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# Thermodynamic database of the phase diagrams in copper base alloy systems

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## Abstract

A thermodynamic database on the phase equilibria of the copper base alloys, including Cu–X binary system and Cu–Fe, Cu–Ni, Cu–Cr base ternary systems has been developed by the Calculation of Phase Diagrams (CALPHAD) method. The thermodynamic parameters describing Gibbs energies of the different phases have been evaluated by optimizing experimental data of phase equilibria and thermodynamic properties. The present thermodynamic database can provide much information such as stable and metastable phase equilibria, phase fraction, liquidus projection and various thermodynamic quantities and so on, which is expected to play an important role in the design of copper base alloys.
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Keywords: D. Phase equilibria; D. Thermodynamic properties

## 1. Introduction

The copper base alloys are widely used in many fields because of their good combination with high thermal and electrical conductivities and high-strength. In particular, Cu base alloys with high performance are required in the field of electronic materials, such as substrate and lead frame in the printed board, interconnection and so on, because the electronic packaging has a tendency to miniaturization [1,2]. In addition, Pb-free micro-soldering alloys to replace conventional Pb–Sn alloys have been designed and developed to meet the requirements arising from environmental and health issues concerning the toxicity of Pb. It has been shown that the bonding properties depend on various kinds of combination between Pb-free solders and Cu base alloys [3]. In order to develop Cu base alloys with high efficiency, a thermodynamic database of Cu base alloys for reliable predictions of liquidus, phase fraction, equilibrium and non-equilibrium solidification behavior, etc. in multi-component

systems is required because it is difficult to obtain these information from available references.

The objective of the present work is to develop the thermodynamic database of the phase diagrams in Cu base alloy systems including Cu–X binary system and Cu–Fe, Cu–Cr, Cu–Ni base ternary systems by the CALPHAD method, and then to introduce some examples of application on the basis of this database.

## 2. CALPHAD Method

In the CALPHAD method, after the appropriate thermodynamic models to describe Gibbs energy of each phase are selected, the thermodynamic optimization is carried out by fitting reliable experimental data including phase equilibria and thermodynamic properties, and thermodynamic database is constructed on the basis of assessed parameters.

In the present work, the Gibbs energies of the liquid, fcc, bcc, hcp and other solid solution phases are described by the subregular solution model with the Redlich–Kister formula [4]. For instance, the Gibbs energy of φ phase in Cu–X–Y

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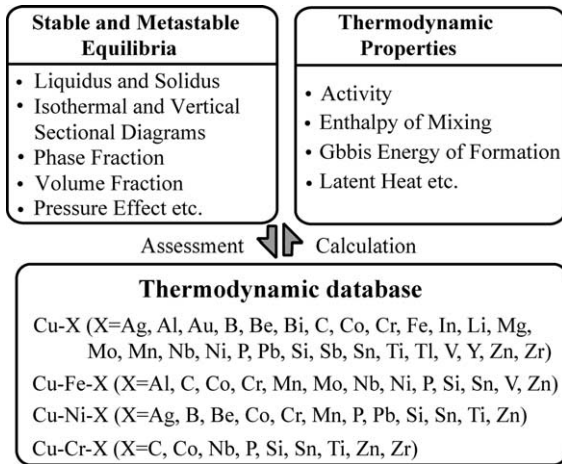E-mail address: ishida@material.tohoku.ac.jp (K. Ishida).

Fig. 1. Outline of the thermodynamic database.

ternary system is expressed as

$$G^\phi = \sum_{i=Cu,X,Y} {}^0G_i^\phi x_i^\phi + RT \sum_{i=Cu,X,Y} x_i^\phi \ln x_i^\phi$$
$$+ \sum_{\substack{i,j=Cu,X,Y \\ (i \neq j)}} L_{i,j}^\phi x_i^\phi x_j^\phi + L_{Cu,X,Y}^\phi x_{Cu}^\phi x_X^\phi x_Y^\phi \quad (1)$$

where ${}^0G_i$ is the Gibbs energy of pure component $i$ in the respective reference state, which is taken from the lattice stability value for pure element compiled by Dinsdale [5]. $x_i$ is the mole fraction of component $i$, and $L_{i,j}$ and $L_{Cu,X,Y}$ are the interaction energies with temperature and composition dependent in binary and ternary systems, respectively.

The Gibbs energies of the ordered bcc phase and intermetallic phases are described by the two-sublattice model [6], which was reported in our previous works [7,8].

## 3. Thermodynamic database

In order to make a reliable thermodynamic assessment, the experimental determination of phase equilibria were conducted in some binary and ternary systems by the present authors [7,9–11]. The thermodynamic optimization of phase equilibria was carried out on the basis of these experimental data and other works reported previously.

