[Paper]

Developing Thermodynamic and Kinetic Databases for Cu-Based Alloy Design

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(Received March 19, 2020 ; Accepted April 6, 2020)

Thermodynamic and kinetic databases are indispensable in providing multicomponent phase diagram and phase transformation data for materials design and process optimization. The recent progress in developing TCCU3 and MOBCU3, the thermodynamic and kinetic databases consisting of 30 elements for copper alloys, is presented in this work. The databases have been validated by ensuring their predictive capability in many multicomponent and industrial alloys following the verification of the assessed binary and ternary systems. It is shown that TCCU3 also contains molar volume data, which can be used to calculate density, coefficient of thermal expansion, and lattice parameter, etc. Applications of these databases in simulating solidification, homogenization, and aging processes are demonstrated and discussed. A case study on high/medium entropy brasses is given in the end to highlight the power of the databases in combination with adequate models.

Keywords: *Cu-based alloy, Database, Modeling, Phase diagram, Simulation, Solidification, Precipitation*

1. Introduction

Phase diagram information and phase transformation kinetics are fundamental for materials design and process optimization. Over decades, the Calphad method[1)2)] has proved indispensable in providing multicomponent phase equilibria and phase diagrams in a computational and efficient way. Its tremendous success relies on the simple and efficient scheme it adopts to model the Gibbs energy of each phase in a multicomponent system, hierarchically from binaries to ternaries and occasionally to quaternaries, and then extrapolating directly to higher-order systems. In this approach, the model parameters can be evaluated by considering both experimental observations and ab initio calculation data and using the optimization module PARROT available in Thermo-Calc[3)]. The method later found its way to describing multicomponent diffusivities through modeling of atomic mobilities[4)], which makes it possible to simulate multicomponent diffusion controlled phase transformations using computational tools such as DICTRA[3)], and to model concurrent nucleation, growth, and coarsening processes of precipitates with TC-PRISMA[5)~7)]. Other thermophysical properties, such as volume, thermal conductivity, and viscosity can also be modeled in a similar fashion. In this work, we present our recent progress in constructing Calphad models and developing TCCU3 and MOBCU3, the thermodynamic and kinetic databases consisting of 30 elements for Cu-based alloys. Some verification, validation, and application results of these databases are demonstrated and discussed against available experiments.

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2. Models

The Calphad method[1)2)] has been used in constructing both thermodynamic and kinetic databases for Cu-based alloys. This method depends strongly on available data, which can be any information relates to the targeted properties, being experimental or theoretical. It is essentially a supervised machine learning approach, incorporating fundamental thermodynamic and kinetic principles/models. A prominent feature of the Calphad models is that a multicomponent property can be extrapolated from the property of binary and ternary systems because the effect of higher-order parameters becomes negligible. Let us take the following substitutional regu-

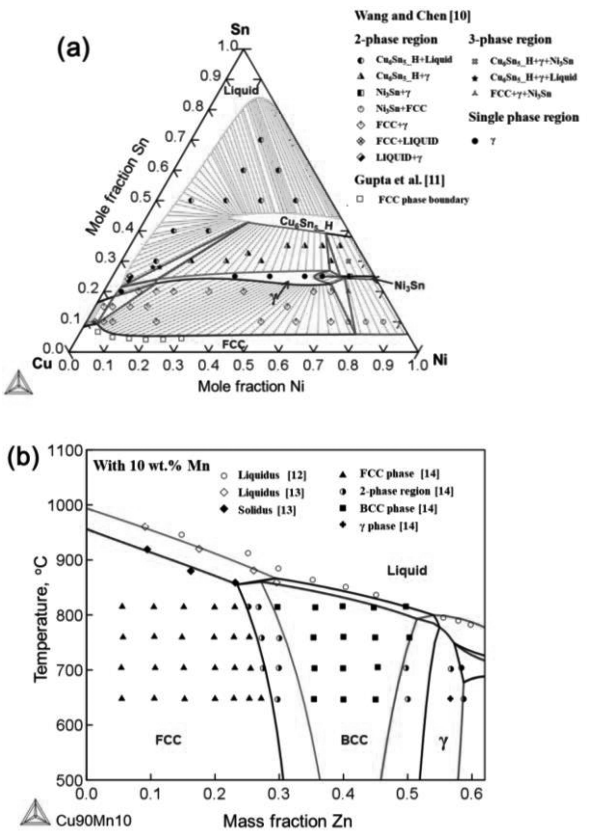

Fig. 1　(a) Calculated isothermal section of Cu-Ni-Sn ternary system at 800℃ along with experimental data[10)11)]; (b) calculated vertical section with 10 wt.% Mn in Cu-Mn-Zn system comparing with experimental data[12)~14)].

