

Thermodynamic Assessments of the Ag-Ni Binary and Ag-Cu-Ni Ternary Systems

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The phase diagram of the Ag-Ni binary system has been evaluated by using the calculation of phase diagrams (CALPHAD) method based on experimental data of the phase equilibria and thermodynamic properties. Gibbs free energies of the liquid and fcc phases were described by the subregular solution model with the Redlich–Kister equation. On the basis of the thermodynamic parameters of the Ag-Ni, Ag-Cu, and Cu-Ni systems, and experimental information of the phase equilibria in the Ag-Cu-Ni system, the thermodynamic assessment in the Ag-Cu-Ni system was carried out. The calculated results in both the Ag-Ni and Ag-Cu-Ni systems are in reasonable agreement with experimental data.

Key words: Ag-Ni system, Ag-Cu-Ni system, thermodynamic assessment, CALPHAD method

INTRODUCTION

Ag-Ni alloys have many applications as magnetic materials,^{1–6} Ag-Cu-based alloys are the most commonly used brazes.^{7,8} In the ceramic packaging, nickel (Ni) pads are usually plated on the ceramic substrates to improve the brazability;^{7,8} therefore, the interfacial reactions between Ag-Cu-based brazes and the nickel pads during the brazing process are important in the ceramic packaging industry. The phase diagrams are important to design materials and understand interfacial reactions. Recently, the present authors developed a thermodynamic database of lead-free solders using the calculation of phase diagrams (CALPHAD) method.^{9–11} The Ag-Ni and Ag-Cu-Ni systems are the basic systems for expanding this database. However, the thermodynamic parameters of the Ag-Ni and Ag-Cu-Ni systems have not yet been exactly calculated. Therefore, thermodynamic assessments of phase equilibria of the Ag-Ni and Ag-Cu-Ni systems are necessary.

The purpose of the present work is (1) to thermodynamically assess the Ag-Ni binary system and (2) to carry out the thermodynamic assessment of phase equilibria in the Ag-Cu-Ni system using the CALPHAD method based on the available experimental data.

THERMODYNAMIC MODELS

No intermediate phases were detected in the Ag-Cu-Ni ternary system and the Ag-Cu, Ag-Ni, and Cu-Ni subsystems, and only the liquid and fcc phases exist in the Ag-Cu-Ni system. The Gibbs free energies of the liquid and fcc phases are described by the subregular solution model with the Redlich–Kister formula,¹² as follows

$$\begin{aligned} G_m^\phi = & \sum_{i=\text{Ag,Cu,Ni}} G_i^\phi x_i + RT \sum_{i=\text{Ag,Cu,Ni}} x_i \ln x_i \\ & + L_{\text{Ag,Cu}}^\phi x_{\text{Ag}} x_{\text{Cu}} + L_{\text{Ag,Ni}}^\phi x_{\text{Ag}} x_{\text{Ni}} \\ & + L_{\text{Cu,Ni}}^\phi x_{\text{Cu}} x_{\text{Ni}} + \Delta^{\text{ex}} G^{\text{tern}}, \end{aligned} \quad (1)$$

(Received June 24, 2007; accepted October 2, 2007; published online October 25, 2007)

where G_i^ϕ is the Gibbs free energy of pure component i in the ϕ phase, x_i is the molar fraction of component i , R is the gas constant, and T is the absolute temperature. The term L_{ij}^ϕ is the interaction parameter between i and j atoms in the i - j binary system, and $\Delta^{\text{ex}}G^{\text{tern}}$ is the excess term due to the interaction between atoms in the ternary system, which can be expressed in the following forms, respectively:

$$L_{ij}^\phi = \sum_{m=0}^n {}^mL_{ij}^\phi (x_i - x_j)^m, \quad (2)$$

$$\Delta^{\text{ex}}G^{\text{tern}} = x_{\text{Ag}}x_{\text{Cu}}x_{\text{Ni}}(x_{\text{Ag}} {}^0L_{\text{Ag,Cu,Ni}}^\phi + x_{\text{Cu}} {}^1L_{\text{Ag,Cu,Ni}}^\phi + x_{\text{Ni}} {}^2L_{\text{Ag,Cu,Ni}}^\phi), \quad (3)$$

where the coefficients of ${}^mL_{ij}^\phi$ and ${}^nL_{\text{Ag,Cu,Ni}}^\phi$ represent the parameters in the sub-binary and ternary systems, respectively, and can be expressed as

$${}^mL_{ij}^\phi = a_m + b_m T, \quad (4)$$

$${}^nL_{\text{Ag,Cu,Ni}}^\phi = a'_n + b'_n T, \quad (5)$$

where a_m , b_m , a'_n , and b'_n are the numerical values, which are optimized based on the experimental data.

