1 Introduction

Contents

For millennia, the advance of human civilization has been closely linked to materials available from the Stone Age through the Bronze and Iron Ages and into the current Information Age. The Information Age is associated with a revolution of technology resulting from significant advances in Si-based semiconductors and other materials. In particular, since 2018 the world has been significantly influenced and changed by the fifth-generation technology standard for cellular networks (5G). Such a network enables users to connect virtually with almost everyone and everything, delivering data among users and machines with much higher speed, lower latency, more reliability, and better availability compared to 4G networks. 5G networks have been utilizing a wide variety of materials, including metals, ceramics, plastics, composites, and materials with low dielectric, high thermal conductivity, and high electromagnetism. In consequence, the continuing technological advancement in current society is strongly dependent on advanced engineering materials that satisfy the ambitious requirements of new products.

The earliest documented materials were the Cu–Sn alloys in ancient China during the Bronze Age (Chang, 1958). The compositions of the "six alloys" (Cu–Sn alloys with the compositions of 17, 20, 25, 33, 40, and 50 wt.% Sn) were determined purely via trial-and-error experiments to guide the casting of various civil and military tools. It is unbelievable that such an empirical approach has persisted for more than three millennia. With the development of computers as well as software and various databases (such as thermodynamic and diffusion databases), computational design of engineering alloys has demonstrated its significant role in efficient developments of new alloys since Kaufman and Bernstein published the book entitled *Computer Calculations of Phase Diagrams* in 1970 (Kaufman and Bernstein, 1970). The interested reader could refer to the following selection of recent (mainly edited) books for more details in the field of computational design (Ashby et al., 2019; Bozzolo et al., 2007; Da Silva, 2019; Horstemeyer, 2012; LeSar, 2013; Raabe et al., 2004; Saito, 1999; Shin and Saal, 2018).

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1.1 Definition of a Few Terms Used in Computational Design of Materials

The goal of this book is to introduce the basic methods used in computational design of engineering alloys and to demonstrate several step-by-step case studies for computational design of these alloys. To facilitate reading, a few most frequently used terms are defined in a more precise way before we proceed to discuss computational design of engineering alloys.

A **model** is an idealization of an actual phenomenon, i.e., an approximate description of a phenomenon based on some empirical and/or physically sound reasoning. A model often begins with a set of concepts, and then it is usually transcribed into mathematical equations from which one can calculate some quantities with a desire to describe some phenomena. For example, a thermodynamic model is usually established according to the crystal structure of one phase in order to calculate its Gibbs energy. Thermodynamic models expressed in different mathematical forms contain adjustable parameters that can be optimized to reproduce many kinds of experimental phase diagrams and thermodynamic properties (activity, heat capacity, enthalpy of mixing, and so on) as well as theoretical data such as first-principles computed enthalpy of formation. The main focus of a model is to create an idealization of an actual phenomenon within an accepted accuracy instead of a strictly true fundamental description of the phenomenon. One may argue that any model is only a picture of reality – not reality itself.

Simulation is a numerical calculation for a modeled system with respect to external and/or internal fields as well as applied constraints. It requires algorithms based on the models and numerical solution strategies that are the backbone of simulation software. Consequently, the simulations are performed by subjecting models to inputs and constraints for the sake of describing an actual phenomenon, such as the solidification of an alloy. The accuracy of a simulation for an actual phenomenon depends on several factors, such as the adequacy of the model, the accuracy in solving sets of equations numerically, and the reliability of input parameters in the equations.

