	(0.445)	(0.113)	(0.442)
$L + \tau \rightarrow (Al) + \varepsilon$	II_2	694	0.331	0.068	0.601
		(680)	(0.307)	(0.088)	(0.605)
$L \rightarrow (Al) + (Zn) + \varepsilon$	I_1	654	0.112	0.016	0.872
		(653)	(0.154)	(0.037)	(0.809)
$L + \beta \rightarrow \varepsilon + \tau$	II_3	917	0.331	0.274	0.395
		(898)	(0.297)	(0.269)	(0.434)
$L + \eta \rightarrow \tau + \theta$	II_4	853	0.668	0.312	0.020
		(853)	(0.659)	(0.316)	(0.025)
$L + \varepsilon' \rightarrow \tau + \eta$	II_5	893	0.628	0.343	0.020
		(893)	(0.626)	(0.352)	(0.002)
$L + \beta \rightarrow \tau + \varepsilon'$	II_6	1010	0.496	0.435	0.069
$L + \gamma^0 \rightarrow \beta + \gamma$	II_7	1226	0.150	0.564	0.286
$L + \gamma + \gamma^0 \rightarrow \beta$	III_1	1197	0.328	0.546	0.126

Compared with assessed experimental data in parentheses when available.

where X_{Al}, X_{Cu}, and X_{Zn} are the mole fractions of the pure components Al, Cu, and Zn, respectively; $G^{0,\Phi}_{Al}$, $G^{0,\Phi}_{Cu}$, and $G^{0,\Phi}_{Zn}$ are the molar Gibbs energies of the components with the structure of Φ; $L^{n,\Phi}_{Al,Cu}$, $L^{n,\Phi}_{Al,Zn}$, and $L^{n,\Phi}_{Cu,Zn}$ (n = 0, 1, 2, …) are the interaction parameters in the binaries Al-Cu, Al-Zn, and Cu-Zn, respectively. The summation of the first three terms on the right-hand side of the above equation represents the reference part of the Gibbs energy. The next term is the ideal mixing term, and the next three summations represent the contributions to the excess Gibbs energy from the three boundary binaries using the Muggianu extrapolation method [75Mug]. The excess Gibbs energies of the constituent binaries are described by Redlich-Kister polynomial [48Red]. The last term represents ternary interactions. Values of the ternary interaction parameters $L^{n,\Phi}_{Al,Cu,Zn}$ (n = 0, 1, 2) are obtained by optimization using available experimental data.

3.2 A Semistoichiometric Approximation for the τ Phase

Using the model $(Al,Cu)_1Al_4Cu_4Zn_1$, the Gibbs energy of the τ phase, formed by mixing two hypothetical stoichiometric compounds $Al_5Cu_4Zn_1$ and $Al_4Cu_5Zn_1$, is represented by:

$$G^{\tau}_m = y'_{Al}\, G^{0,\tau}_{Al:Al:Cu:Zn} + y'_{Cu}\, G^{0,\tau}_{Cu:Al:Cu:Zn} + \frac{1}{10}RT(y'_{Al}\ln y'_{Al} + y'_{Cu}\ln y'_{Cu}) + y'_{Al}y'_{Cu}[\Sigma\, L^{n,\tau}_{Al,Cu:Al:Cu:Zn}(y'_{Al} - y'_{Cu})^n] \quad \text{(Eq 2)}$$

where y_{Al} and y_{Cu} are the site fractions of components Al and Cu in sublattice 1; $G^{0,\tau}_{Al:Al:Cu:Zn}$ and $G^{0,\tau}_{Cu:Al:Cu:Zn}$ are the molar Gibbs energies of the compounds $Al_5Cu_4Zn_1$ and $Al_4Cu_5Zn_1$, respectively; $L^{n,\tau}_{Al,Cu:Al:Cu:Zn}$ (n = 0, 1, 2) are the parameters to be obtained by optimization for describing the interactions between atoms Al and Cu in sublattice 1.

