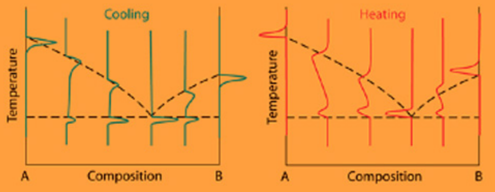
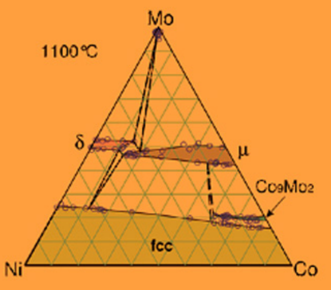
Methods for Phase Diagram Determination





J.-C. Zhao (Editor)

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Preface

When I was approached by Elsevier to put together a book on phase diagram determination, I immediately responded with a positive answer and a book plan. Such a book, in my opinion, is long overdue. There have been several books in recent years on thermodynamic calculations of phase diagrams using the CALculation of PHAse Diagrams (CALPHAD) approach, but only a thin conference proceedings volume on *Experimental Methods of Phase Diagram Determination* edited by J.E. Morral, R.S. Schiffman, and S.M. Merchant and published by the Minerals, Metals and Materials Society (TMS) in 1994. This new book will help offset such imbalance, and emphasize the importance of experimental determination of phase diagrams. Since the Gibbs energy functions in CALPHAD assessments are optimized from experimental phase diagrams and a few thermodynamic measurements (when available), accurate experimental phase diagrams are essential for reliable CALPHAD modeling that is one of the foundations for computational design of multicomponent materials.

Phase diagram determination is both a scientific study and an art in a certain sense, because experience and good practice can play an important role in the quality of the results. The feeling that the "art" part is gradually fading away has been bothering me for quite some time. Hopefully, this book will archive some of the art.

Another important consideration in putting this book together is the need for a comprehensive reference book on the subject, which surprisingly did not exist. I was very encouraged by the positive comments from anonymous reviewers on the book plan. Their comments include words such as "As for the subject matter of the proposed book, indeed it is high time to have an up-to-date book on that subject, which is very central to MSE [materials science and engineering]". An effort has been made in creating this reference book to allow researchers to quickly find various methods in a single volume and to select specific methods for their own research. This volume also serves as a state-of-the-art overview of the subject. Each chapter tries to provide descriptions of the techniques, their underlying principles, their pros and cons, interpretation and reliability of the results, and a number of real examples. The book also covers determination of phase diagrams containing order–disorder transitions, magnetic transitions, as well as phase diagrams in non-metallic systems such as ceramic systems, slags, and hydrides. Traditional well-known techniques such as the equilibrated alloy method and recent developments such as diffusion multiples are covered. The editor hopes this book will serve as an introduction for researchers new to the field and as a refresher for the experienced researchers.

In Chapter 1, Smith provides an introduction to phase diagrams and to this book. He starts with a brief history of the establishment and early application of the phase rule from Gibbs' thermodynamics, and the developments in the twentieth century applying optical and electron microscopy as well as X-ray diffraction to phase diagram experimental inputs are then discussed to emphasize the importance of reliable experimental data as expressed in the classic cliché, *garbage in equals garbage out*. The phase rule and its importance in phase diagram construction are then discussed along with basic rules for generating reliable experimental data. Also discussed in this chapter are some past efforts in compilation of phase diagram data.

Chapter 2 stresses the importance of understanding the basic phase transformation kinetics in determination and assessment of phase diagrams. The cooling process always shifts the phase transformation temperature away from the equilibrium phase boundary toward lower temperatures, and the opposite is true for the heating process. Real examples are used to show that the shift can be very pronounced for solid–solid phase equilibrium transitions at low temperatures; and the heating data are no better than the cooling data if equilibrium is not reached at low temperatures before heating. The difficulty associated with slow decomposition of some high-temperature phases, especially intermetallic compounds, is also discussed with real examples. This problem has not been adequately discussed before. The slow decomposition kinetics is often manifested as a widening of the composition region of a stoichiometric phase or line compound in a phase diagram. This chapter emphasizes that caution must be used in the determination of phase diagrams at relatively low temperatures.

