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HEP Series in Materials Science and Engineering

Yonghua Rong

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微观组织的分析电子显微学表征（英文版）

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To Prof. T. Y. Hsu (Zuyao Xu) for his 90th birthday

Foreword

Characterization of Microstructures by Analytical Electron Microscopy (*AEM*) reflects the teaching and research expertise of its author, Prof. Yonghua Rong, and it is a valuable resource for students and practicing researchers in the fields of transmission electron microscopy (TEM) and materials science. Professor Rong began microstructural characterization by TEM in 1980, and since then, he has concentrated on application of TEM to problems in phase transformations and the role of dislocations in deformation. This expertise is clearly reflected throughout the book, with detailed analyses that explain how to determine the stacking-fault probability in f.c.c. crystals based on the diffraction spot shift in Section 3.9.3, predict an arbitrary diffraction pattern based on the orientation relationship between phases in Inconel 718 alloy in Section 4.1.2, determine crystal structures by crystal symmetry analysis in Section 4.3.10, and determine dislocation dissociation reactions in Al_3Ti-based alloy in Section 5.2.5, for example. Importantly, these analyses are not just summarized, but explained in detail including the relevant mathematics, so the reader can understand exactly how to perform the analyses. Throughout his career, Professor Rong has taught courses relevant to *Characterization of Microstructures by Analytical Electron Microscopy* (*AEM*). For example, he taught "X-ray Diffraction and Electron Microscopy" for undergraduate students at Shanghai Jiao Tong University from 1986 to 1994, (from 1994 to 1995, he was at Lehigh University as a senior visiting scholar where he investigated the Inconel 718 alloy mentioned above), and from 1996 to the present, he has taught "Fundamentals of Materials Science" for undergraduate students and co-authored an accompanying textbook. Since 2000 he has also taught "Analytical Electron Microscopy" for graduate students at Shanghai Jiao Tong University and authored an accompanying textbook. Professor Rong's strengths as a teacher are apparent throughout *Characterization of Microstructures by Analytical Electron Microscopy* (*AEM*), as evidenced by the careful development of each chapter, which contains all of the information necessary to obtain a good working knowledge of the TEM, and how to use it to solve important problems in materials science. Equally beneficial to the reader are the many excellent figures that have been included to clearly illustrate the important concepts being presented. Although there are a number of good books on analytical electron microscopy, few possess both the breadth and depth of topics presented in *Characterization of Microstruc-*

tures by Analytical Electron Microscopy (AEM), particularly as related to phase transformations and the role of dislocations in deformation, where this book will become a valuable reference to students and researchers. For example, Chapter 4 provides the matrix algebra necessary to perform a variety of diffraction and crystallographic analyses relevant to multiphase materials, and Chapter 5 presents thorough developments of both kinematical and dynamical treatments of electron diffraction and imaging applied to various dislocation reactions and planar defects in alloys. *Characterization of Microstructures by Analytical Electron Microscopy (AEM)* reflects the many years of outstanding research performed by Prof. Younhua Rong and his colleagues at Shanghai Jiao Tong University, and it is a great pleasure for me to recommend this important book to students and researchers in materials science and related fields.

James M. Howe
University of Virginia, May 2011

Preface

Since Ernst Ruska and Max Knoll constructed the first transmission electron microscope (TEM) in Germany 80 years ago, the development of TEM technology was so quick that a more powerful TEM-analytical electron microscope (AEM) came out. AEM attaches energy dispersive spectrometer (EDS) or/and electron energy-loss spectroscope (EELS) and has become popular in study of materials science, especially FEG (field emission gun)-AEM began to be popular after the advent of nanoscience. FEG-AEMs provide opportunity to obtain one-to-one quantitative information on the microstructures consisting of morphology-structure-composition in materials linking down to atomistic level, and such an *in situ* comprehensive analysis is indispensable for understanding the properties of materials. Phase transformation and deformation are two important approaches to improve the properties of materials. The so-called phase transformation is the microstructural change from one to another. As a result, the characterization of microstructures is the basis of studying phase transformation. Among various instruments, only AEMs can be so far used to obtain the *in situ* comprehensive information of microstructures in nanometer scale. On the other hand, dislocations produced by deformation play an important role in mechanical properties of materials, especially in metallic materials. The determination of natures of dislocations is necessary in explaining materials' mechanical behaviour. These two fields the author is interested in are focused in this book.