EXPERIMENTAL INFORMATION

The Ag-Ni System

The experimental phase diagram of the Ag-Ni system was assessed by Singleton and Nash.¹³ There is a eutectic reaction [L \rightarrow fcc (Ni) + fcc (Ag)] at 960°C and a monotectic reaction [L1 \rightarrow fcc (Ni) + L2] at 1435°C. The Ag-rich liquidus in the temperature range from 1000 to 1370°C was investigated by Stevenson and Wulff,¹⁴ from whose experimental data the liquid compositions at the monotectic temperature are fixed at about 3 and 96.11 at.% Ag, respectively, and the liquid composition at the eutectic temperature is 99.679 at.% Ag. The maximum solid solubility of Ag in the fcc (Ni) phase is estimated to be 1 at.%.

Although Ni and Ag have the same fcc crystal structure and the small difference of atom radii (within 15%), the solubilities of Ag in fcc (Ni) phase and Ni in fcc (Ag) phase are very limited. Tammann and Oelson¹⁵ and Ladet et al.¹⁶ investigated the solubility of Ni in the fcc (Ag) phase. Both of their results revealed that there is a miscibility gap of the solid solution in this binary system. Colinet and

Table I. Thermodynamic Parameters in the Ag-Cu-Ni Ternary System

Phase	Thermodynamic Parameters (J/mol)	Reference
Liquid (Ag, Cu, Ni)	${}^0L_{\text{Ag,Cu}}^{\text{liquid}} = 17,384.37 - 4.46438T$	28
	${}^1L_{\text{Ag,Cu}}^{\text{liquid}} = 1660.74 - 2.31516T$	28
	${}^0L_{\text{Cu,Ni}}^{\text{liquid}} = 12,048.61 + 1.29893T$	29
	${}^1L_{\text{Cu,Ni}}^{\text{liquid}} = -1861.61 + 0.94201T$	29
	${}^0L_{\text{Ag,Ni}}^{\text{liquid}} = 54,055.6 - 2.2T$	This work
	${}^1L_{\text{Ag,Ni}}^{\text{liquid}} = -1910$	This work
	${}^0L_{\text{Ag,Cu,Ni}}^{\text{liq}} = 118,140 - 88T$	This work
	${}^1L_{\text{Ag,Cu,Ni}}^{\text{liq}} = -62,830 + 54T$	This work
	${}^2L_{\text{Ag,Cu,Ni}}^{\text{liq}} = -85,600 + 34T$	This work
	${}^0L_{\text{Ag,Cu}}^{\text{fcc}} = 36,772.58 - 11.02847T$	28
	${}^1L_{\text{Ag,Cu}}^{\text{fcc}} = -4612.43 + 0.28869T$	28
	${}^0L_{\text{Cu,Ni}}^{\text{fcc}} = 8047.72 + 3.42217T$	29
	${}^1L_{\text{Cu,Ni}}^{\text{fcc}} = -2041.3 + 0.99714T$	29
	${}^0T_{\text{c}}^{\text{fcc}} = -935.5$	29
${}^1T_{\text{c}}^{\text{fcc}} = -594.9$	29	
${}^0\beta^{\text{fcc}} = -0.7316$	29	
${}^1\beta^{\text{fcc}} = -0.3174$	29	
${}^0L_{\text{Ag,Ni}}^{\text{fcc}} = 54,620.4 + 3.1T$	This work	
${}^1L_{\text{Ag,Ni}}^{\text{fcc}} = 2800$	This work	
${}^0L_{\text{Ag,Cu,Ni}}^{\text{fcc}} = -850,00$	This work	
${}^1L_{\text{Ag,Cu,Ni}}^{\text{fcc}} = -68,278 + 86T$	This work	
${}^2L_{\text{Ag,Cu,Ni}}^{\text{fcc}} = -93,694 + 68T$	This work	

