

# Thermodynamic calculation of phase equilibria in the Cu–Ni–Zn system

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## Abstract

A ternary system of Cu–Ni–Zn has been thermodynamically analyzed based on extensive experimental information and reasonable thermodynamic modeling work by using the CALPHAD approach. A self-consistent set of thermodynamic parameters has been obtained, and the experimentally determined phase equilibria in the whole composition range except for the Zn-rich portion have been critically reproduced. The thermodynamic description established in this work can be used in predicting the phase relationships and thermodynamic properties in the Cu–Ni–Zn system.

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## 1. Introduction

Both Ni and Zn are the elements most commonly alloyed with Cu, and the ternary system of Cu–Ni–Zn is one of the basic systems for metals such as copper–nickel alloys, nickel silver and some types of brass and bronze. Although many investigations of the phase equilibria in the Cu–Ni–Zn system have been reported, there is still a lack of an overall thermodynamic description of the complete ternary system. The present work then, attempts to provide such a thermodynamic analysis for this system based on a close study of available ternary experimental information and reasonable thermodynamic modeling work.

In this work, the binary thermodynamic assessments done by Mey [1] for the Cu–Ni system, by Kowalski and Spencer [2] for the Cu–Zn system, and by Vassilev et al. [3] for the Ni–Zn system have been basically accepted. However, for the calculation of ternary solid solutions, some binary phases in both Cu–Zn and Ni–Zn systems have to be remodeled. The ternary phase relationships, except for those in the very Zn-rich region, have been well experimentally studied by numerous investigations [4–10], and

will be critically described in this work. On the other hand, the ordering phenomenon within the  $\alpha$ -CuNiZn is rather complicated due to the strongly attractive interaction of the nearest Ni–Zn and Cu–Zn pairs and the weakly repulsive one of the Cu–Ni. Though some measurements [11] have indicated that a ternary ordering around Cu<sub>2</sub>NiZn exists in this system, the relative transformations are still not very clear, and hence the ordering in the fcc region which occurs at low temperatures will not be discussed in this work.

## 2. Available experimental information

Table 1 lists the crystal phases included in the Cu–Ni–Zn system with information on their structures. The system was evaluated by Chang et al. in 1979 [12], in which a liquidus projection and an isotherm at 775 °C were provided mainly based on the work of Yamaguchi and Nakamura [5], and Schramm [6]. Fig. 1 shows the evaluated isotherm at 775 °C, where the  $\gamma$  phases in the binary Cu–Zn and Ni–Zn systems, both with a Cu<sub>5</sub>Zn<sub>8</sub> structure, form a ternary continuous solid solution. In this work, the order–disorder transformation between bcc\_A2 ( $\beta$ ) and bcc\_B2 ( $\beta'$ ) will not be taken into account, thus another ternary continuous solid solution

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Table 1  
Structural information on the crystal phases in the Cu–Ni–Zn system

Phase	Strukturbericht designation	Prototype
$\alpha$	A1	Cu
$\beta$	A2	W
$\beta'$	B2	CsCl
$\beta_1$	L1 <sub>0</sub>	AuCu
$\gamma$	D8 <sub>2</sub>	Cu <sub>5</sub> Zn <sub>8</sub>
$\delta$ (Cu–Zn)	...	...
$\varepsilon$ (Cu–Zn)	A3	Mg
NiZn <sub>8</sub>	...	...
(Zn)	A3	Mg

with bcc structure, consisting of  $\beta$  and  $\beta'$  fields, should be present. The region below is referred to as  $\beta$ .

Several other determinations are available on the phase equilibria in the Cu- and Ni-rich portions. Bauer and Hansen [4] provided a series of analysis results by microscopic observation for the phase equilibria between  $\alpha$ ,  $\beta$  and  $\gamma$  near the Cu–Zn side at 400, 600 and 800 °C. Haworth and Hume-Rothery [7] determined the  $\alpha/\beta$  equilibrium at 672 °C by microscopic examination combined with chemical analysis. Mayall and co-workers [9,10] did systematic research at 600 °C by using X-ray technique for structural analysis and atomic absorption spectrometer for composition determination, and as a result, the phase relationships in this isotherm covering the phase regions of  $\alpha$ ,  $\beta$  and  $\beta_1$  have been well constructed. Besides these, a series of investigations on multiphase diffusion at 775 °C have been performed in the Cu–Ni–Zn system [8,13,14]. Though most of these investigations were not for phase diagram determination, their results have verified the isotherm of 775 °C shown in Fig. 1. It should be noted that, there is a general agreement among the various investigations mentioned above, and from a composite of their findings, the phase relationships from 600 to 800 °C in the Cu–Ni–Zn system can be well understood.

