THERMODYNAMIC DATABASES FOR ALLOY PHASE DIAGRAMS

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ABSTRACT

Thermodynamic databases for phase diagrams recently developed by the authors' group are reviewed. These databases contain a set of thermodynamic parameters in some alloy systems and offer stable and metastable phase diagrams and thermochemical properties of each phase by coupling the computer software. This kind of approach referred as CALPHAD method will be most useful for materials design and development of materials.

Introduction

Phase diagrams have played an important role for understanding and development of various kinds of materials so far. However it has become difficult to construct a whole range of the phase constitution just only by experimental methods because a large amount of time and job is required to determine the phase relations, especially in multicomponent systems. That is a main reason a computer calculation of phase diagrams has recently been performed and some alloy databases have been developed in the European countries and the United States[1].

In the general case, these databases are coupled with the computer program of phase diagrams and construct the integral thermochemical database(ITD). Main purpose of the ITD is to give a reliable information on the phase relationship and thermochemical properties to the users quickly. Since the experimental information of ternary or higher order systems are generally limited, it would be very useful if phase equilibria in such systems could be predicted thermodynamically. In this kind of integral system, the large scale of thermodynamic databases is being constructed under an international collabolation during the last decade.

In this paper, some thermodynamic databases for several practical materials developed by our group are presented.

Calculation of Phase Diagrams by the CALPHAD Approach

Because a phase diagram is the manifestation of the thermodynamic properties of a system, the correct set of thermodynamic descriptions for the individual phases yield a calculation of more reliable phase diagram than the hand-drawn ones. This method is so called the CALPHAD (CALculation of PHAse Diagram) approach[2]. To compute phase equilibria in the multi-component system, it is necessary to obtain the thermodynamic functions in each phase precisely by careful modelling of the Gibbs energy functions in the objective system. In the current research, the ordinary regular solution model and sublattice model[3] are usually adopted considering the simplicity of handling of the model and the expansibility to the higher order systems.

Thermodynamic parameters necessary to consist the Gibbs energy functions are evaluated based on the various experimental information on phase boundary compositions, specific heats, activities, heats of formation and so on. Once the thermodynamic properties were known, it would be possible not only the temperature-composition phase diagrams but also many other metastable extensions of phase equilibria, the driving force of precipitation, effect of high pressure on the phase boundaries and so on.

Examples of the Thermodynamic Databases and Calculations

(1) Microalloyed Steels

A small amount of additives like Nb, Ti and V to the steels has been found to retard the coarsening of the grains by the pinning effect of precipitation of the fine carbides or nitrides, which causes the significant increase in the strength of the materials. However, precise phase diagrams needed for the microstructural control of microalloyed steels have not been well established. This is mainly due to difficulty of the determination of the solubility of the precipitates by a conventional experimental method. CALPHAD approach for the phase diagrams of microalloyed steels based on the synthesis and analysis of the limited experimental information on phase boundaries and thermodynamic data have been carried out[4-8].

Fig.1 (a) through (c) show the effect of addition of Nb, Ti and V on the carbon limitation of the austenite single phase region in the Fe-C binary phase diagram, which reveals that a small amount of the order of 0.01wt% addition of these elements makes the significant effect on the phase boundaries. Effect of P, S and B on the austenite single phase region is also presented in Fig.1(d) through (f), respectively[7,8]. In this respect, a construction of phase diagram by the CALPHAD method is regarded a powerful tools to obtain the exact phase relationship in the steels.