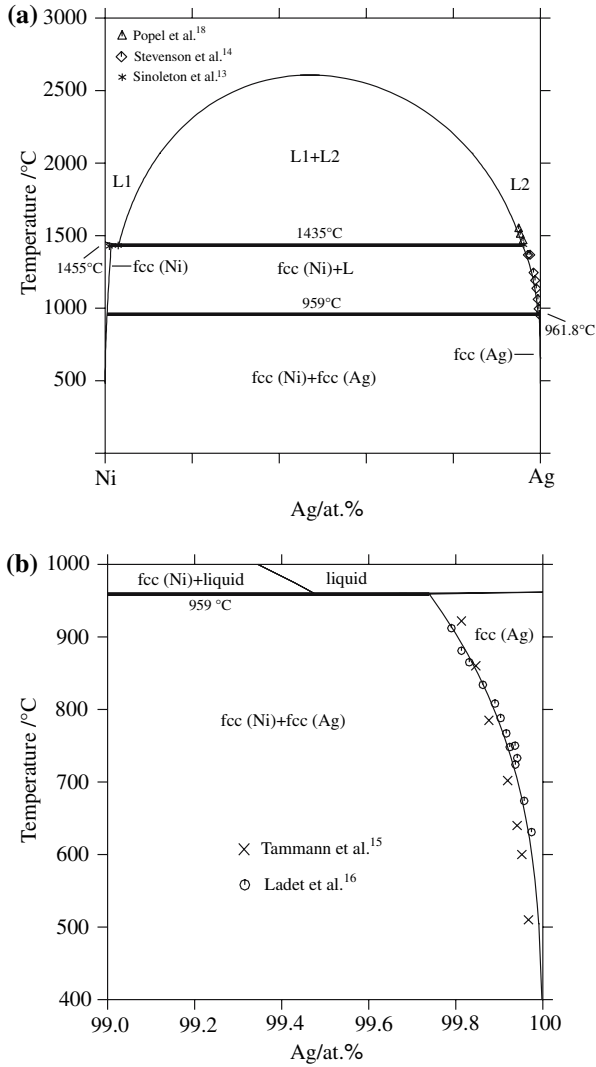


Fig. 1. (a) The calculated phase diagram for the Ag-Ni system and (b) a magnified portion of the Ag-rich side with the experimental data.

Pasturel¹⁷ calculated the highest critical temperature (about 4000 K) of the miscibility gap of the metastable fcc phase using theoretical calculations. A liquid miscibility gap is also found; however, there is little experimental information except those in Ref. 18.

Recently, Saeed et al.¹⁹ measured the mixing enthalpies in the liquid alloys at 1500°C, indicating that the mixing enthalpies are positive for all

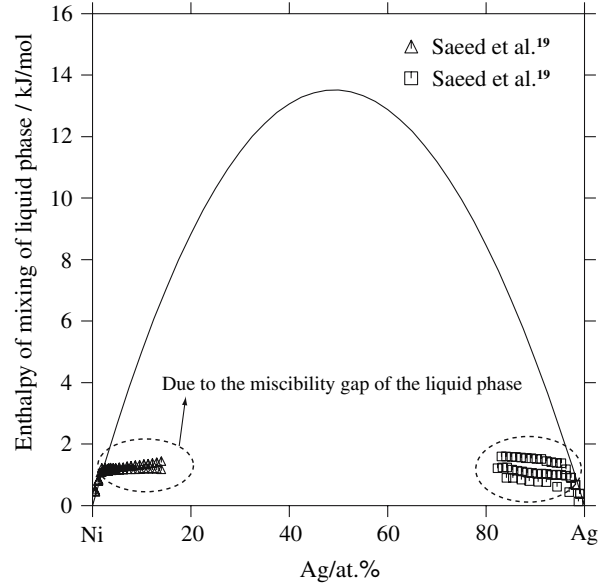


Fig. 2. The calculated mixing enthalpy of the liquid phase at 1500°C in the Ag-Ni system compared with the experimental data reported by Saeed et al.¹⁹ Reference state: Ag (liq), and Ni (liq).

compositions. From extrapolation of these experimental data, Saeed et al.¹⁹ gave the maximum value to be about 13.5 kJ/mol at 40 at.% Ag, although such an extrapolation has uncertainty due to the limited solubility range on either side.

Zolla and Spaepen²⁰ reported the mixing enthalpies of the solid phase in two films with compositions of 5.8 and 9.6 at.% Ni based on differential scanning calorimetry (DSC) measurements. The films were deposited by using a dual-gun electron beam evaporator. The values of the mixing enthalpies extrapolated from the DSC measurements of 5.8 and 9.6 at.% Ni were 3.3 ± 0.04 and 4.6 ± 0.09 kJ/mol, respectively.