3.3 A Three-Sublattice Model for the γ^0 Phase

The γ^0 phase was modeled as $(Al,Cu)_1(Al)_4(Cu)_8$ in the Al-Cu binary by [93Sau]. By adding Zn in the first two sublattices for describing the ternary solubility of the γ^0 phase, it is thus treated as $(Al,Cu,Zn)_1(Al,Zn)_4(Cu)_8$ in the ternary. Its Gibbs energy is represented by:

$$G^{\gamma 0}_m = y'_{Al}y''_{Al}\, G^{0,\gamma 0}_{Al:Al:Cu} + y'_{Cu}y''_{Al}\, G^{0,\gamma 0}_{Cu:Al:Cu} + y'_{Cu}y''_{Zn}\, G^{0,\gamma 0}_{Cu:Zn:Cu} + y'_{Zn}y''_{Zn}\, G^{0,\gamma 0}_{Zn:Zn:Cu} + y'_{Al}y''_{Zn}\, G^{0,\gamma 0}_{Al:Zn:Cu} + y'_{Zn}y''_{Al}\, G^{0,\gamma 0}_{Zn:Al:Cu} + RT\left[\frac{1}{13}(y'_{Al}\ln y'_{Al} + y'_{Cu}\ln y'_{Cu} + y'_{Zn}\ln y'_{Zn}) + \frac{4}{13}(y''_{Al}\ln y''_{Al} + y''_{Zn}\ln y''_{Zn})\right] \quad \text{(Eq 3)}$$

where y'_i and y''_i are the site fractions of pure component i in sublattices 1 and 2, respectively; $G^{0,\gamma 0}_{Al:Al:Cu}$, $G^{0,\gamma 0}_{Cu:Al:Cu}$, $G^{0,\gamma 0}_{Cu:Zn:Cu}$, $G^{0,\gamma 0}_{Zn:Zn:Cu}$, $G^{0,\gamma 0}_{Al:Zn:Cu}$, and $G^{0,\gamma 0}_{Zn:Al:Cu}$ are the molar Gibbs energies of the compounds Al_5Cu_8, Al_4Cu_9, Cu_9Zn_4, Cu_8Zn_5, $Al_1Cu_8Zn_4$, and Al_4Cu_8Zn, respectively. The values of the $G^{0,\gamma 0}_{Al:Al:Cu}$ and $G^{0,\gamma 0}_{Cu:Al:Cu}$ were those by [93Sau] for describing the γ^0 phase in the Al-Cu binary. The values of the $G^{0,\gamma 0}_{Cu:Zn:Cu}$, $G^{0,\gamma 0}_{Zn:Zn:Cu}$, $G^{0,\gamma 0}_{Al:Zn:Cu}$, and $G^{0,\gamma 0}_{Zn:Al:Cu}$ are to be obtained by optimization for reproducing the stable temperature range of the γ^0 phase in the ternary.

4. Optimization of Model Parameters

As stated in section 3, thermodynamic description of the ternary is developed from descriptions of the constituent bina-

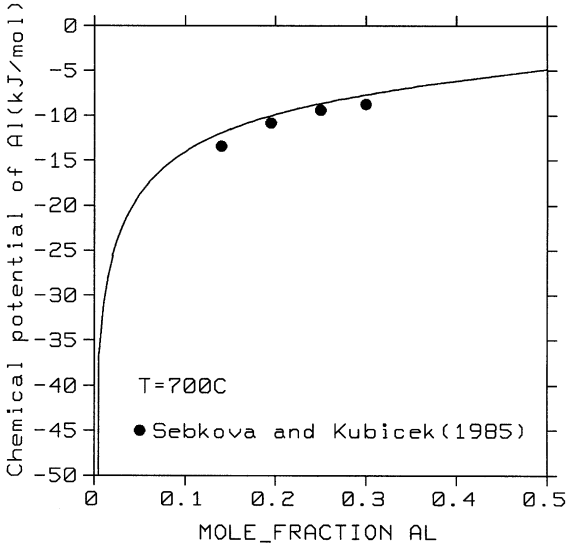

Fig. 4(a) Comparison of calculated chemical potential of Al in liquid state at 700 °C in the section at 7.5 at.% Cu with experimental data [85Seb], referring to Al(L).