A **database** is an organized set of data that is stored in a computer and can be accessed, managed, updated, and used in many ways. Various types of databases are reported for the systems of interest, resulting in different definitions for the databases. According to a recent analysis for engineering alloys (Li et al., 2018), three kinds of databases are defined for these alloys: the original technological database, the evaluated technological database, and the scientific database. The first type of database is usually a compilation of one or several typical quantities, such as hardness and toughness during one or several processes, such as homogenization and age hardening. The second type of database is the critically evaluated technological database, eliminating inaccurate values. The last type of database (i.e., the scientific database) is the most important database for engineering alloys. This scientific database is based on physically sound models, and the parameters in the database are obtained by fitting accurate experimental and/or theoretical data for targeted systems. Thermodynamic and thermophysical databases (for example, diffusion coefficient, interfacial energy, and thermal conductivity) are the typical scientific databases.

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Armed with powerful materials design software, these databases can be utilized to design alloy composition, optimize the heat treatment schedule, simulate microstructural evolution, and predict mechanical and other properties.

The term **materials design** may have different meanings for different readers. Olson presented a very deep and wide definition for this term (Olson, 1997; 2000). In view of the four cornerstones (i.e., processing, structure, property, and performance) in materials science and engineering, **our definition for materials design** is to establish relationships among these four cornerstones through computationally based approaches implemented with experimental and/or empirical approaches for the sake of yielding materials with the desired sets of properties and performances to meet the needs of users. Materials design will be more powerful when modeling and simulation tools are integrated with experiments, as highly stressed in integrated computational materials engineering (ICME) (ICME, 2008) and the Materials Genome Initiative (MGI) (MGI, 2011), which will be briefly described in the next subsection.

1.2 The Past and Present Development of Computational Design of Engineering Materials

The computational design of engineering materials dates back to 1970, when the calculation of phase diagrams (CALPHAD) approach was developed by Kaufman and Bernstein (Kaufman and Bernstein, 1970), who advanced the pioneering work on phase diagram calculations by Van Laar (1908) and Meijering (1950). The major justification for such a statement is that almost all engineering materials are multicomponent and multiphase systems, and the CALPHAD approach is the only one that can deal with such complex systems.

However, it should be mentioned that before the birth of the CALPHAD approach, there were a few important milestones for alloy design, such as the Hume-Rothery rule (Hume-Rothery, 1967). This rule utilizes information about atomic size, valence, electronegativity, and crystal structure to predict phase formation, being applicable to both solid substitutional and interstitial solutions. Due to its empirical feature, this rule can only be used as component selection criteria instead of alloy composition optimization, which is usually the first step for computational design of engineering alloys.

Another approach for alloy design is the phase computation (PHACOMP) method, which was developed by Boesch and Slaney (1964). This method utilizes the average number of electron vacancies in the metal d band above the Fermi level to predict phase stability of the harmful topologically close-packed (TCP) phases. One modification for the original PHACOMP method is the so-called d orbital method (Matsugi et al., 1993), in which the d orbital energy level of alloying transition metal and the bond order are used as indicators for the occurrence of TCP phases. Although the electron vacancies in the d orbital method can be obtained through quantum mechanical electronic structure calculations, the average number of electron vacancies and the bond order are only approximate, affecting the validity of

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the method. One more obvious shortcoming for the PHACOMP method and its other revised form (Morinaga et al., 2003) is that the criterion for judging phase stability is independent of temperature. Due to the preceding drawbacks, the PHACOMP method and its modified form cannot be used for design of multicomponent and multiphase engineering alloys in which temperature dependence of phase stability should be considered.

This is why we consider the aforementioned book entitled *Computer Calculation of Phase Diagrams* by Kaufman and Bernstein (1970) as the outstanding milestone for computational design of engineering alloys. This book leads to the birth and development of the CALPHAD approach. According to Lukas et al. (2007), a comprehensive definition for CALPHAD is that the "CALPHAD method" means the simultaneous use of all available experimental and theoretical data to assess the parameters in Gibbs energy models selected for individual phases. Armed with powerful software tools, such as Pandat (www.computherm.com) and Thermo-Calc (www.thermocalc.com), which are based on the principles and concepts of thermodynamics, this method can be used to calculate phase diagrams and various thermodynamic properties in multicomponent systems within all the composition and temperature ranges. The successful use of CALPHAD for materials design relies on reliable thermodynamic databases. Reliability means that the properly selected thermodynamic models and optimized parameters can reproduce both thermodynamic and phase stability experimental data as well as first-principles or other theoretically calculated data. Recently, the CALPHAD method has been broadened to include a range of fundamental phase-level thermophysical properties. In conjunction with other computational methods, such as the phase-field method and the finite element method, the CALPHAD method has shown its importance for process and phase transformation simulations. Due to these unique features, thermodynamics, which is the theoretical basis for CALPHAD, was regarded as the fundamental building block for simulation-supported materials design (McDowell et al., 2010).