The Ag-Cu-Ni System

The phase diagram in this system was first studied by Cesaris,²¹ who measured the temperatures of the phase transformation, and later updated by Guertler and Bergmann,²² who determined the isothermal sections at temperatures of 700, 900, 1250, 1300, 1400, and 1440°C. Siewert and Heine²³ thought that the experimental values reported by Cesaris²¹ and Guertler and Bergmann²² may including errors due to areas of contamination

Table II. Invariant Reactions of the Ag-Ni System

Reaction	Type	Composition of the Respective Phases (at.% Ag)			Temperature (°C)	Reference
		1	2	3		
L1 → fcc (Ni) + L2	Eutectic	3	~1	96.11	1435	13
		3.1	1.4	95.8	1435	This work
L → fcc (Ni) + fcc (Ag)	Monotectic	99.68	<1	99.8	960	13
		99.5	0.45	99.8	959	This work

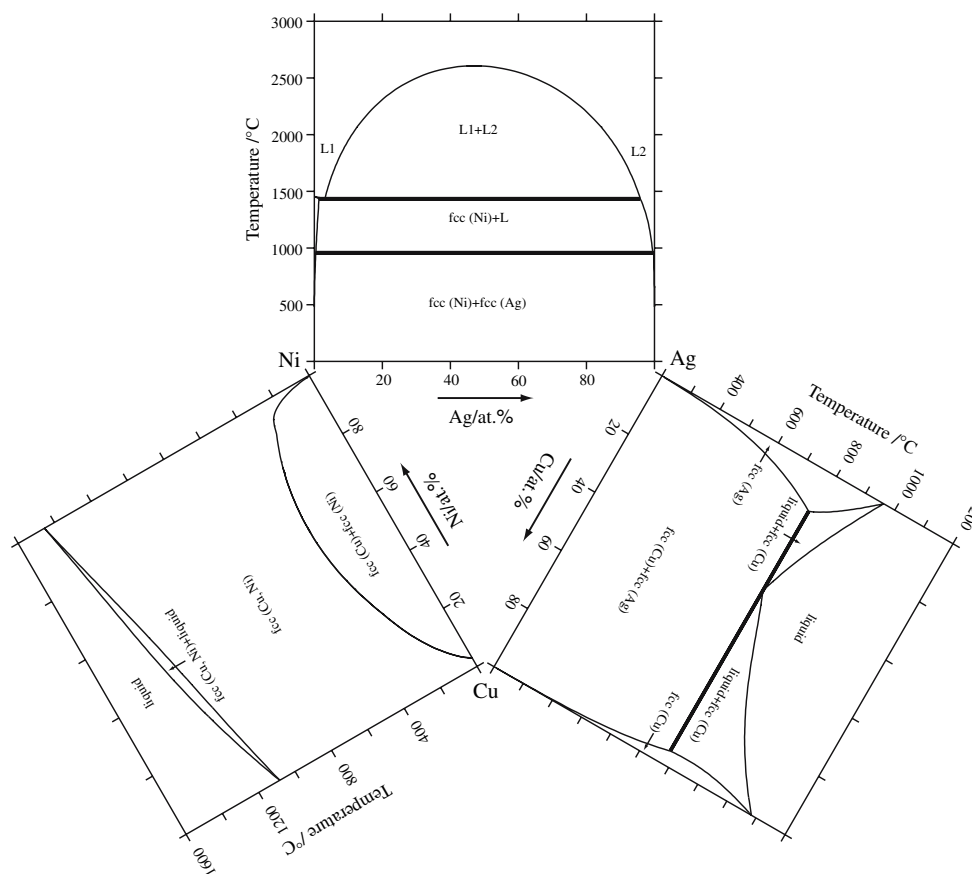


Fig. 3. Calculated binary phase diagrams used for the Ag-Cu-Ni system.

by oxygen, the determination of the composition of the phases, and quenching of the large samples rapidly enough to prevent further diffusion. Based on advances in the technique and equipment, Siewert and Heine²³ redetermined the phase diagrams at 800 and 900°C. Their results for solubility²³ might be more accurate than those reported by Cesaris²¹ and Guertler and Bergmann,²² except that the isothermal section at 900°C shows some differences from the accepted Ag-Cu phase diagram.²⁴ Recently, Luo and Chen²⁵ studied the phase equilibria at temperatures of 700, 795, and 860°C, by using X-ray diffractometer (XRD), scanning electron microscopy (SEM), and electron probe microanalysis (EPMA). Kubaschewski²⁶ reviewed the phase diagram in the Ag-Cu-Ni system based on previous literature. According to the chemical analysis data by Guertler and Bergmann,²² the liquid miscibility gap extends from the Ag-Ni binary system into the ternary up to approximately 48 at.% Cu at 1250°C.²⁶

CALCULATED RESULTS AND DISCUSSION

Optimization of Phase Equilibria

Although in previous studies the isothermal sections at the temperatures of 700, 795, and 860°C were calculated, the thermodynamic parameters

were obtained directly from the three binary Ag-Cu, Ag-Ni, and Cu-Ni systems without any ternary interaction parameters.²⁵ Luo and Chen only listed the approximate parameters of the Ag-Ni binary system and did not show the details in Ref. 25.