Fig. 1 shows the scheme of the present thermodynamic database of the copper base alloys, which provides various information on phase diagrams and thermodynamic properties such as liquidus, solidus, isothermal and vertical
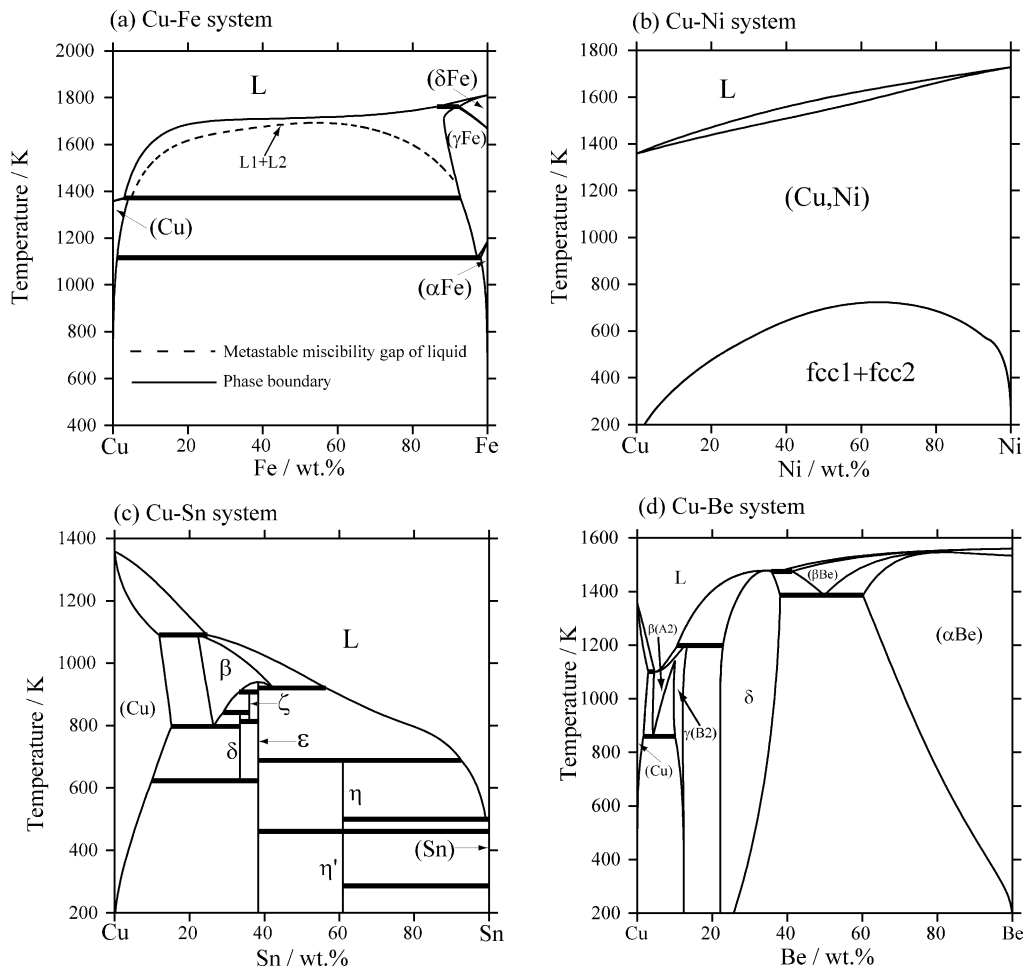


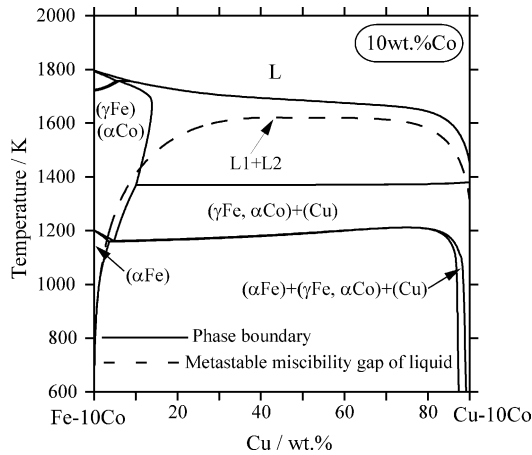Fig. 2. Calculated phase diagrams in the Cu–X binary systems.

Fig. 3. Calculated vertical section diagram including the metastable miscibility gap of the liquid phase in the Cu–Fe–Co system.

sections, mole fraction of constituent phases, activity, enthalpy of mixing, Gibbs energy of formation and so on. Furthermore, this database also has a potential application to design copper base alloys, and to simulate the interface reaction between solder and substrate by combining the thermodynamic database for micro-solder alloys [12].