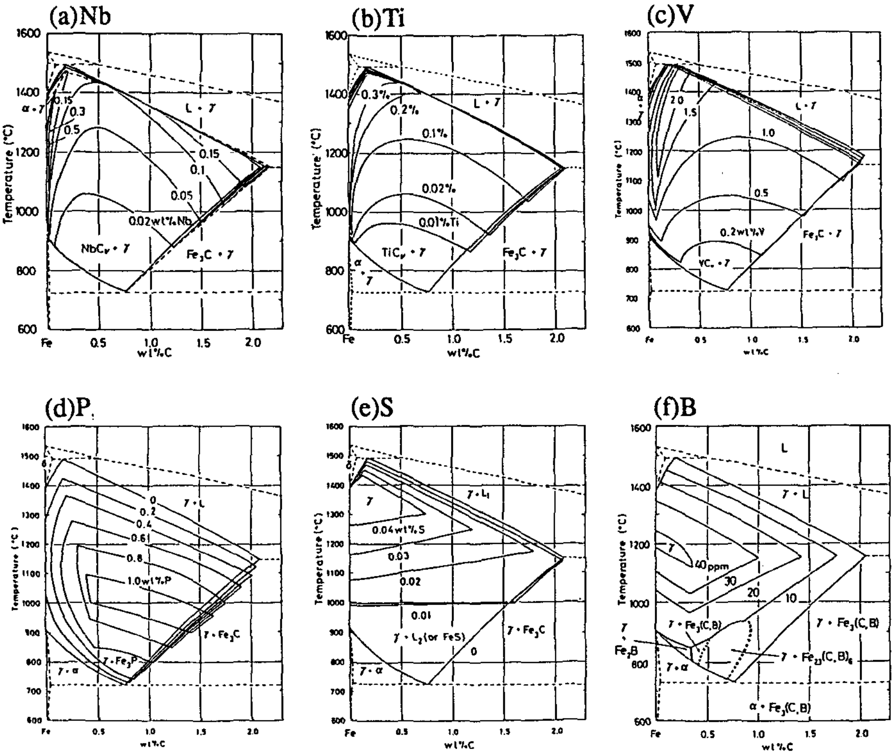

Fig. 1 Effect of some elements on the carbon limitations of the austenite single phase region in the Fe-C binary phase diagram. (a)Nb, (b)Ti, (c)V, (d)P, (e)S and (f)B.

(2) Stainless Steels

The major phase constituents of stainless steels are ferrite(α), austenite(γ) and martensite(α') and there have been some attempts to predict these phase constitutions using Cr and Ni equivalents. The Schaeffler's diagram, for instance, has widely been used. The CALPHAD analysis of phase diagram in the Fe-Ni-Cr base alloys containing various elements such as C, N, Mo, Mn, Si and Al enable to predict the more reliable phase relations between the ferrite, austenite, liquid and some carbides.

Fig.2 (a) shows an example of the calculated vertical section diagrams for the typical duplex stainless steel. The figure shows that this kind of stainless steel has a wide range of (ferrite+austenite) two-phase region, and thus the alloy compositions can be selected easily to obtain variation of volume ratio between these two phases. A distribution behavior of these elements between ferrite and austenite in the steel is calculated in Fig.2 (b), in which a comparison with the experimental values is included.

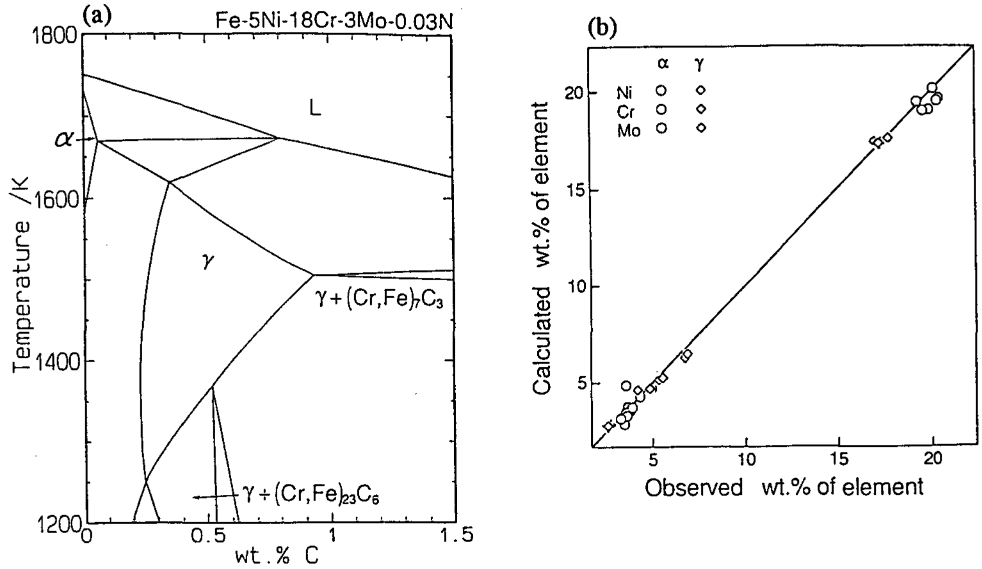

Fig.2 Thermodynamic calculation using the database for the stainless steels, (a) vertical section diagram and (b) distribution coefficient between ferrite and austenite in the Fe-5%Ni-18%Cr-3%Mo-0.03%N-C steel.