In the present work, the optimization of the thermodynamic parameters of the various phases in the Ag-Ni system was performed with the parrot module of the Thermo-Calc package, which uses various types of experimental data for the optimization process.²⁷ The experimental data taken from the phase diagram of the Ag-Ni system revised by Singleton and Nash,¹³ and the thermodynamic properties¹⁹ were used as inputs to the program. Each selected piece of information was assigned a certain weight according to its importance, which was changed by trial and error during the assessment, until most of the results were within the expected uncertainty limits.

In the assessment of the Ag-Cu-Ni ternary system, the thermodynamic parameters of the Ag-Cu and Cu-Ni binary systems were taken from the previous literature.^{28,29} The thermodynamic parameters of the liquid and fcc phases in the Ag-Cu-Ni ternary system were optimized on the basis of the isothermal sections and liquidus projection, since no thermodynamic properties were reported for this ternary system.

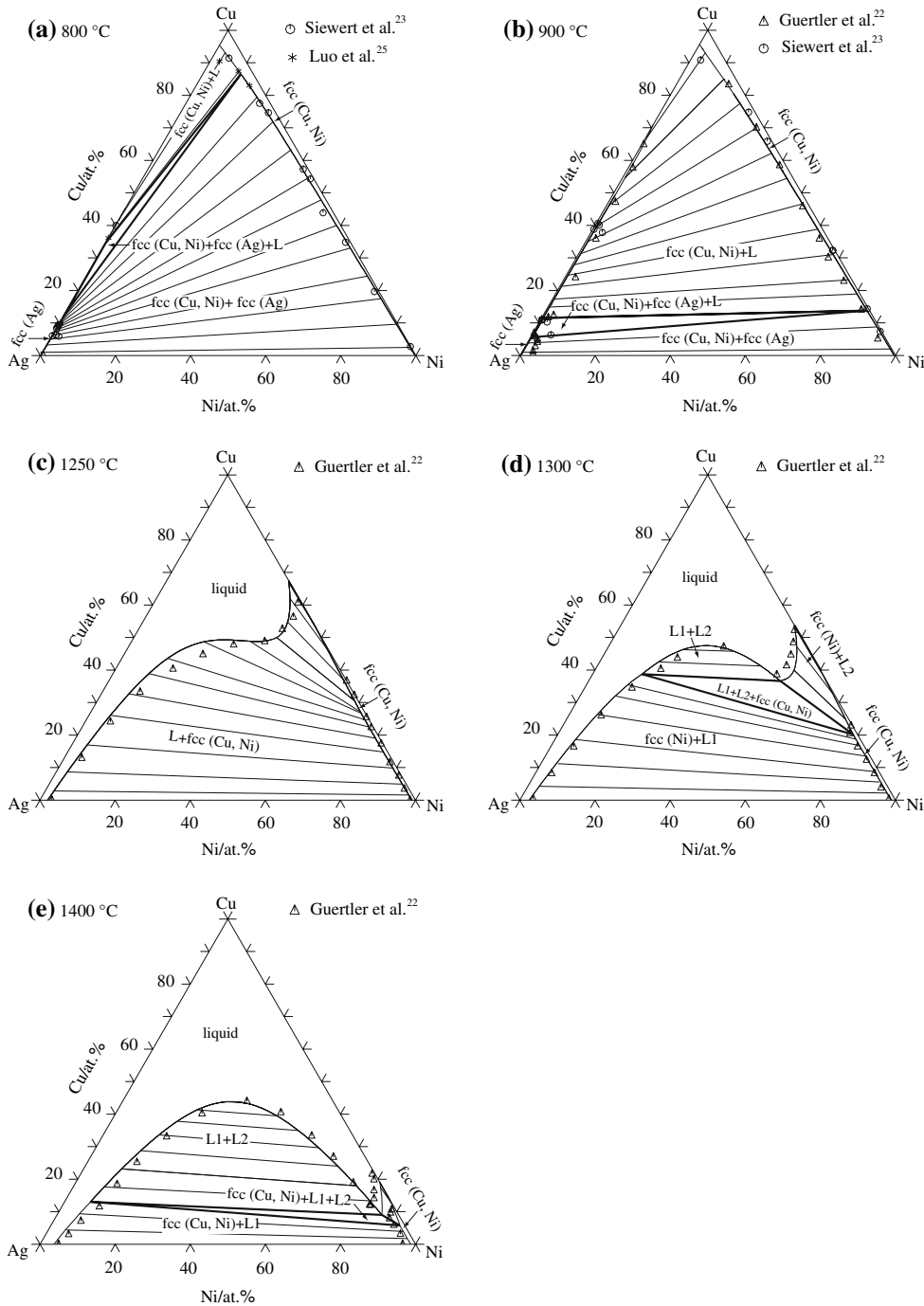