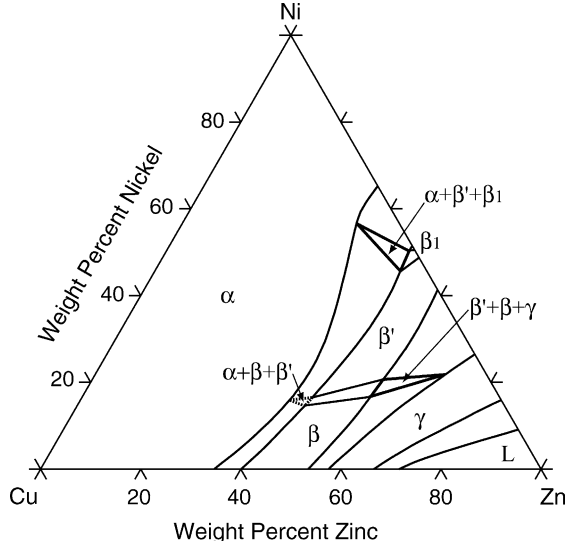


Fig. 1. Evaluated isotherm of the Cu–Ni–Zn system at 775 °C [12].

Very few thermodynamic data have been reported for the Cu–Ni–Zn system. The activity of Zn at 727 °C in the  $\alpha$  field of the Cu-rich region has been determined by measuring the vapor pressure of Zn [15,16]. Based on these data, Sisson and Dayananda [14] evaluated and also calculated the isoactivity curves of Zn at 775 °C. Another measurement was done by Sugino and Hagiwara [17], in which the activities of Zn in dilute Cu–Ni–Zn melt at 1100 and 1150 °C were determined by measuring the vapor pressure of Zn.

### 3. Thermodynamic modeling and optimization

As discussed above, a ternary continuous  $\gamma$  phase exists in this system. This requires that the  $\gamma$  phase should be described by compatible models in both Cu–Zn and Ni–Zn systems. In the original binary assessments, however, it was described by a four-sublattice model  $(\text{Cu,Zn})_8(\text{Cu,Zn})_8\text{Cu}_{12}\text{Zn}_{24}$  in the Cu–Zn [2] and  $(\text{Ni,VA})_4(\text{Ni,Zn})_{22}\text{Ni}_4\text{Zn}_{22}$  in the Ni–Zn system [3]. These two models are incompatible and remodeling work before a ternary calculation is necessary. Since the present calculation is one part of work to develop a thermodynamic database for multi-component copper alloys [18], a model selected should not only be thermodynamically reasonable, but also be feasible in applications. It has been found that the Cu<sub>5</sub>Zn<sub>8</sub> type of  $\gamma$  phase can be soluble with a large solubility of Al, Cu, Fe, Ni, Si and Zn, all of which are commonly used alloying elements in copper alloys and will be included in our database. To describe such a high-order phase, a four-sublattice model, despite its being more physically meaningful in reproducing the atomic occupation, is obviously too complicated. Moreover, the  $\gamma$  phase usually has a large homogeneity range, and its Gibbs energy changes smoothly with composition. These factors suggest that the best selection should be a substitutional solution model to describe the  $\gamma$  phase in this work.

Since bcc\_A2 and bcc\_B2 were treated as one disordered phase, the CsCl type of  $\beta'$  phase in the Ni–Zn system was remodeled. Also in the Ni–Zn system, the L1<sub>0</sub> type of  $\beta_1$ , originally described by  $(\text{Ni,Zn})(\text{Zn,VA})$ , was remodeled by a two-sublattice model  $(\text{Ni,Zn})(\text{Ni,Zn})$  in the binary system. For the ternary  $\beta_1$  phase, Cu was permitted to enter the Ni sublattice, leading to  $(\text{Cu,Ni,Zn})(\text{Ni,Zn})$ , according to its homogeneity range as determined by Mayall and co-workers [9,10]. No phase diagram data are available for the Zn corner, thus the  $\varepsilon$  phase in the Cu–Zn and the NiZn<sub>8</sub> in the Ni–Zn system were treated as binary phases.