For the past two decades, the computational design of engineering materials has focused on the following three aspects: multiscale/multilevel modeling methodologies for more quantitative materials design, more user-friendly simulation software, and high-quality scientific databases (i.e., thermodynamic and thermophysical databases). In order to demonstrate the major aspects for materials design in detail, a flow chart for through-process simulation and experimentation with aluminum alloys during the whole heat treatment schedule is presented in Figure 1.1 (Du et al., 2017). The first-principles method, phase-field method, and finite element method are typical nano-, meso-, and macro-level simulation methods, respectively. The Kampmann–Wagner numerical (KWN) model (Kampmann and Wagner, 1984), which is the basis of the one-dimensional precipitation simulation package, is included in this figure due to its high computational efficiency for design of engineering alloys. The CALPHAD method can cover the micro to meso levels of phase transformation in engineering alloys. As shown in Figure 1.1, these multiscale numerical simulations from nano (10^{-10}–10^{-8} m), micro (10^{-8}–10^{-4} m), meso (10^{-4}–10^{-2} m), to macro (10^{-2}–10 m) were utilized to describe multiscale structures and their response to mechanical properties

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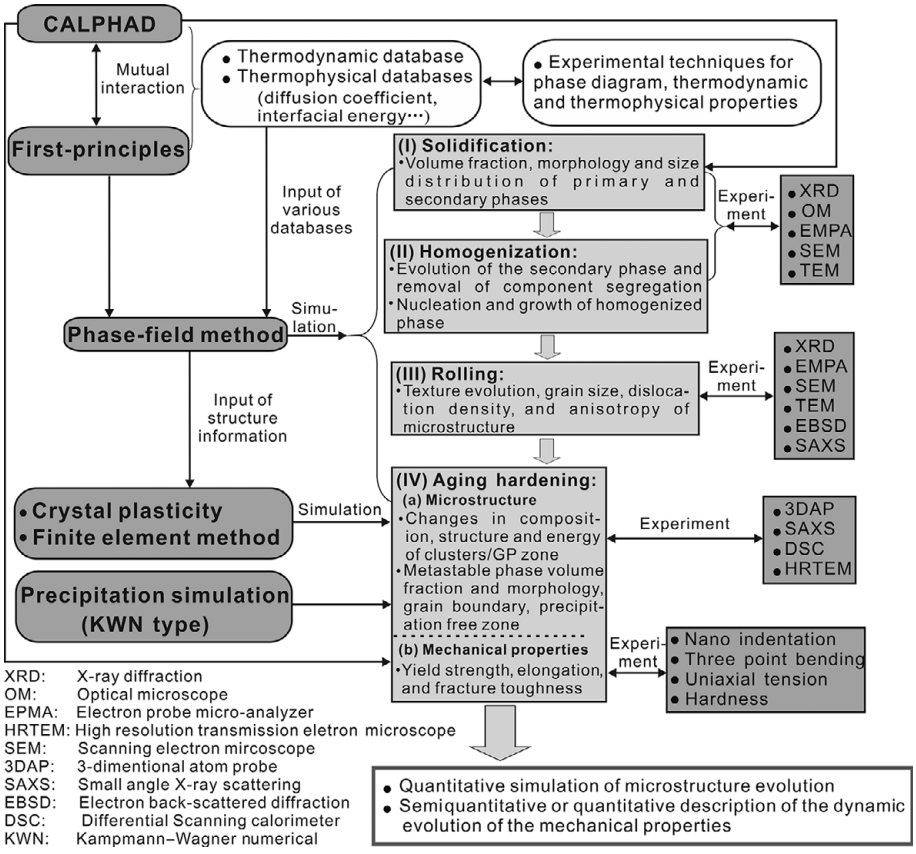