Fig. 4. Calculated isothermal sections at (a) 800°C, (b) 900°C, (c) 1250°C, (d) 1300°C, and (e) 1400°C for the Ag-Cu-Ni system with the experimental data.

All the thermodynamic parameters in the Ag-Cu-Ni ternary system are listed in Table I. The Gibbs free energies of the pure components are taken from the Scientific Group Thermodata Europe (SGTE) database.³⁰

The Ag-Ni System

The phase diagram calculated for the Ag-Ni system is shown in Fig. 1, compared with all the

experimental data used in the present optimization. It is seen from Fig. 1a that the calculated results are in good agreement with the experimental data reported by Stevenson and Wulff¹⁴ and Popel and Kozhurkov,¹⁸ and the highest critical temperature of the miscibility gap of the liquid phase is estimated to be 2607°C at about 47 at.% Ag. Figure 1b shows a magnified portion of the calculated phase diagram in the Ag-rich side between 400 and

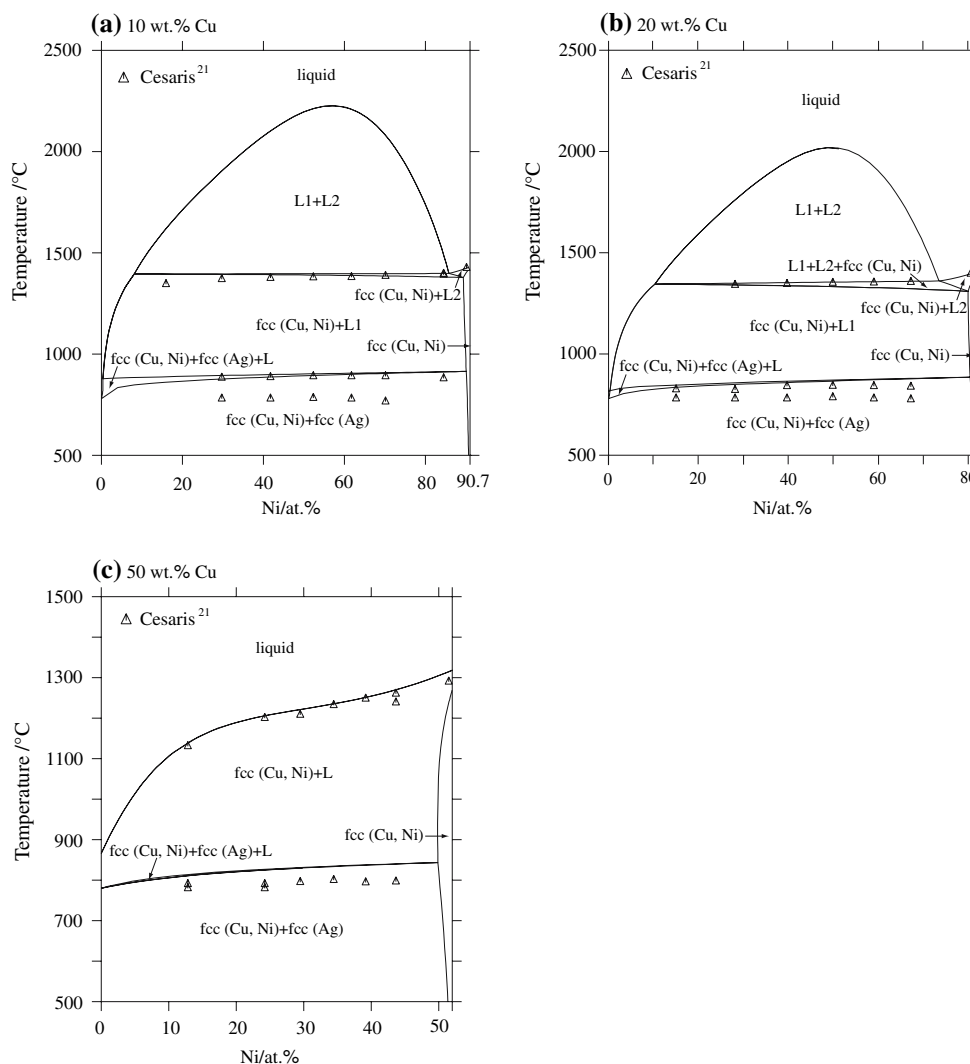


Fig. 5. Calculated vertical sections at (a) 10 wt.% Cu, (b) 20 wt.% Cu, and (c) 50 wt.% Cu for the Ag-Cu-Ni system with the experimental data.