The optimization work was done with the Parrot module contained in the Thermo-Calc databank system [19]. The pure elements in their stable structures at 25 °C were chosen as the reference states for the system. The thermodynamic functions for the stable and metastable states were taken from the SGTE database [20].

Table 2  
Thermodynamic parameters obtained in this work for the Cu–Ni–Zn system

Liquid: (Cu, Ni, Zn)	${}^0L_{\text{Ni,Zn:Ni}}^{\beta_1} = -3395.03364 + 8.48315937T$
${}^0L_{\text{Cu,Ni,Zn}}^L = +60,000 - 30T$	${}^0L_{\text{Ni:Ni,Zn}}^{\beta_1} = {}^0L_{\text{Ni,Zn:Ni}}^{\beta_1}$
${}^1L_{\text{Cu,Ni,Zn}}^L = +30,000$	${}^0L_{\text{Ni,Zn:Zn}}^{\beta_1} = -9729.64622 + 5.79730282T$
${}^2L_{\text{Cu,Ni,Zn}}^L = -63,000$	${}^0L_{\text{Zn:Ni,Zn}}^{\beta_1} = {}^0L_{\text{Ni,Zn:Zn}}^{\beta_1}$
Fcc_A1 ( $\alpha$ ): (Cu, Ni, Zn)	${}^0L_{\text{Cu:Ni,Zn}}^{\beta_1} = -15,000$
${}^0L_{\text{Cu,Ni,Zn}}^{\text{Fcc\_A1}} = -8614 + 15T$	${}^1L_{\text{Cu:Ni,Zn}}^{\beta_1} = +5000$
${}^1L_{\text{Cu,Ni,Zn}}^{\text{Fcc\_A1}} = +55,000 - 20T$	$\gamma$ : (Cu, Ni, Zn)
${}^2L_{\text{Cu,Ni,Zn}}^{\text{Fcc\_A1}} = -55,000 + 10T$	${}^0G_{\text{Cu}}^{\gamma} = +5000 + {}^0G_{\text{Cu}}^{\text{Fcc\_A1}}$
Bcc_A2 ( $\beta$ ): (Cu, Ni, Zn)	${}^0G_{\text{Ni}}^{\gamma} = +10,000 + {}^0G_{\text{Ni}}^{\text{Fcc\_A1}}$
${}^0L_{\text{Ni,Zn}}^{\text{Bcc\_A2}} = -93,229.1431 + 30T$	${}^0G_{\text{Zn}}^{\gamma} = +10,000 + G_{\text{Zn}}^{\text{Hcp\_A3}}$
${}^1L_{\text{Ni,Zn}}^{\text{Bcc\_A2}} = -15,243.375 + 20.721995T$	${}^0L_{\text{Cu,Ni}} = +10,000$
${}^2L_{\text{Ni,Zn}}^{\text{Bcc\_A2}} = +107,770.361$	${}^0L_{\text{Cu,Zn}}^{\gamma} = -68,907.5809 + 8.67897055T$
${}^0L_{\text{Cu,Ni,Zn}}^{\text{Bcc\_A2}} = +115,000$	${}^1L_{\text{Cu,Zn}}^{\gamma} = +50,929.7595 - 12.6041406T$
${}^1L_{\text{Cu,Ni,Zn}}^{\text{Bcc\_A2}} = +217,000$	${}^2L_{\text{Cu,Zn}}^{\gamma} = +42,871.5071 - 30T$
${}^2L_{\text{Cu,Ni,Zn}}^{\text{Bcc\_A2}} = -205,000$	${}^0L_{\text{Ni,Zn}}^{\gamma} = -76,447.5239 + 7.25980486T$
$\beta_1$ : (Cu, Ni, Zn) <sub>1</sub> (Ni, Zn) <sub>1</sub>	${}^1L_{\text{Ni,Zn}}^{\gamma} = +73,547.0089 - 21.8036134T$
${}^0G_{\text{Cu:Ni}}^{\beta_1} = +10,000 + {}^0G_{\text{Cu}}^{\text{Fcc\_A1}} + {}^0G_{\text{Ni}}^{\text{Fcc\_A1}}$	${}^2L_{\text{Ni,Zn}}^{\gamma} = -119,121.737 + 19.1717902T$
${}^0G_{\text{Ni:Ni}}^{\beta_1} = +2{}^0G_{\text{Ni}}^{\text{Fcc\_A1}}$	${}^0L_{\text{Cu,Ni,Zn}}^{\beta_1} = +230,000$
${}^0G_{\text{Zn:Ni}}^{\beta_1} = -43,082.6129 + 3.99394891T + {}^0G_{\text{Ni}}^{\text{Fcc\_A1}} + {}^0G_{\text{Zn}}^{\text{Fcc\_A1}}$	${}^1L_{\text{Cu,Ni,Zn}}^{\beta_1} = +130,000$
${}^0G_{\text{Cu:Zn}}^{\beta_1} = -25,500 + {}^0G_{\text{Cu}}^{\text{Fcc\_A1}} + {}^0G_{\text{Zn}}^{\text{Fcc\_A1}}$	${}^2L_{\text{Cu,Ni,Zn}}^{\beta_1} = +10,000$
${}^0G_{\text{Ni:Zn}}^{\beta_1} = -43,082.6129 + 3.99394891T + {}^0G_{\text{Ni}}^{\text{Fcc\_A1}} + {}^0G_{\text{Zn}}^{\text{Fcc\_A1}}$	
${}^0G_{\text{Zn:Zn}}^{\beta_1} = +2{}^0G_{\text{Zn}}^{\text{Fcc\_A1}}$	