## 4. Application of the thermodynamic database

### 4.1. Calculation of phase equilibria

As an example, Fig. 2 shows the calculated phase diagrams in some Cu–X binary systems. It is seen that a metastable miscibility gap of the liquid phase and the stable miscibility gap of the fcc phase exist in the Cu–Fe and Cu–Ni systems, respectively. The complex phase equilibria in the Cu–Sn system can also be calculated and the miscibility gap of the β (B2)+γ (A2) is well reproduced in the Cu–Be system due to the ordering of the bcc phase in the Cu-rich portion.
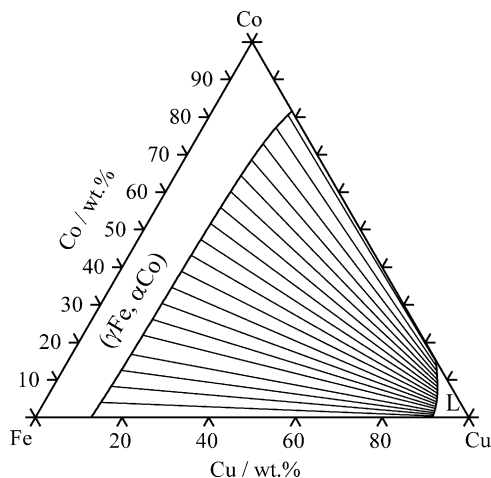


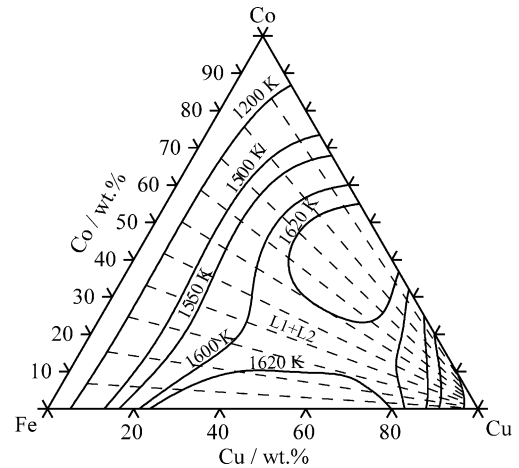Fig. 4. Calculated isothermal section diagram of the Cu–Fe–Co ternary system at 1573 K.



Fig. 5. Calculated metastable miscibility gap of the liquid phase in the Cu–Fe–Co system.

Figs. 3–5 show the calculated isothermal and vertical section diagrams in the Cu–Fe–Co system, in which not only the stable phase equilibria, but also metastable miscibility gap of the liquid phase can be calculated on the basis of the present database.

### 4.2. Application for alloy design

#### 4.2.1. Solubility in copper base alloys

The change of solubility in the fcc phase in the Cu-rich portion due to addition of alloying element is useful information in the design for high strength copper base alloys utilizing precipitation hardening. Typical example of the effect of Ni on the solubility in fcc phase in the Cu–Be alloy is shown in Fig. 6. Comparing to the Cu–Be binary system, the solubility of Be in the fcc phase is remarkably reduced due to the addition of Ni, which means that the notable effect of the precipitation hardening may be obtained in the Cu–Be–Ni system.
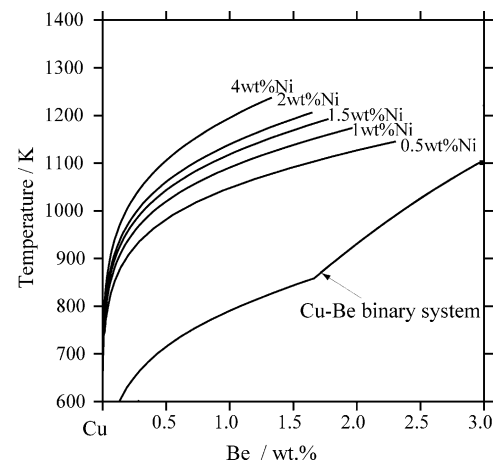


Fig. 6. Calculated solubility line of fcc phase for Cu-rich corner in Cu–Be–Ni system.
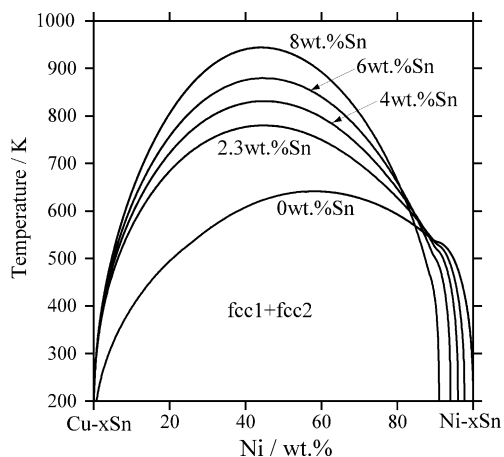
Fig. 7. Calculated metastable miscibility gap of the fcc phase in the Cu–Ni–Sn system.