1000°C with the experimental data,^{15,16} where the calculated solid solubility of Ni in the fcc (Ag) phase (Fig. 1b) reproduces the experimental data very well. The calculated highest critical temperature of the miscibility gap of the metastable fcc phase is about 3783°C (4056 K), which is in agreement with the theoretical calculation (about 4000 K) reported by Colinet and Pasturel.¹⁷ All invariant reactions in the Ag-Ni system are summarized in Table II, in which the experimental data are also listed for comparison.

Figure 2 shows the calculated mixing enthalpy of the liquid phase at 1500°C with the experimental data,¹⁹ based on the present thermodynamic parameters. A reasonable agreement is obtained between the calculated and experimental results. The calculated maximum value of the mixing enthalpy of the liquid phase is about 13.5 kJ/mol at 50 at.% Ag, which is in good agreement with the extrapolated value (13.5 kJ/mol) based on the experi-

mental data.¹⁹ However, a kink in the experimental results (Fig. 2) was observed due to the miscibility gap of the liquid phase.¹⁹

The mixing enthalpy of the fcc phase is calculated. The calculated mixing enthalpies of the compositions of 5.8 and 9.6 at.% Ni are about 3.2 and 5 kJ/mol, respectively, which are in agreement with the data reported by Zolla and Spaepen.²⁰

The Ag-Cu-Ni System

Figure 3 shows the calculated binary phase diagrams used in the Ag-Cu-Ni system. Seven calculated isothermal sections of this system at temperatures of 800, 900, 1250, 1300, and 1400°C are shown in Fig. 4 compared with the experimental data. A good agreement between the experimental data and calculations is obtained except for the sections at 900°C (Fig. 4b) and 1250°C (Fig. 4c), where the discrepancies were caused by the difference between the experimental data and calculated