Chapter 1 provides the basic knowledge of an AEM, including signals used, structure and functions of AEM as well as the principle of imaging, magnifying and diffracting. Spherical-aberration-corrected TEMs developed recently are also introduced. In Chapter 2, traditional techniques and special techniques of specimen preparation are presented. In Chapter 3, the geometric condition of electron diffraction in reciprocal space is derived and the features of diffraction patterns of polycrystals and single-crystals are described. Systematic tilting technique and its applications are emphasized. In this chapter, both the determination of stacking fault probability in HCP and FCC crystals based on the diffraction spot shift due to stacking faults and the prediction of diffraction patterns of long period stacking order structures occupy considerable space in this chapter. Chapter 4 presents mathematics analysis in electron diffraction and crystallography. In this chapter, transformation matrices of orientation relationships and mathematics description of characteristic parameters of coincidence site lattice are derived in detail. Three methods for the prediction of orientation relationships between different phases, edge-to-edge matching, invariant line strain model and O-line model, are described in detail. In order to understand the systematic extinction in electron diffraction caused by crystallographic symmetry, the basic knowledge of crystallography is introduced. Chapter 5 refers to diffraction contrast. The classification of electron image contrasts and imaging modes are introduced. Kinematical and dynamical equations of diffraction contrast in perfect and imperfect crystals are derived, and determination methods of natures of stacking faults and dislocations are illustrated. An example of computer simulation of a superdislocation based on two-beam dynamical theory is given in this chapter. Chapter 6 presents the high resolution and high spatial resolution of AEM, including high resolution TEM and its applications, convergent beam electron diffraction and its applications, EDS and EELS. Three kinds of advanced AEMs are briefly introduced, and they are negative C_s imaging technique, atomatic resolution Z-contrast imaging technique and electron holography, respectively.

The famous textbooks or monographs by the renowned microscopists are referred to throughout this book, and they are *Electron Microscopy of Thin Crystals* by P. Hirsch, A. Howie, D. W. Pashley, M. J. Whelan, *Electron Microscopy of Materials, an Introduction* by M. von Heimendahl, *Transmission Electron Microscopy of Materials* by G. Thomas and M. J. Goringe, *Transmission Electron Microscopy: A Textbook for Materials Science* by D. B. Williams and C. B. Carter, *Transmission Electron Microscopy and Diffractometry of Materials* by B. Fultz and J. M. Howe, *Introduction to Conventional Transmission Electron Microscopy* by M. D. Graef, *High-Resolution Electron Microscopy for Materials Science* by D. Shindo and K. Hiraga, *Analytical Electron Microscopy for Materials Science* by D. Shindo and T. Oikawa, and *Progress in Transmission Electron Microscopy: Concepts and Techniques 1* Eds. by X. F. Zhang and Z. Zhang.

I would like to thank researchers who have contributed significantly to the knowledge in this book. I would like to apologize to those works have been indirectly cited in this book without being listed in the references. This situation appears in the "examples" subsections in Chapter 3, 4, 5 and 6, which are selected to demonstrate the applications of the theory and technique presented in this book. The origins of these examples have been acknowledge by the references at the end of these subsection titles. Therefore, the references cited in the original papers for these case studies are not explicitly listed in this book to save space. Besides, in examples I have almost excerpted sentences in the references so as to reflect research status at that time and the original meaning of the authors in the references.

As a leader of "Theory of Phase Transformation and Its Applications" group recombined by Prof. T. Y. Hsu, I would like to acknowledge members in our group for their contributions to this book. They are Prof. Xuejun Jin, Associate Prof. Zhenghong Guo, Associate Prof. Qingping Meng and Dr.

Xiaodong Wang. I sincerely appreciate my graduate students: Xinsheng Liao, Ying Wang, Jiao Man, particularly, Weizong Xu, Yangxin Li, Zheliang Hu and Meihan Zhang, who spent a lot of time to type and treat plenty of figures and tables. Without their help, this book would not be published in time. The author is grateful to Prof. Gengxiang Hu and Prof. T. Y. Hsu(Zuyao Xu) who gave me useful help in dislocation theory and phase transformation theory when I worked in their group successively. I would like to thank Prof. Yongrui Wang and Prof. Shipu Chen for their help when I was beginner in TEM 30 years ago. I would like to express the gratitude to my old friends: Prof. Jin Zou (now in Australia), Dr. C. L. Jia (in Germany) and Dr. Yongxiang Guo (in America) who encouraged me to write this book and provided the results of their studies. Special acknowledgements are given to my wife, Peili Shu, and to my son, Jackson Rong, for their patience and sustaining support during several years of my evening, weekend and holiday work.