lar solution model for the Gibbs energy of a phase in an n-component system as an example,

$$G_m = \sum_{i}^{n} x_i\, {}^{o}G_i + RT \cdot \sum_{i}^{n} x_i \ln(x_i) + \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} x_i x_j L_{ij} + \sum_{i=1}^{n-2} \sum_{j=i+1}^{n-1} \sum_{k=j+1}^{n} x_i x_j x_k L_{ijk} + \cdots, \qquad (1)$$

where G_m is the molar Gibbs energy of a phase with the composition x_i, ${}^{o}G_i$ is the molar Gibbs energy of pure element i, and L_{ij}, L_{ijk} and ⋯ are so-called interaction parameters. The maximum absolute value for those interaction terms occurs at the equiatomic compositions and it decreases exponentially upon the increase of n. Consequently, the higher order interaction terms are less and less important and can be ignored if not absurdly large values for the interaction parameters are adopted.

It should be mentioned that more elaborate models such as the compound energy formalism and order-disorder model[8)] have been used for intermetallic phases. Models for composition and temperature dependences of atomic mobilities and chemical diffusivities have been described in detail in our recently published paper[9)].

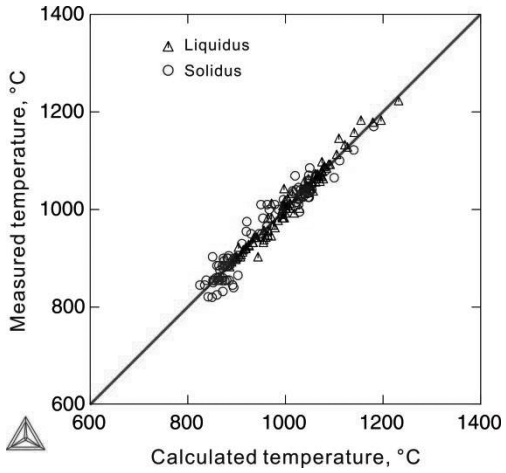

Fig. 2　Comparison of calculated liquidus and solidus temperatures of various commercial copper alloys with those determined by experiments[15)].

Since all sorts of data are used in the process of parameter optimization, the Calphad method possesses another remarkable advantage : the cross checking between different datasets is automatically done and the inconsistences, if any exist, can be revealed. Therefore, the resulting collections of model parameters, i.e. databases, are always self-consistent.

3. Databases

The currently released version of the Cu-based alloys databases are TCCU3 and MOBCU3, which contain 30 elements : Ag, Al, Au, As, B, Be, Bi, C, Ca, Cd, Co, Cr, Cu, Fe, Ge, Mg, Mn, Mo, Nb, Ni, O, P, Pb, Pt, Se, Si, Sn, Ti, Zn, and Zr. In TCCU3, descriptions of 133 binary and 50 ternary systems, where 257 various solution and intermetallic phases exist, have been included. In MOBCU3, assessed atomic mobility data is available for the liquid and fcc solution phases. Coupling TCCU3 and MOBCU3, we can obtain the full matrices of various diffusion coefficients for any composition/temperature and simulate many metallurgical processes, ranging from solidification, homogenization, to precipitation hardening. Verification and validation results for MOBCU3 have already been demonstrated in our recently published paper[9)] and will not be repeated in this work. For TCCU3, here we provide a few illustrations.

3.1 Verification

During the development process and just before the release of the databases, the thermodynamic descriptions for all assessed binary and ternary systems are verified by making calculations of phase diagrams and thermochemical properties for comprehensive comparisons with available experimental or theoretical information. Fig. 1 (a) depicts the calculated isothermal section of the Cu-