(3) III-V and II-VI Alloy Semiconductors

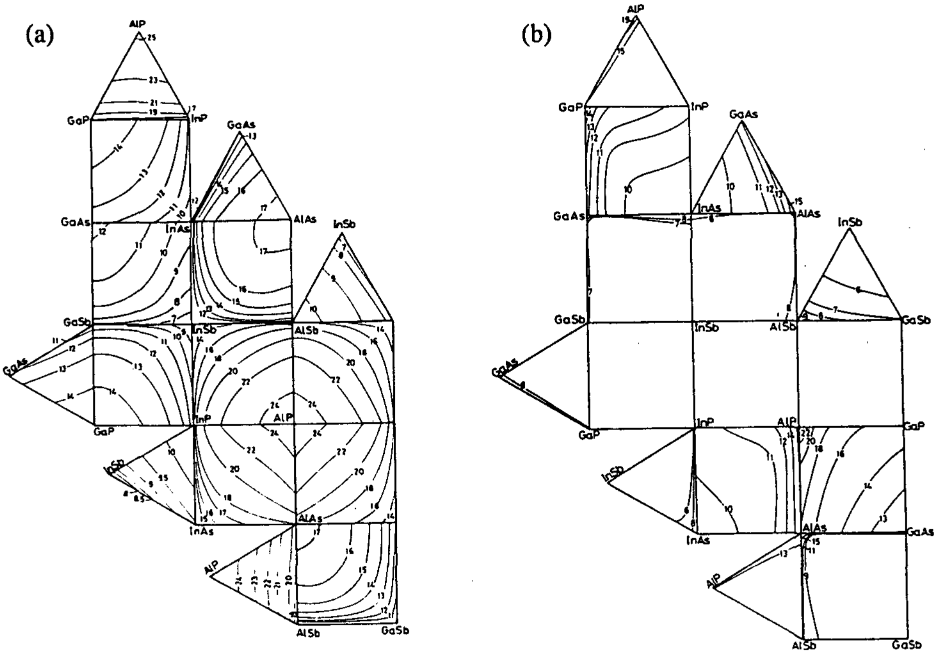

Fig.3 (a) Liquidus and (b) solidus surfaces of the 15 III-VI quaternary systems.

Multicomponent alloy semiconductors are being used increasingly in application to optoelectronic devices, because their lattice constants and band gap energies can be easily changed by selecting the proper compositions of alloys. In both the liquid phase epitaxy (LPE) and vapor phase epitaxy (LPE) techniques for growing alloy semiconductor crystals, phase diagrams play a key role in controlling the chemical composition of the crystals. For instance, phase equilibria between liquid and solid is the basis of the LPE growth. Also, it has been recognized that the existence of a miscibility gap has a significant problem because it prevents the growth of a uniform solid solution. However, experimental data of the phase equilibria are limited to a very restricted region of temperature and composition, especially in multicomponent alloy systems. Thus, if phase equilibria could be predicted with fair accuracy, it would be useful for the practical design of alloy semiconductors.

In the circumstances, the database has been coupled with the simple calculation program to obtain the phase equilibria between the solid compounds and the liquid phase[9]. This system has three parts: (i) a database containing thermodynamic parameters, (ii) a computer program for calculating phase equilibria, (iii) a computer program for a graphic display on the personal computers. Lattice parameter and band gap calculations are also included as a supplement.

Typical examples of the calculation on the liquidus and solidus surfaces of the 15 III-V quaternary systems are shown in Fig.3(a) and (b), respectively[9]. Fig.3(b) shows that a compound phase with various compositions can be easily obtained from the III-III-P-As, III-III-III-Sb and III-III-III-As systems,i.e., the solid solution of the compound phase is widely formed in these systems. Isothermal sections of the miscibility gaps in the 15 II-VI quaternary systems are presented in Fig.4[10]. The origin of miscibility gap in (A,B,C)X type compounds (triangular shapes in Fig.4) is mainly attributed to the difference in lattice parameters of the component compounds, while in the (A,B)(X,Y) type compounds (square shapes in Fig.4) it is attributed mainly to the difference in relative stabilities of the binary compounds.