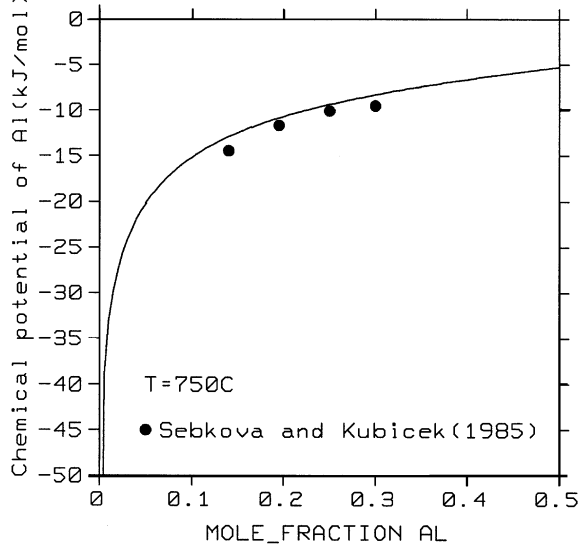

Fig. 4(b) Comparison of calculated chemical potential of Al in liquid state at 750 °C in the section at 7.5 at.% Cu with experimental data [85Seb], referring to Al(L).

ries: Al-Cu by [93Sau], Al-Zn by [93Che], and Cu-Zn by [93Kow], which are believed to be the best descriptions available for these systems. However, the two binary γ phases, γ-Al_4Cu_9 and γ-Cu_5Zn_8, which are isomorphous and form continuous solid solution in the ternary, were represented by totally different models. The γ-Al_4Cu_9 phase was described by a three-sublattice model as $Al_4Cu_8(Al,Cu)_1$ [93Sau], while the γ-Cu_5Zn_8 phase was described by a four-sublattice model as $(Cu,Zn)_8(Cu,Zn)_8Cu_{12}Zn_{24}$ [93Kow]. These two models are incompatible and cannot be used to describe the thermodynamic properties of the γ phase in ternary Al-Cu-Zn. The ternary γ phase has rather complex structure, and in the present study the authors chose to describe it as a disordered bcc phase because the Gibbs energies of the two binary γ-Al_4Cu_9 and γ-Cu_5Zn_8 phases change smoothly with composition. These two binary γ phases were remodeled, while the model parameters of all other phases in the two binaries were kept the same as in the original description. Hypothetical lattice stabilities were used for the γ phases instead of those for bcc structures. The calculated phase diagrams of the Al-Cu and Cu-Zn as well as the Gibbs energies of the two binary γ phases in their stable regions with the new parameters are the same as those with the parameters given by [93Sau] and [93Kow]. It is worth noting that the authors did also try to use a consistent compound energy model to describe the thermodynamic properties of the γ phase, but did not feel the requisite complexity is necessary in the present case.

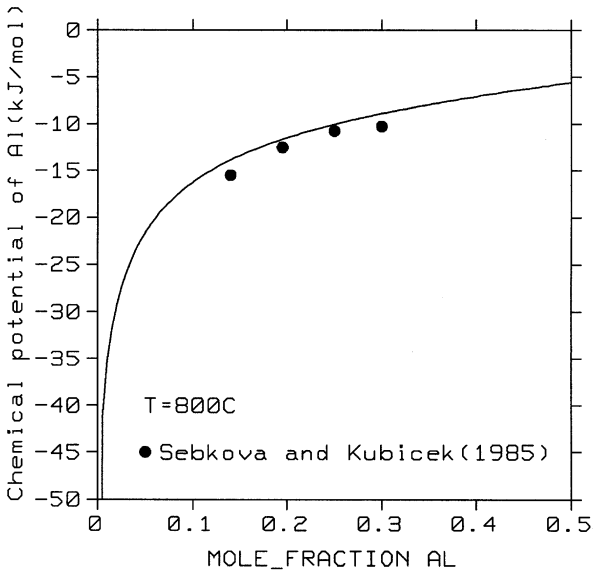

Fig. 4(c) Comparison of calculated chemical potential of Al in liquid state at 800 °C in the section at 7.5 at.% Cu with experimental data [85Seb], referring to Al(L).

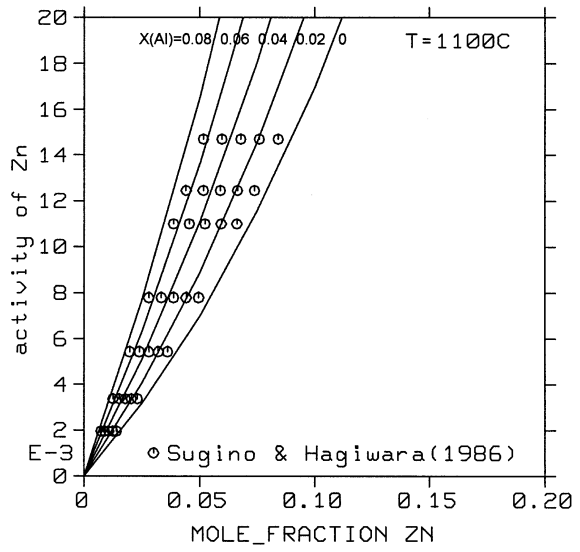

Fig. 5(a) Comparison of calculated activity of Zn in liquid state at 1100 °C in Cu-rich alloys with experimental data [86Sug], referring to Zn(L).