Okamoto and Massalski, two of the most experienced experts in the world on phase diagram assessments and compilations, illustrate the many correct and incorrect phase diagram features they have seen when performing phase diagram assessments. Based on previous publications of theirs, Okamoto and Massalski use many real examples in Chapter 3 to explain the correct phase diagram topology based on thermodynamics. It is important to understand these features in order to correctly construct phase diagrams from experimental observations and to avoid mistakes that can be easily made when drawing phase boundary lines across experimental data points.

Zhan, Du and Zhuang in Chapter 4 explain the most widely used method – the equilibrated alloy method – for phase diagram determination. They use very simple examples to illustrate the step-by-step process, including alloy preparation, homogenization heat treatment, and determination of phases and phase equilibria via isothermal (static) measurements or cooling/heating (dynamic) experiments. Ample detail is provided to ensure high-quality alloy preparation through induction melting, arc melting, or a powder metallurgy route. The heat treatment process has also been discussed in detail, especially regarding the necessity for long-term heat treatment for low-temperature solid–solid phase equilibria, and the quenching process that is often used to freeze the high-temperature equilibria for analysis at ambient temperature. The determinations of the Cu–Nd binary system, the Al–Be–Si and the Al–Mn–Si ternary systems, and the Al–C–Si–Ti quaternary system are then shown as real examples. Common issues and solutions associated with the equilibrated alloy method are discussed at the end of the chapter to ensure high-quality data.

Chapter 5 is essentially the NIST (National Institute of Standards and Technology) guide to DTA and heat-flux DSC measurements of alloy melting and freezing. Several years in drafting, this chapter provides the most comprehensive solidus of phase diagrams. The chapter along with its appendices provides valuable information and insight into the DTA and DSC processes, especially the fundamental thermodynamics and kinetics governing these processes. This chapter is a "must read" for those who use or intend to use DTA and DSC measurements to construct phase diagrams.

Kodentsov, Bastin and van Loo in Chapter 6 describe the application of diffusion couples in phase diagram determination. They first explain the principles of the diffusion couple method, the process of making diffusion couples, and basics of the electron probe microanalysis (EPMA). Real examples are then used to illustrate two types of diffusion couples that are used for phase diagram determination, namely the semi-infinite ones and "sandwich" diffusion couples with a thin foil in the middle. The latter configuration is not widely used, but has high potential and advantages in both efficiency and simple sample fabrication. They discuss in detail the various error sources and methods to correct them, again using many real examples encountered in their laboratory. Their examples of missing phases and impurity stabilized extra phases are especially worth noting. Diffusion couples are a powerful way to determine phase diagrams, especially high-temperature isothermal sections. This chapter is a "must read" for those considering using this methodology.

In Chapter 7, a novel diffusion-multiple approach is introduced with real examples. Using a hot isostatic pressing (HIP) process, one can put several pieces of metals together to form several diffusion couples and triples in a single "diffusion multiple" to determine isothermal sections of several systems. The key considerations and steps in making good diffusion multiples are discussed first to stress the importance of sample preparation. The analysis steps involving imaging and phase identification, EPMA, and extraction of tie lines are then discussed. It is shown that two plots, one composition profile (composition–distance plot) and one composition path (composition–composition plot), are essential for reliable interpretation of the experimental results obtained from very concentrated areas of diffusion multiples. The practices used to reduce the chances of errors are discussed at the end of the chapter. By following the many recommendations specified in this chapter, one can determine phase diagrams with high efficiency while maintaining high quality.

Chang and Yang in Chapter 8 describe a novel approach in accelerated phase diagram determination/assessment by coupling CALPHAD modeling with selected experiments. This is a very important and promising direction for multicomponent phase diagram research. Taking advantage of available thermodynamic assessments of many binary (and some ternary) systems, one can perform a preliminary assessment of a ternary (or a higher order) system by assuming there are no ternary (or higher order) compounds and that the solubilities of the elements in the binary (or the higher order) compounds are negligible. Such an approximate assessment is used to predict a phase diagram of interest which guides the selection of key alloy compositions to maximize the significance of the input data points. The phase equilibrium information obtained from the selected alloys is then used to improve the thermodynamic model parameters for better description of the ternary (or the higher order) system. The authors use real examples such as Mg–Al–Sc and Mo–Si–B–Ti systems to illustrate how the process works. Some systems may need multiple iterations to develop a reliable thermodynamic description. This methodology