Figure 1.1 Flow chart for through-process simulation and experiment of Al alloys during solidification, homogenization, rolling, and age strengthening.

during the whole research and development (R&D) process of aluminum alloys. Similarly, time scales can range from femtoseconds of atomic vibrations to decades for the use of products. As a strong tie to multiscale simulations, various materials characterizations are needed to serve as validation for the accuracy of simulations or to perform decisive experiments based on the simulation results. Transmission electron microscope (TEM) / three-dimensional atom probe (3DAP), scanning electron microscope (SEM) / electron probe microanalyzer (EPMA) / electron backscatter diffraction (EBSD), and optical microscope (OM) are typically the nano-, micro-, and meso-level structure characterization methods. Consequently, computational design of engineering materials is often considered the most powerful approach when it is integrated with experiments. In Figure 1.1, thermodynamic and thermophysical databases are also indicated. These scientific databases are key inputs for various simulations based on the CALPHAD, phase-field, and finite element methods, just to mention a few.

Recently, the concurrent design of materials and product was described (McDowell et al., 2010). To reflect this idea, a simple but comprehensive diagram is presented in

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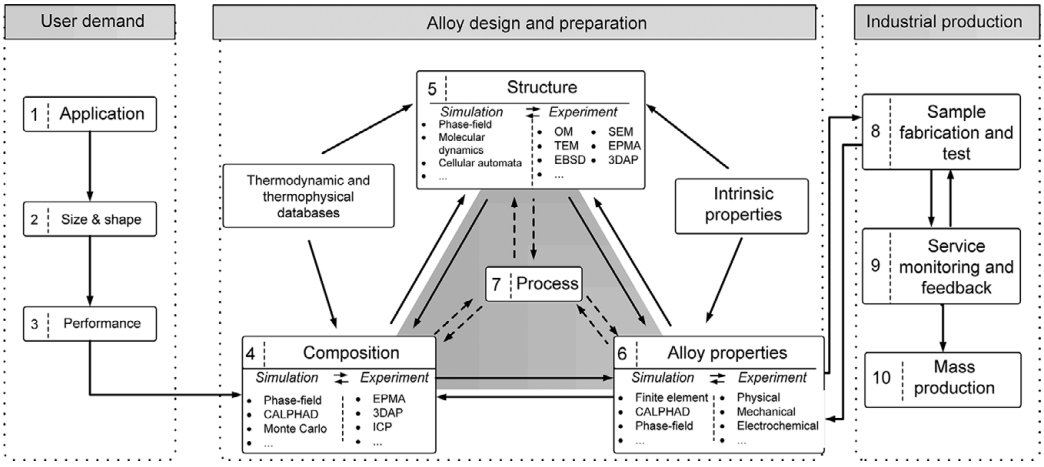

Figure 1.2 Three stages (user demand, alloy design and preparation, and industrial production) for the development of engineering materials.

Figure 1.2, where three stages (user demand, alloy design and preparation, and industrial production) for development of engineering alloys are shown and linked to each other.