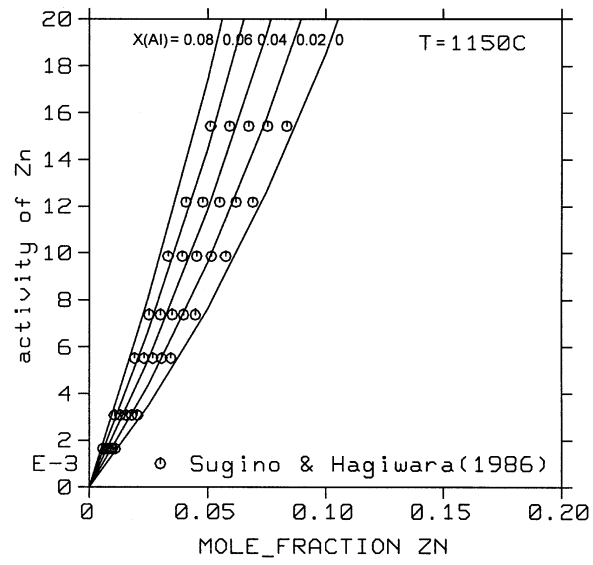

Fig. 5(b) Comparison of calculated activity of Zn in liquid state at 1150 °C in Cu-rich alloys with experimental data [86Sug], referring to Zn(L).

The model parameters were optimized on the basis of phase equilibrium and thermodynamic data available in the literature using Thermo-Calc [85Sun]. The lattice stability data of the pure components are from the SGTE database [91Din]. As stated in section 2, the measured thermodynamic properties and the liquidus and solidus close to the Al-Zn side are believed to be reliable, while the invariant reactions and the phase equilibria in the Cu-rich region are less certain. Therefore, the measured thermodynamic properties and the experimental liquidus and solidus close to the Al-Zn side have been given more weight in the optimization than the invariant reaction data. The optimized model parameters are presented in Table 3. Table 4 lists all the calculated invariant equilibria. The calculated diagrams are presented in Fig. 4 to 8. Considering the uncertainty in the experimental data, the calculated results are in good agreement with experimental data.

5. Results and Discussion

Figure 4(a) to (c) show comparisons of the calculated chemical potentials of Al in the liquid state for the section at 7.5 at.% Cu with the experimental values of [85Seb] at 700, 750, and 800 °C, respectively. Figures 5(a) and (b) show comparisons of the calculated activities of Zn in the liquid state with the experimental values of [86Sug] at 1100 and 1150 °C with five constant Al contents ranging from 0 to 8 at.%. The comparisons show good agreement between the calculated values and experimental data. Figures 6(a) to (c) show three calculated isopleths, one with a constant Cu content of 20 wt.%, two with constant Zn contents of 20 and 40 wt.%, respectively. In these isopleths, the calculated phase boundaries are in good agreement with the available experimental data of [41Kos3]. The agreement between the calculated results and experimental data as shown in Fig. 4 to 6 suggests that the model parameters obtained in the present study are reasonable.

A comparison of the calculated isotherms at 700 and 500 °C given in Fig. 7(a) and (c) with the assessed diagrams given in Fig. 2 and 3 shows agreement for the experimentally established phase equilibria. Figure 7(b) shows the calculated phase equilibria at 600 °C, which are also in accord with experimental results. It is understood that the calculated phase boundaries of the τ phase would be different in view of the assumption made in describing this phase to be a semistoichiometric phase. There are also differences between the calculated and assessed phase equilibria due to the fact that modeling approximations neglect such things as the solubilities of Zn in the θ, ε', η, and ζ phases.