The binary phases were optimized by using their thermodynamic properties and relative phase diagram data, as cited in the work of Kowalski and Spencer [2] and Vassilev et al. [3]. The ternary optimization began with fitting the phase equilibria between  $\alpha$ ,  $\beta$ ,  $\beta_1$  and  $\gamma$  in the isotherms from 600 to 800 °C. After that the parameters for the liquid were determined based on the liquidus data from Yamaguchi and Nakamura [5], and the evaluated liquid projection provided by Chang et al. [12]. The obtained thermodynamic model parameters in this work are listed in Table 2. For simplicity, those binary parameters provided in

the assessments for the Cu–Ni [1], Cu–Zn [2] and Ni–Zn [3] systems were omitted.

#### 4. Results and discussion

The remodeling work performed in the binary Cu–Zn and Ni–Zn systems was successful, and the details will not be discussed here. For the ternary calculated results, agreement with all phase diagram data and thermodynamic properties discussed above was obtained. Due to a limitation

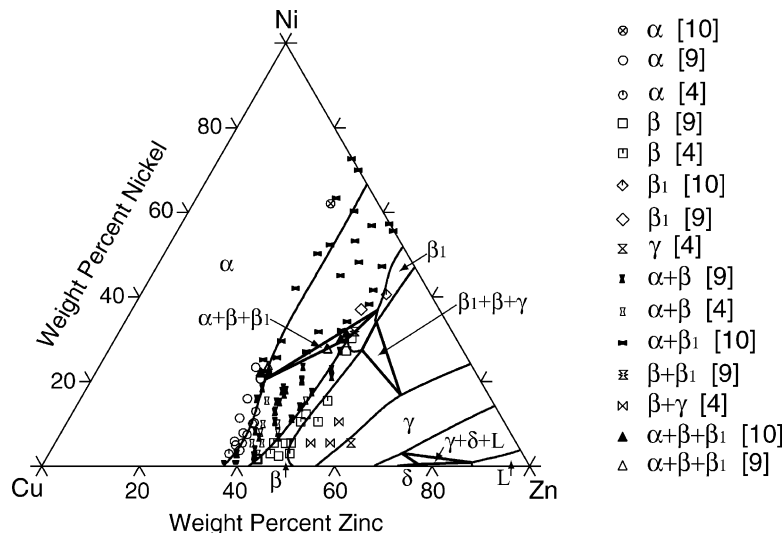


Fig. 2. Comparison of the calculated isotherm at 600 °C with various experimental investigations [4,9,10].