Following the strategies similar to those described in Figures 1.1 and 1.2, many new engineering alloys have been developed recently. By establishing the relationships among processing, structure, properties, and performance by means of the integrated computational materials design (ICMD) technique enhanced with experiment, Olson and his colleagues developed the ultrahigh-strength steel Ferrium S53 in only 8.5 years (McDowell et al., 2010). The development of this steel would need more than 15 years by the traditional and costly experimental approach. Gottstein (2007) introduced the scientific concept Integral Materials Modeling (IMM) to guide the development for a variety of materials, including Al alloys and steels. According to IMM, the properties of terminal materials can be predicted from the information about materials chemistry and various processing conditions. The unique feature for IMM is that the microstructural evolution through the whole processing chain is traced to manipulate the final microstructure needed at the end of the processing chain for the sake of predicting the corresponding properties. Most recently, using a through-process simulation (the CALPHAD and finite element methods) and calculation-guided key experiments, Qiu et al. (2019) developed a high-performance chemical vapor deposition (CVD) hard coating in two years. In their work, the CALPHAD calculations predict the phases and their compositions accurately by means of the computed CVD phase diagrams, where the phase regions are shown for the given temperature and gas mixtures. Finite element simulations predict temperature field, gas distribution field, and the deposition rate of hard coating. The costly experimental work was significantly reduced with these simulations.

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In 2008, the promising engineering approach ICME was announced by the National Research Council in the USA. Its goal is to optimize materials, processes, and component design, prior to the fabrication of components, by linking models at multiple length and time scales into a holistic system. The successful application of ICME (ICME, 2013; Schmid-Fetzer, 2015) in industry supports the MGI announced in June 2011 by US President Barack Obama. The goal of MGI is to discover, develop, and manufacture advanced materials at least twice as fast as was possible at the time through the integration of three platforms: high-throughput calculations, high-throughput experiments, and databases. Kaufman and Ågren (2014) mentioned that "a materials genome is a set of information encoded in the language of thermodynamics that serves as a blueprint for a material's structure."

Recently, materials informatics (Rajan, 2008) has shown its role to speed up the discovery of new materials. By using data mining and visual analysis of databases, materials informatics could extract and/or establish quantitative relationships among the four cornerstones of materials science and engineering much faster than the current materials design methods. Future prospects for ICME, MGI, and materials informatics will be addressed in Chapter 13 of the book.

1.3 The Structure of the Book

This book is intended to be an introductory as well as a reference book for computational design of various engineering materials. The text of the book is divided into two parts, and each chapter in these two parts has its special focus. The first part, comprising Chapters 1–6, presents broad but not deep introductions to basic computational methods used in materials design. For more detail about these methods, the interested reader could refer to the references recommended in each chapter. Our intent is to provide a concise but sufficient background in the theory of these methods so that the readers of this book can understand case studies of the representative engineering materials. One very short case study is integrated in each chapter of Chapters 2–6, while detailed case studies for selected engineering materials are described in the second part (Chapters 7–12) via a step-by-step strategy.

The balance of this book is well realized by the interplay between theory described in part one and practice demonstrated in part two. It is our hope that this book will (1) help to attract and prepare the next generation of materials design modelers, whether modeling is their principal focus or not; and (2) encourage readers, in particular undergraduates, graduates, and engineers, to apply these methods for materials design.

This first chapter briefly introduces the past and present development of computational design of engineering materials. The scope and structure of the book are also described.

Chapter 2 gives a short introduction to density functional theory (DFT) and molecular dynamics (MD). These methods are typically atomistic simulation methods. The chapter demonstrates how to calculate some basic materials properties through the

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first-principles method. One case example of material design through atomistic methods is included.

In Chapter 3, firstly a brief introduction to the phase-field method and cellular automaton is presented. These methods are typical mesoscale methods for materials design. Secondly, the integration of phase-field method and/or cellular automaton with CALPHAD, MD, crystal plasticity computations, and machine learning is stressed. One case study for material design mainly based on phase-field simulation and machine learning is addressed.

Chapter 4 presents fundamental concepts in the crystal plasticity and finite element method. Crystal plasticity can be integrated with finite element method to describe the mechanical response of crystalline materials, from single crystals to engineering components. The finite element method is widely used as a macroscale method in engineering. One case study of plastic deformation-induced surface roughening in Al polycrystals will be described by means of the crystal plasticity finite element method.