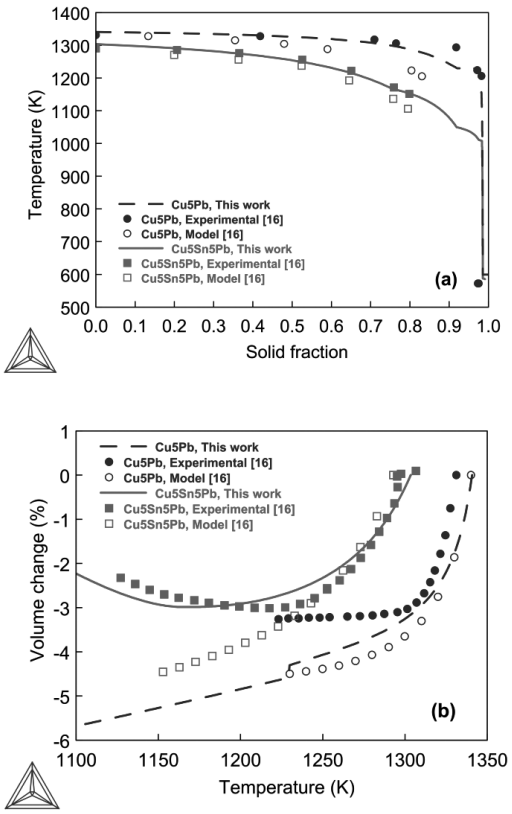

Fig. 3　Predicted and experimental[16] (a) solid fractions and (b) volume changes in Cu-5Pb and Cu-5Sn-5Pb (wt.%) alloys.

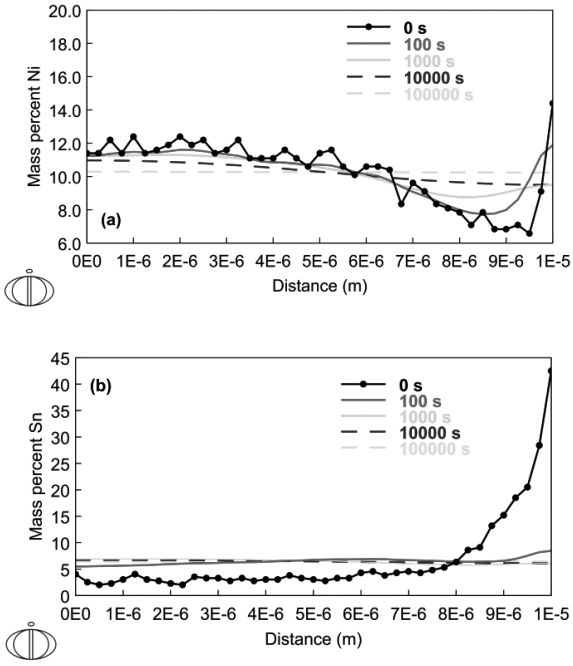

Fig. 4　Simulated evolution of the composition profile of a) Ni and b) Sn in the Cu-9Ni-6Sn (wt.%) alloy homogenized at 1073 K with the experimental data at 0 s from Reference 17.

Ni-Sn ternary system at 800℃. The experimental data from Wang and Chen[10] and Gupta et al.[11] are also presented in the figure, showing a good agreement between calculated and experimental results. Fig. 1 (b) presents the vertical section along 10 wt. % Mn in the Cu-Mn-Zn system together with the reported measurements[12)~14)], and it confirms that most of the experimental data can be reproduced.

3.2　Validation

To validate the database, information about phase transformation, phase amount, phase composition or alloying element distribution during cooling/heating or annealing for various industrial Cu-alloys has been collected and compared with our equilibrium calculation or kinetic simulation results using TCCU3. As an example, the melting and solidus temperatures are critical parameters needed for the determination of processing conditions by industry. The liquidus and solidus temperatures of more than 100 multicomponent commercial copper alloys were calculated to validate the reliability of TCCU3. Figure 2 presents the comparison of the calculated liquidus and solidus temperatures with those from experimental determinations[15)]. For most of the liquidus points, the agreement is excellent. The average difference for the solidus points is slightly larger, but well acceptable considering their larger uncertainty in the measurements.

4.　Applications

Due to space limitations, only four application examples are given below.

4.1　Solidification

Korojy et al.[16)] measured and modeled the solid fraction and volume change during solidification of the Cu-5Pb and Cu-5Sn-5Pb (wt.%) alloys. Using TCCU3 and the Scheil Solidification Simulation module in the Thermo-Calc software package, we can readily calculate these quantities. The results are shown in Fig. 3 together with the experimental and modeling data of Korojy et al.[16)]. As can be easily seen, the predicted solid fraction evolution agrees very well with the experimental data. Our simulated solidification shrinkage for the Cu-5Sn-5Pb (wt.%) alloy catches the same behavior as the measurement, while Korojy et al.'s model cannot. This success indicates the high fidelity of our thermodynamic database TCCU3.