The calculated liquidus projection shown in Fig. 8 is next compared with the assessed one in Fig. 1. In addition to these two diagrams, the calculated temperatures and liquid compositions for all the invariant reactions involving the liquid as well as the assessed values are summarized in Table 4. Although the general features of the calculated liquidus projection are in accord with those of the assessed one, there are discrepancies between the calculated temperatures and compositions of the liquid and the experimental data for the invariant reactions II_1, II_2, II_3, II_4, II_5, and I_1. For example, the calculated temperature for II_1 is only 3 °C higher than the assessed value while the calculated composition of the liquid differ appreciably from the assessed one. Because all the invariant reactions in the Al-Zn side ex-

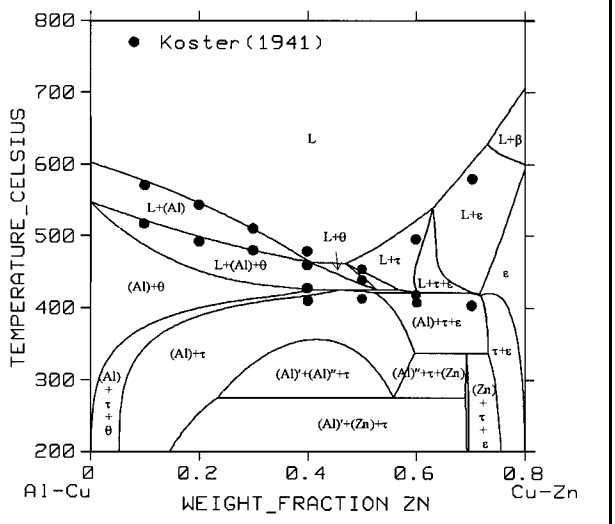

Fig. 6(a) Comparison of calculated isopleth at 20 wt.% Cu with experimental data [41Kos3].

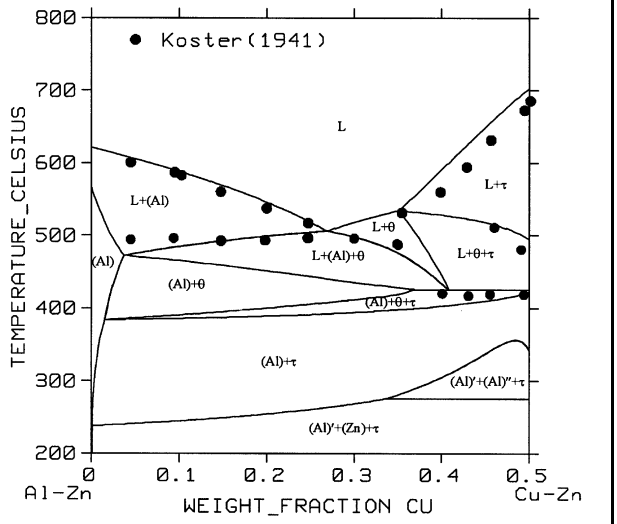

Fig. 6(b) Comparison of calculated isopleth at 20 wt.% Zn with experimental data [41Kos3].

cept I_1 involve the τ phase, which still has large uncertainty with respect to its compositional stability, the differences between the calculated values and the assessed ones could be due to the approximation made with respect to the compositional stability of the τ phase. For the invariant reactions in the Cu-rich region, such as II_7 and III_1, no supporting experimental data are available. It is obvious that additional experimental measurements are required before the phase equilibria of this system are established over wide ranges of composition and temperature. However, it is of interest to note that there is good agreement between the calculated results and experimental data for the chemical potentials of Al given in Fig. 4(a) to (c), the activities of Zn given in Fig. 5(a) and (b), and the isopleths given in Fig. 6(a) to (c). On the basis of the composite evidence, the authors conclude that the calculated liquidus projection given in Fig. 8 as well as the calculated invariant reactions given in Table 4 could be more reliable than the assessed data given in Fig. 1 and Table 2. Until more experimental data become available, they should be used with caution.

6. Conclusion

A thermodynamic description of the Al-Cu-Zn system is developed based on the descriptions of its three constituent binaries and ternary experimental phase equilibrium and thermodynamic data available in the literature. The agreement between the model-calculated results and experimental data for several isopleths and chemical potentials of Al and Zn in the liquid state suggests that the current description is reasonable.