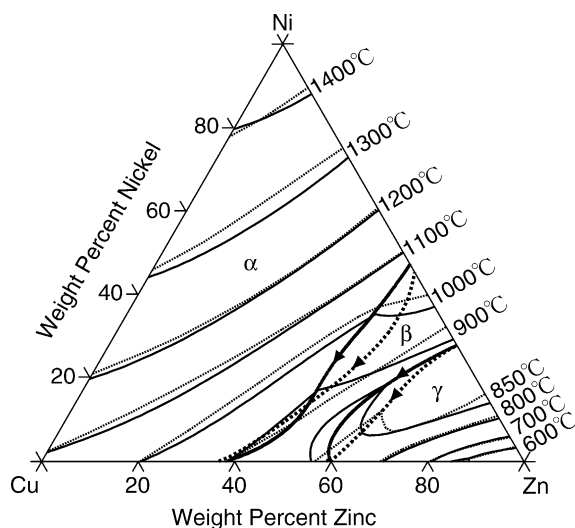


Fig. 3. Comparison of the calculated liquidus (thin solid) and monovariant curves of the liquid (thick solid) with the evaluated ones (dotted) by Chang et al. [12].

of space, only the typical ones are shown here. Fig. 2 is the calculated isothermal section at 600 °C compared with various experimental determinations [4,9,10]. Overall, agreement between the calculation and the experiments is fairly good except for a difference as to the location of the phase boundary  $\alpha/\alpha + \beta_1$ . On the Ni–Zn side, according to the currently accepted Ni–Zn phase diagram [21], the solubility of Zn in  $\alpha$ -Ni is 32.5 wt% at 600 °C, which is close to the present calculation and larger than the measurement by Mayall [10] which is about 27 wt%. So, the phase boundary  $\alpha/\alpha + \beta_1$  defined by Mayall [10] was considered to be slightly deviated to the lower Zn side, thus was not critically reproduced in this work.

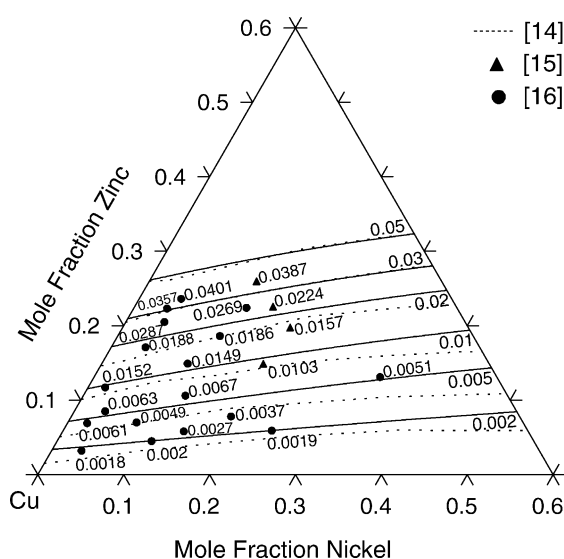


Fig. 4. Calculated isoactivity curves of Zn in the  $\alpha$ -CuNiZn at 727 °C compared with the measurements at 727 °C [15,16], and the evaluated isoactivity curves of Zn at 775 °C [14]. The numbers within the triangle are the values of  $a_{Zn}$ , referred to pure liquid Zn.

Fig. 3 shows the calculated liquidus and monovariant curves of the liquid, together with the evaluated results by Chang et al. [12] shown in dotted lines for comparison. Except for some differences which occur at 850 °C, agreement between the calculation and the evaluation is within experimental uncertainty. At 850 °C, the present calculation agrees well with the direct measurements of Yamaguchi and Nakamura [5].

Fig. 4 shows the calculated isoactivity curves of Zn within the  $\alpha$  phase region at 727 °C compared with the measurements [15,16] and the evaluated isoactivity curves of Zn [14]. The sample compositions of those measurements are marked by the characters in the Gibbs triangle with their activity values denoted nearby. It should be mentioned that although these data were not used in the optimization, the calculation can reproduce them reasonably, and the agreement with the evaluated curves is also good. This fact indicates that the calculation is thermodynamically reasonable and can serve as a guide in predicting the phase relationships and thermodynamic properties in the Cu–Ni–Zn system.

## 5. Conclusions

A thermodynamic analysis of Cu–Ni–Zn system was done and a consistent set of thermodynamic parameters for this system was obtained. The phase relationships covering the whole composition range except for the Zn-rich portion, including the three continuous solid solutions of  $\alpha$ ,  $\beta$  and  $\gamma$ , as well as the  $L1_0$  type of  $\beta_1$  phase, were well thermodynamically described. In addition, it was proved that the thermodynamic properties in the Cu–Ni–Zn system can be predicted by using the thermodynamic description herein reported.

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