Yonghua Rong
Minhang Campus
Shanghai Jiao Tong University
February 22, 2011

Contents

Chapter 1 Analytical Electron Microscope (AEM)

Transmission electron microscope (TEM) with the function of composition analysis is called analytical electron microscope (AEM).

The AEM history is briefly introduced from the first enlarged electron images performed by Ruska and Knoll to spherical aberration-corrected TEM constructed by Haider et al., also including the development of various techniques, such as convergent-beam electron diffraction (CBED), high resolution TEM (HRTEM) image, X-ray spectroscopy (EDS) and electron energy-loss spectroscopy (EELS).

Signals used by AEM are from various interactions between the specimen and the high-energy incident electrons, of which main signals are elastically scattered (transmitted and diffracted) electrons, characteristic X-ray and inelastic scattering electrons for EELS. A fundamental difference between TEM and light microscope lies in electron beam and electromagnetic lenses, and in the former they replace light beam and glass lenses in the latter. The electron wavelength, as a function of acceleration voltage, is very short compared to the visual light wavelength. A single electromagnetic lens possesses the nature of thin glass lens and can be used to focus electron beam and obtain electron image although it also has spherical aberration, astigmatism and chromatic aberration. However, the focal length of an electronmagnetic lens can continuously be adjusted by varying the excitation current of the lens, and this property easily change magnification of TEM and exchange its modes. TEM consists of the illumination system, specimen chamber inserted with a specimen goniometer, imaging system, viewing and recording system. The exchange between image mode and diffraction mode in TEM can be easily carried out by varying the excitation current of intermediate lens. The theoretical resolution limit of TEM is about 0.2 nm, and is much better than that of light microscope due to very short electron wavelength. TEM exhibits much larger depth of focus and depth of field than light microscope owing to much smaller aperture semiangle for TEM. In the late 1990s, Haider et al. succeeded in constructing a hexapole corrector system to compensate the spherical aberration of the objective lens of a 200 kV TEM, which realizes the improvement of the point resolution from 0.24 nm to better than 0.14 nm.

1.1 Brief introduction of AEM history

In this section, the history of analytical electron microscope (AEM) is briefly introduced to let us know issues microscopists thought of and the contributions the pioneers made, which is favorable for us to devote ourselves to the development of the electron microscopes and electron microscopies. The main content of this section is written based on Ref. [1-4].

Since Louis de Broglie proposed the idea of the wave-particle duality in 1923 and Hans Busch discovered that a rotationally symmetric, inhomogeneous magnetic field could be conceived of as a lens for an electron beam in 1926—1927, like a glass lens for a light beam. Since then the theoretical fundamentals of an electron microscope have been built. The idea for an electron microscope was first proposed and patented by Rudenberg in Siemens Corporation in 1930. The idea to use electron beams to produce enlarged images was first carried out in 1932 by two independent research groups: Knoll and Ruska (Technical University of Berlin) who produced a magnetic-type electron microscope, and Bruche and Johannson (AEG-Research Institute of Berlin) who produced an electrostatic type. Knoll and Ruska's work was the most crucial step, for which Ruska won the Nobel Prize in 1986. By 1939, the first commercial transmission electron microscope (TEM) from Siemens Corporation, based on the improvements of Ruska's work, was introduced. Perfect electron microscope could be mass produced from the beginning of the 1950s.

The electron microscope was first used in the investigation of medical-biological materials. For the studies of metallic materials an indirect replica technique was introduce by Hans Mahl in 1940. The most important development took place in the late 1940s when Heidenreich first thinned aluminum foils to electron transparency in 1949. This work was subsequently developed by Bollman in Switzerland and Hirsch and co-workers in Cambridge, UK in the mid-1950s. Cambridge group also developed the theory of electron diffraction contrast so that various lattice defects, early described theoretically or indirectly demonstrated, could finally be directly observed, such as dislocations, stacking faults, precipitates and the orientation relationship between a precipitate and its parent phase. In these studies, the selected area electron diffraction (SAED), bright field image and dark field image techniques were employed. Heating, cooling, deformation holders were used to *in situ* dynamic observation, such as the change in structure of the specimen, the growth of grains, the dissolution of particles, and movement and multiplication of dislocations.

After that, the development of TEM can satisfy the applications of various techniques in materials science, such as convergent-beam electron diffraction (firstly used by Walther Kossel and Gottfried Mollenstedt in 1938), high-resolution image (the crystal lattice images with dislocations were first observed by James Menter in 1956), X-ray spectroscopy (Manne Siegbahn, winner of Nobel Prize for his work on X-ray spectroscopy in 1924), electron