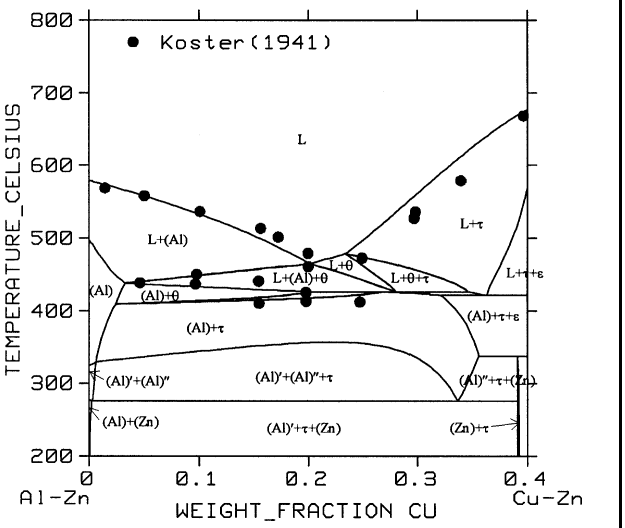

Fig. 6(c) Comparison of calculated isopleth at 40 wt.% Zn with experimental data [41Kos3].

However, discrepancies do exist between the calculated phase equilibria and the assessed values that were obtained based on limited experimental data. It is clear that additional

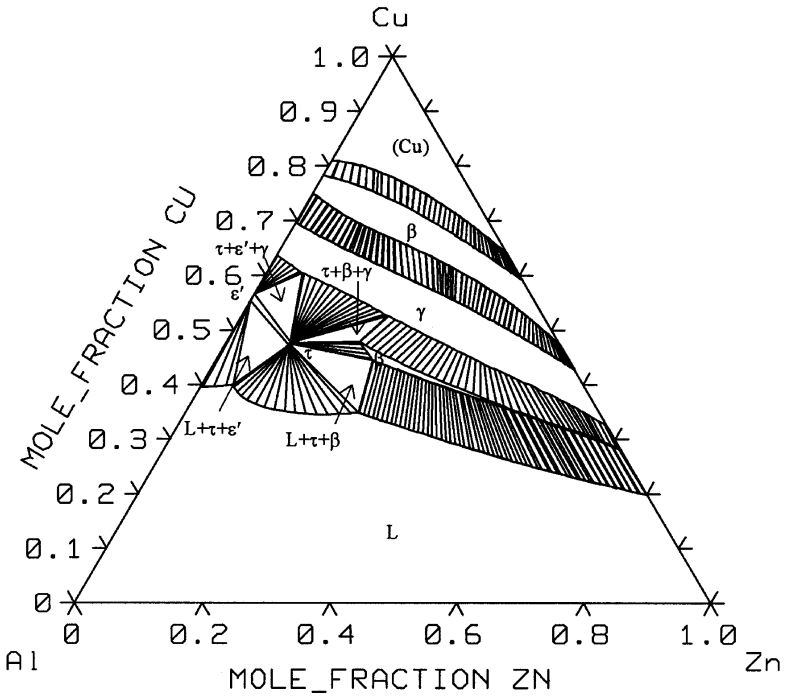

Fig. 7(a) Calculated isothermal section at 700 °C.

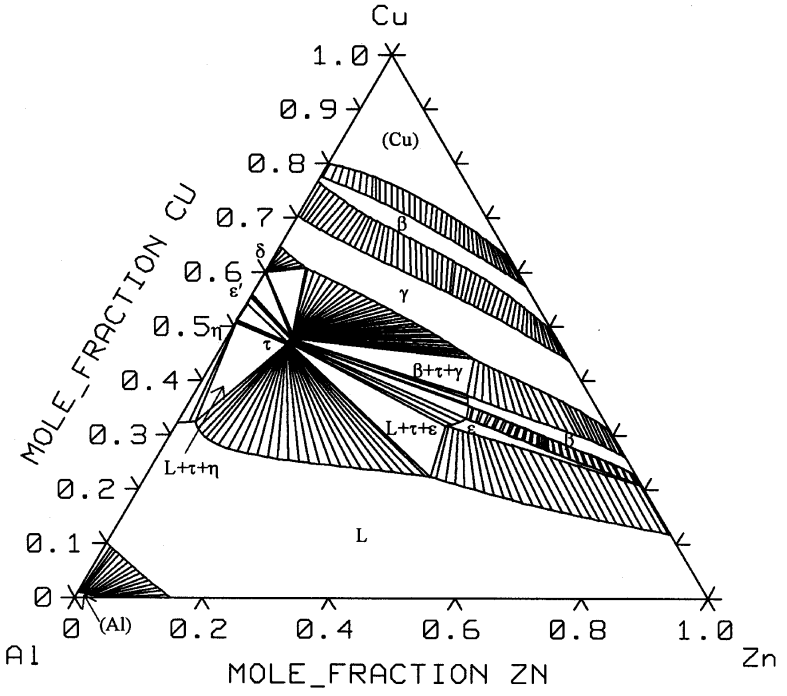

Fig. 7(b) Calculated isothermal section at 600 °C.