Chapter 5 presents a fundamental introduction to computational thermodynamics and the CALPHAD method, followed by a strategy to establish a consistent thermodynamic database. Such a database is highly needed for efficient material design of engineering material. A few case studies for Al and Mg alloys design are described using solely thermodynamic databases or extended CALPHAD-type databases. The aspects in these case studies include calculations of both stable and metastable phase diagrams, property diagram calculation, and Scheil solidification simulations, as well as extended simulations of solidification and heat treatment in Al and Mg alloys.

In Chapter 6, a few important thermophysical properties (diffusion coefficient, interfacial energy, viscosity, volume, and thermal conductivity) are very briefly described. The procedure to establish thermophysical databases is also described from a material design point of view. One case study for material design mainly using thermophysical properties is demonstrated.

Part two begins with Chapter 7, demonstrating a step-by-step material design for two representative steels, the S53 ultrahigh-strength and high-corrosion resistance steel as well as the AISI H13 hot-work tool steel. The materials design for these steels based on a hybrid approach of thermodynamic calculations, precipitation simulations, first-principles calculations, and the finite element method will cover the selection of alloy composition, optimal combination of the heat treatment schedule, control of the microstructure, and the correlation of structure properties.

Chapter 8 describes a few case studies for material design of Al and Mg alloys. Two case studies for Al alloy design were described through computations using the thermodynamic database and extended CALPHAD-type databases (atomic mobility and kinetic databases). In the first case study on cast alloy A356, the solidification simulation involving microsegregation modeling is presented. The second case study on wrought alloy 7xxx presents heat treatment simulations based on precipitation kinetics. In the case of Mg alloys, the first two case studies present the simulations of solidification path and T6 heat treatment of AZ series Mg alloys using solely

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thermodynamic databases. The third case study describes the computational design and development of Mg–Al–Sn and AT72 alloys by means of both thermodynamic database and extended CALPHAD-type databases. The last case study is on biomedical Mg alloy implants, presenting the state-of-the-art bioresorbable Mg alloy stent to cure coronary artery disease, the development of which utilized the CALPHAD method.

In Chapter 9, two case studies for the design of single crystal Ni-based superalloy and Ni–Fe-based superalloy for A-USC are demonstrated. The computational methods used in the case studies are thermodynamic calculations, the property prediction model, the multistart optimization algorithm, and machine learning.

In Chapter 10, three types of cemented carbides (gradient cemented carbide, ultrafine cemented carbide, and WC–Co–NiAl cemented carbide) are designed according to thermodynamic calculations, diffusion modeling, phase-field simulations, and the finite element method. The calculations cover the selection of alloy composition, optimal combination of the heat treatment schedule (such as temperature, time, and atmosphere), control of the microstructure, and the correlation of structure properties. In comparison with the time-consuming and costly experimental approach, these simulation-driven materials designs led to the development of these industrial products in three years.

Chapter 11 demonstrates a step-by-step material design for TiAlN-based CVD and PVD hard coatings. The utilized methods include thermodynamic calculations, diffusion modeling, first-principles calculations, phase-field simulations, computational fluid dynamics, and the physically sound structure-property model. The designed materials have found their industrial applications.

In Chapter 12, two case studies for energy materials (hydrogen storage material and lithium battery) are demonstrated. The dominant methods employed in the two case studies are first-principles calculations and thermodynamic calculations.

In Chapter 13, the main contents of the book are summarized, followed by highlighting computational designs of four other engineering materials not covered in the preceding chapters and discussing future directions and key challenges for materials design.

Appendix A provides a summary of ancillary materials available online at Cambridge University Press. These are pertinent data files and step-by-step instructions for hands-on experience of the reader with the simulation tools and examples discussed in the book.

Appendix B compiles the notation in three tables of symbols for the entire book. For the reader's benefit, the equation numbers where these symbols are defined are given as well as the SI-units.

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