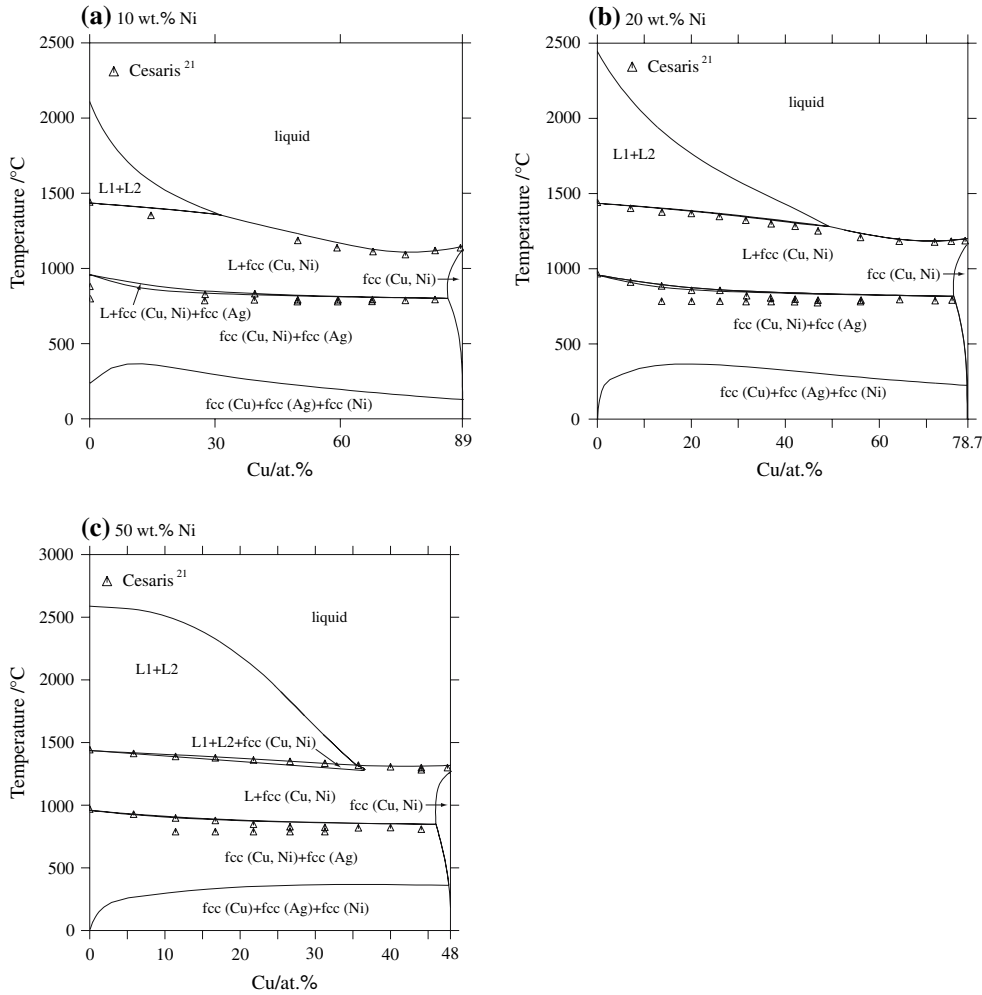


Fig. 6. Calculated vertical sections at (a) 10 wt.% Ni, (b) 20 wt.% Ni, and (c) 50 wt.% Ni for the Ag-Cu-Ni system with the experimental data.

phase diagrams in the Ag-Ni and Ni-Cu systems.²⁹ The solubility of Ni in the fcc (Ag) phase obtained from Guertler and Bergmann²² is obviously greater than that from the experimental results¹³ and the present calculated results. A miscibility gap of the liquid phase is observed in the isothermal section at 1300°C, agreeing with the experimental data. From Fig. 4d and e, it is seen that the region of the miscibility gap of the liquid phase becomes larger with increasing temperature, and the shape of the miscibility gap is in accordance with experimental results.²² Figure 5 shows the calculated vertical sections at 10, 20, and 50 wt.% Cu compared with the experimental data,²¹ from which it is seen that the region of the miscibility gap of the liquid phase decreases with increasing composition of Cu. The calculated vertical sections at 10, 20, and 50 wt.% Ni are also shown in Fig. 6 with the experimental data. The reasonable agreement between the experimental and calculated results is obtained. It should be noted that there are some differences between the calculated and experimental data in Figs. 5 and 6. Further experimental work is needed

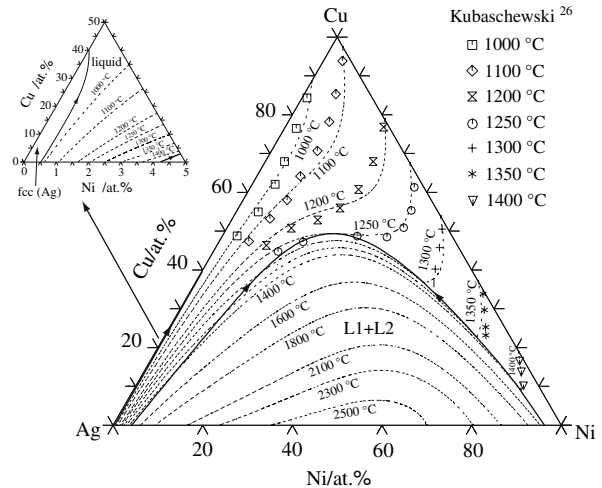


Fig. 7. Calculated liquidus projection of the Ag-Cu-Ni system with the experimental data.

to verify the present calculated results. Figure 7 shows the calculated liquidus projection of the Ag-Cu-Ni system, where the calculated liquid miscibility

gap exists from the Ag-Ni system up to about 49 at.% Cu at 1250°C, which is in reasonable agreement with the experimental results.²⁶

CONCLUSIONS

Thermodynamic assessments of the Ag-Ni binary and Ag-Cu-Ni ternary systems were carried out on the basis of the available experimental information in the literature. A consistent set of optimized thermodynamic parameters was derived for describing the Gibbs free energy of each solution phases in the Ag-Ni binary and Ag-Cu-Ni ternary systems, leading to good agreement between calculation and most of the experimental data found in literature.

ACKNOWLEDGEMENTS

This work is jointly supported by the National Natural Science Foundation of China (Grant No. 50425101), The Ministry of Science and Technology of China (Grant No. 2004CCA0420), The Ministry of Education of China (Grant Nos. 20050384003 and 105100), and the Fujian Provincial Department of Science & Technology (Grant No. 2005HZ1015). Support from a Core Research for Evolutional Science and Technology (CREST), Japan Science and Technology Agency (JST), and Xiamen Bureau of Science & Technology (Grant No. 02ZZ20055016) are also acknowledged.

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