4.2　Homogenization

As-cast chemical segregations are usually inevitable and have to be reduced or removed by the homogenization heat treatment. This process can be simulated by using DICTRA[3)] in order to optimize the temperature

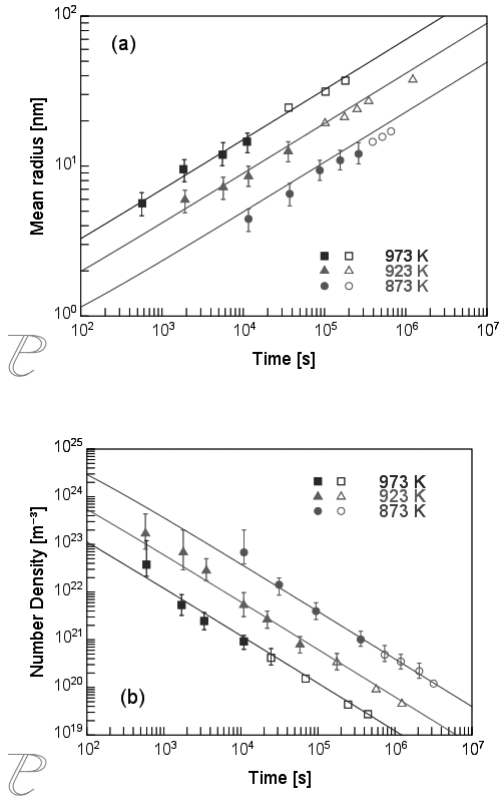

Fig. 5　Simulated and experimental[18] (a) mean radius and (b) number density of fcc Co-Fe precipitate in Cu－0.68 at.%Co－1.52 at.%Fe alloy annealed at 973, 923, and 873 K. The solid symbols are for spherical particles ; and the open symbols are for cuboid particles.

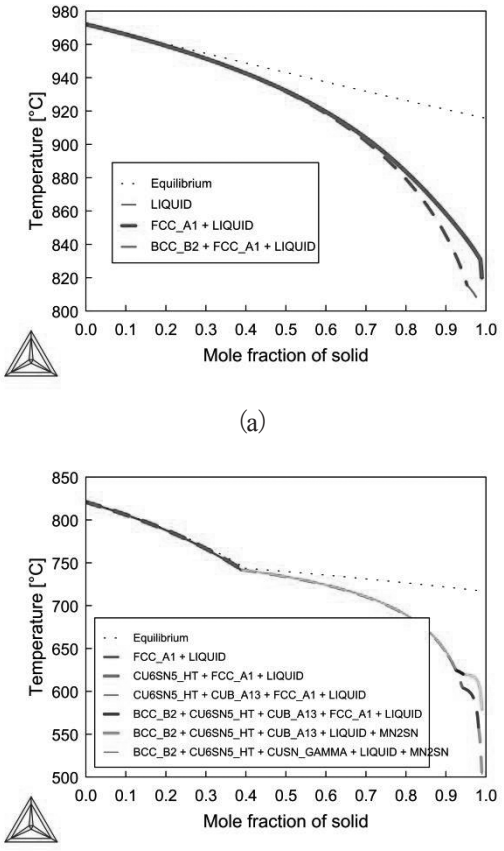

Fig. 6　Solidification simulation results for high/medium entropy brasses a) $Cu_2ZnMnNi$ and b) $Cu_2ZnMnNiSn_{0.45}$.

and time for the sake of energy efficiency. Fig. 4 shows the simulation results for the temporal evolution of the composition profiles of Ni and Sn in the as-cast Cu-9Ni-6Sn (wt.%) alloy annealed at 1073 K. The initial experimental composition profile and the secondary dendrite arm spacing are taken and estimated, respectively, from the work by Basak and Krishnan[17]. According to our prediction, while the inhomogeneity of Sn almost disappears by 1000 s, a slight segregation of Ni remains until 10000 s because of the slower diffusion of Ni.

4.3　Precipitation

Precipitation hardening is the most common heat treatment process that makes materials stronger. The strengthening effect depends on the resulting particle size and particle number. With a combination of thermodynamic and kinetic databases, the average size and number density, as well as volume fraction of a precipitate, can be predicted by using TC-PRISMA[5)～7)9)], the Precipitation Simulation module in Thermo-Calc for simulating concurrent nucleation, growth, and coarsening of particles. In Fig. 5, the particle size and number density at various temperatures were obtained for the fcc Co-Fe precipitate in alloy Cu－0.68 at.% Co－1.52 at.% Fe with the use of the TCCU3 and MOBCU3 databases. In our simulation, homogeneous nucleation is assumed and an interfacial energy value of 0.22 J/ m^2 is adopted, all based on Watanabe et al.'s experimental observation[18]. The excellent agreement between our predictions and Watanabe et al.'s measurements validates both the thermodynamic database TCCU3 and the kinetic database MOBCU3. It proves again the unique power of the Calphad software and databases in multicomponent alloy design and process optimization.