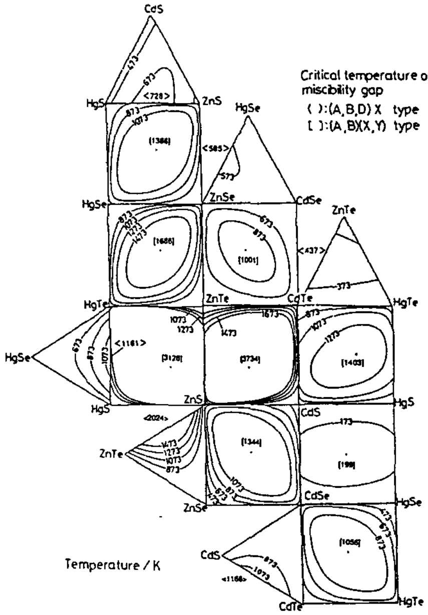

Fig.4 Isothermal Sections of the miscibility gaps in the 15 II-VI quaternary systems

(4) Ni-base Superalloys

Phase equilibria in the Ni-rich portions of the Ni-base superalloys have fundamental interest for the alloy design. The γ' phase contributes a major part of strengthening by the well-known anomalous positive temperature dependence of flow stress, while β phase is used for the surface coating because of its high oxidation resistance. Therefore phase relationship concerned with the ordered phases of Ni aluminides, γ'(Ni_3Al:L1_2 structure) and β(NiAl:B2 structure) play a key role on the practical design of high temperature materials. Systematic investigations have been performed not only on the experimental determination of phase relation between γ, γ' and β phases by diffusion couple technique but also on the thermodynamic analysis.

Based on the information, construction of the database for phase diagrams of Ni-base superalloys is now in progress. By using this, it is possible to compute the phase equilibria between the γ(A1), γ', η(Ni_3Ti:D0_{24}), β and Heusler(L2_1) phases in the ternary Ni-Al-X (X=Ti,Fe,Cr,Co,Mn etc.) and multicomponent systems. Figs.5 and 6 show the isothermal section diagrams of Ni-Al-Ti and Ni-Al-Cr ternary systems, respectively[11].

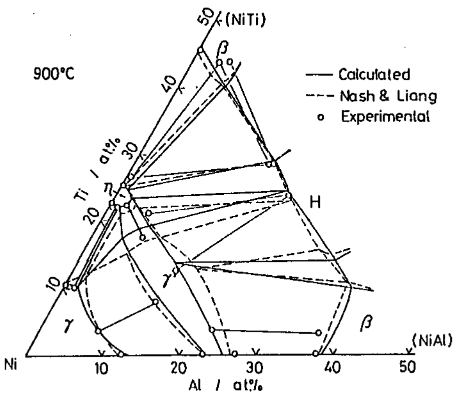

Fig.5 Isothermal section diagram of Ni-Al-Ti ternary system at 900°C.

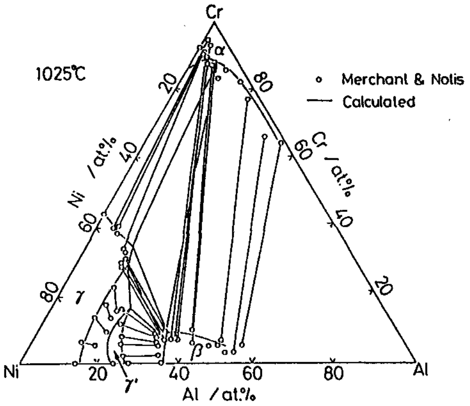

Fig.6 Isothermal section diagram of Ni-Al-Cr ternary system at 1025°C.

(5) Carbonitrides Ceramics Materials

Carbides and nitrides composed of IVa (Ti,Zr,Hf) and Va(V,Nb,Ta) elements have a NaCl type of structure, which show the characteristic features like the high melting point, high hardness, high elasticity and high thermal conductivity. Being made a best use of these characters, the compounds have been applied to the coating materials on the tool steels, sintering composites as Cermet and so on.

Recently these carbides and nitrides tend to be used as complex solid solutions on the purpose of obtaining better wear resistance. However, few experimental works on the phase relations and thermodynamic properties can be found in the complex materials due to the difficulty to prepare the specimens and to obtain the reliable data. To avoid the difficulty to attain the equilibrium state due to sluggish diffusion in the carbide and nitride, the phase equilibria of carbonitrides has been investigated through the iron matrix at the usual experimental temperatures. Since solubility of Fe in the NaCl type carbonitrides is negligible small, the existence of Fe does not affect the phase equilibria in the composite materials and this method has a great advantage for obtaining the equilibrium state rapidly. By using the experimental results, the database for carbonitrides ceramics materials has been developed.