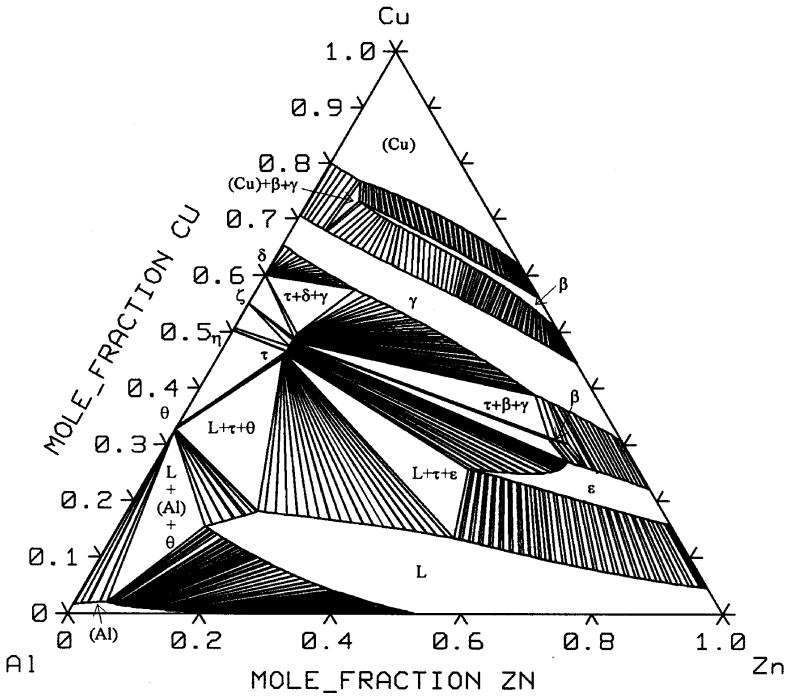

Fig. 7(c) Calculated isothermal section at 500 °C.

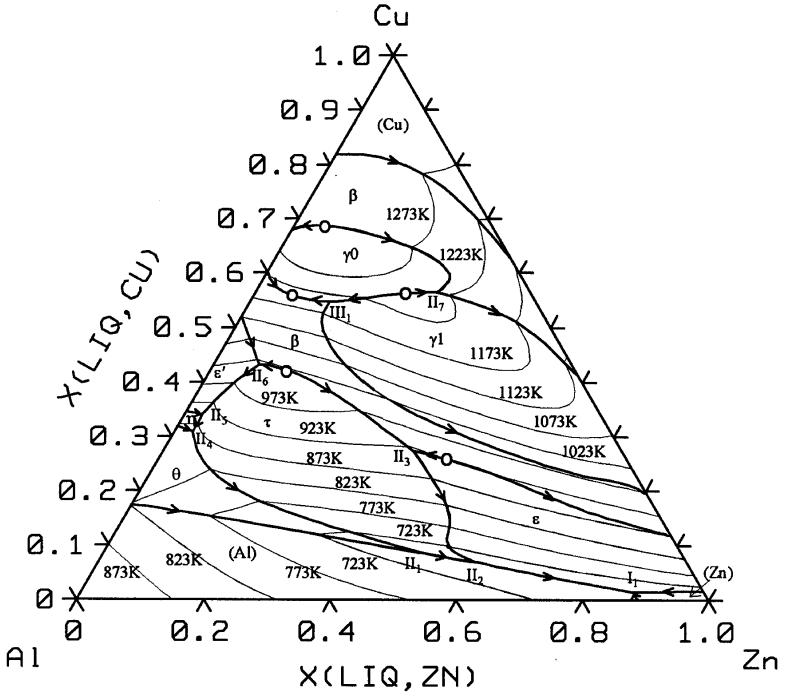

Fig. 8 Calculated liquidus projection.

experimental investigations are needed before a definitive knowledge on the phase equilibria of this system over wide ranges of composition and temperature is obtained. In the absence of additional experimental data, it is believed that the calculated phase equilibria in compositions away from the Al-Zn side should be used for practical applications with caution instead of the assessed data. This conclusion is reached on the basis of agreement obtained between the calculated results and experimental data for several isopleths and thermodynamic properties of the liquid phase.

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