4.4　High/Medium Entropy Brasses

Traditional alloys usually consist of a single principal element with the addition of small fractions of other alloying elements. Not surprisingly, many existing databases reflect this fact accordingly. In contrast to the traditional practice, the TCCU3 and MOBCU3 databases were developed in a more ambitious way where not only the phase equilibria around the corner of the principal element were included, but also those over the whole composition range in each assessed binary and ternary system. This means the databases could also be suitable for exploring compositionally concentrated regions in a multicomponent system.

Table 1 Simulated and experimental results on the constitutive phases in as-cast high/medium entropy brasses.

	Scheil	Scheil+BD*	Exp.[19]
CuZnMnNi	Fcc+Bcc	Fcc+Bcc	Fcc+Bcc
Cu_2ZnMnNi	Fcc+Bcc	Fcc	Fcc
Cu_3ZnMnNi	Fcc+Bcc	Fcc	Fcc
Cu_4ZnMnNi	Fcc+Bcc	Fcc	Fcc
CuZnMnNi$Sn_{0.2}$	Fcc+IMs**	Fcc+IMs**	Bcc
Cu_2ZnMnNi$Sn_{0.45}$	Fcc+IMs**	Fcc+IMs**	Fcc+IMs**

*BD = Back diffusion　　**IMs = Intermetallics

Recently, Nagase et al.[19] designed several high/medium entropy brasses according to some reported empirical rules and examined experimentally the constituent phases in the as-cast alloys. As we all know today, the configurational entropy rarely dominates phase stabilities, and it is the Gibbs energy that determines the stability of a thermodynamic phase. A Calphad thermodynamic database consists of the Gibbs energy as a function of composition and temperature over the whole composition range for each phase and is ideal for predicting the relative stability of different phases in the equilibrium state. In reality, many high/medium entropy alloys in their as-cast state without long-time annealing are in a non-equilibrium state, and in this case, kinetic databases can play an important role. Here we try to simulate the solidification process of six alloys studied by Nagase et al.[19] and compare the predictions with measurements. In Fig. 6, the solidification curves (temperature vs. fraction of solids) are plotted for the alloys Cu_2ZnMnNi and Cu_2ZnMnNi$Sn_{0.45}$ as an example, while those for CuZnMnNi, Cu_3ZnMnNi, Cu_4ZnMnNi, and CuZnMnNi$Sn_{0.2}$ are omitted due to limitations of space. The dotted curves are the equilibrium calculation results ; the dashed curves are the Scheil simulation results ; and the solid curves are the results from using the modified Scheil model[20] implemented in Thermo-Calc since version 2020a. This model uses both thermodynamic and kinetic data from TCCU3 and MOBCU3, and takes into account the back diffusion in the primary solid phase in an effective and efficient way. It runs much faster than a DICTRA simulation. As expected, the Scheil with back diffusion results always lie between two extreme scenarios : the equilibrium one assuming infinitely fast diffusion in both the liquid and solid phases and thus always attaining equilibrium and the conventional Scheil one assuming infinitely fast diffusion in only the liquid phase but no diffusion in the solid phases. Comparing with Nagase et al's experimental results[19] in Table 1, we can easily see that the Scheil with back diffusion model shows significant improvement over the conventional Scheil model. It should be pointed out that both models are not successful with regard to the alloy CuZnMnNi$Sn_{0.2}$, which is probably not a surprise considering the fact that not all constitutive ternary systems in the Cu-Zn-Mn-Ni-Sn quinary system are assessed and included in the databases. An improved prediction is expected when the missing ternaries are available in the coming upgrade of the databases.

5. Summary

A thermodynamic database TCCU3 and its compatible atomic mobility database MOBCU3 have been developed for Cu based alloys. These databases can be applied to calculate accurate stable and metastable phase equilibria, and simulate almost all important physical metallurgy processes, such as solidification, homogenization, and precipitation. A bold application is also demonstrated for the design of high/medium entropy brasses.

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