### 4.2.2. Copper base alloys with spinodal decomposition

The spinodal-type Cu base alloys of the fcc phase are also potential candidates for the new type Cu base practical materials with high strength. Therefore, the effect of alloying element on the miscibility gap is important in alloy design. Fig. 7 shows the effect of Sn on the miscibility gap of the fcc phase in the Cu–Ni system (see Fig. 2(b)). The miscibility gap becomes more stable with increasing Sn content, which is an effective guide for microstructure design by using spinodal decomposition.

### 4.2.3. Egg-type core powders

Fe–Cu and Fe–Cu–C base powder compacts are widely used for automotive, electric and industrial machinery, and they are fabricated by the liquid phase sintering of mixtures of iron, graphite and copper elemental powders, but there are problems with dimensional variations caused by the swelling of the graphite and copper powders [13]. Most recently, the present authors developed the powders with an egg-type core microstructure in immiscible alloy systems by conventional gas atomization [14]. A sample of powder with the composition
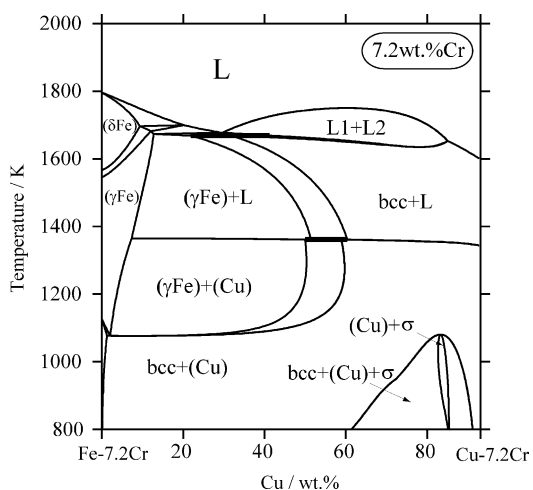


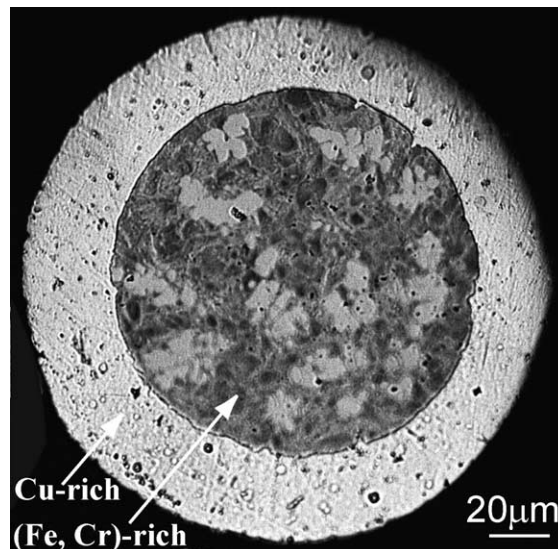Fig. 8. Calculated vertical section diagram of the Cu–Fe–Cr (wt%) system.



Fig. 9. Microstructure of the Cu–32.4Fe–7.2Cr–0.4C (wt%) alloy powder.

of the Cu–32.4Fe–7.2Cr–0.4C (wt%) was prepared, whose composition was designed to fall into the stable miscibility gap in the liquid phase, as indicated in the vertical section (Fe–7.2Cr)–(Cu–7.2Cr) of the phase diagram calculated using the thermodynamic database as shown in Fig. 8, where the effect of carbon is neglected. Fig. 9 shows the egg-type core microstructure of this alloy powder with (Fe, Cr)-rich as a core and Cu-rich as a periphery. The egg-type core powder as a segregation-free iron powder is expected to improve dimensional accuracy. On the other hand, this egg-type powder with a high thermal and electrical conductivities for the Cu-rich periphery, and a high strength and hardness in the (Fe, Cr)-rich core. Such an attractive powder is also expected for developing electrical materials and other functional materials.

## 5. Summary

A thermodynamic database of the phase diagrams in copper base alloy systems including Cu–X binary system and Cu–Fe, Cu–Cr, Cu–Ni base ternary systems were developed. This database can provide much information such as phase diagrams, thermodynamic properties, and liquidus projection, etc. and it is indicated that this database is useful tool for the design of structure and functional copper base alloys.

## Acknowledgements

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