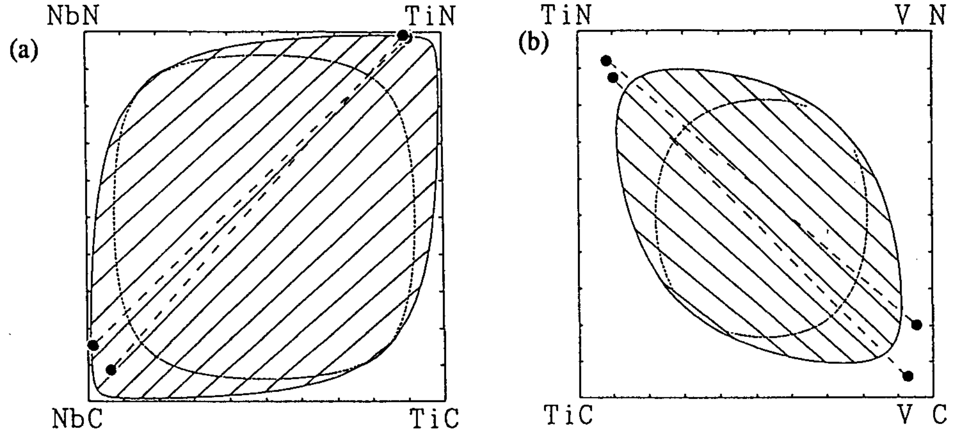

Fig.7 Miscibility gaps in the (a) (Ti,Nb)(C,N) and (b) (Ti,V)(C,N) quaternary systems at 1000°C .

Fig.7 (a) and (b) are the calculated miscibility gaps in the (Ti,Nb)(C,N) and (Ti,V)(C,N) quaternary systems at 1000°C, respectively. In the figures the solid circles are the experimental points examined by the method. The dominant factor of these immiscibilities is attributed to the difference of the stabilities between the components, as well as for II-VI alloy semiconductors.

(6) Solder Materials

The Pb-Sn alloys are generally used for the solder materials. However, to endure a variety of imposed conditions, several additional elements are contained in the microsoldering materials employed in the modern electronic devices. For instance, Bi and Sb or In are the representative additives to the solder alloys. In these devices, melting points of the solder alloys should be carefully selected, and thus multi-component alloys of which melting points vary widely are required in practice.

The database for the solder materials can calculate the melting points, phase relations and thermochemical properties of a certain alloy immediately, so it presents basic solutions to the selection of solder alloys. Fig.8 shows the liquidus surface of the Sn-Bi-Sb ternary alloy calculated by coupling the database with the phase diagram computation software Thermo-Calc[12] developed in Sweden.

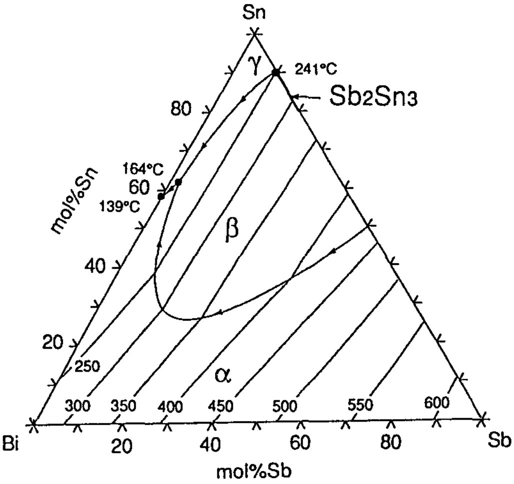

Fig.8 Liquidus surface of the Sn-Bi-Sb ternary system.

Conclusions

This paper has presented a review on the thermodynamic databases recently developed by our group. The CALPHAD method employed here gives us a powerful technique to construct the multi-component alloy phase diagrams of the practical materials. Therefore there is no doubt that this kind of computer generated phase diagram will act as a guidance to the materials design and development in future.

However it is worth noticing that whether the computer assisted calculation will be successful or not depends strongly on the selected experimental data and a careful assessment piled up step by step and also depends on the international collaboration to extend the network of database.

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