This book investigates the various causes of thermodynamic instability in metallic microstructures. Materials theoretically well designed for a particular application may prove inefficient or even useless unless stable under normal working conditions. The authors examine current experimental and theoretical understanding of the kinetics behind structural change. The different changes are analysed on the basis of the different driving forces for structural change: chemical, strain, interfacial, gradient etc. In each case the currently accepted mechanisms are described, analysed kinetically and then the analysis is tested against experimental evidence.

The entire text of the first edition of this popular textbook has been updated in this second edition, and a completely new chapter on highly metastable alloys has been added by a new co-author. There are practically no thermodynamically stable metallic materials of importance to materials scientists, and the degree to which the kinetic stability of the material outweighs the thermodynamic instability is therefore very important. The useful working life of the material depends on this balance, and changes that increase total entropy or decrease free energy are nearly always possible. If, therefore, the structure is initially produced to an optimum, such changes will degrade the properties of the material.

A comprehensive and well-illustrated text, accompanied by ample references, this volume will allow final year undergraduates, graduate students and research workers in related fields to investigate in detail the stability of microstructure in metallic systems.
Stability of microstructure in metallic systems

Second edition

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Preface to the first edition

Man’s use of materials, both as a craft and more recently as a science, depends on his ability to produce a particular microstructure with desirable properties in the material when it has been fabricated into a useful object. Such a microstructure occurs, for example, in a steel crankshaft heat-treated for maximum strength, a glass lens heat-treated for fracture resistance or a small crystal of silicon containing non-uniform distributions of solute acting as a complex electronic circuit. Such microstructures are almost always thermodynamically unstable. This situation arises since for any alloy there is only one completely stable structure and there is an infinite number of possible unstable microstructures. The one with the best properties is therefore almost always one of the unstable ones. The desired structure is usually produced by some combination of heat-treatment, solute diffusion and deformation, in the course of which the transformation is arrested, normally by cooling to room temperature, at the right time to obtain the optimum structure. The success of these processes, many of which were derived from craft skills, to give materials with good strength, toughness, electrical properties, etc., is an essential part of current technology. There is, however, a price to be paid in that all these structures are potentially unstable, so that the structures can, and frequently do, transform with time into less desirable forms, especially if used at elevated temperatures.

The science of phase transformations is concerned with transformations to the desired microstructure and equally with the instability of this microstructure. The science of phase transformation has greatly advanced in the last thirty years, both with improved metallographic techniques and the development of successful quantitative theories of the mechanisms and kinetics of structural change. These subjects have been discussed in many excellent textbooks and review articles which have
enabled the student to keep well up to date with advances in the subject. However, the emphasis in almost all these publications has been on the processes occurring during heat-treatments that are intended to produce the particular microstructures with desirable properties. The correlation of these properties, usually mechanical but sometimes magnetic or electrical, with microstructure has also been reviewed frequently. The stability of the microstructure produced by heat-treatment has, however, received no systematic consideration in textbooks. Microstructural stability is a topic that has been the subject of considerable research activity and in many cases the state of knowledge is already very extensive and frequently the agreement between theory and experiment is remarkably good. Despite these scientific successes and the importance and interest of the subject, there has been only limited incorporation of the state of knowledge into general textbooks of physical metallurgy and no book, as far as is known to the authors, has been published with microstructural stability as its main concern.

The present volume was written to try to correct this shortcoming by providing a book that would summarise the main elements of the current understanding of the stability of microstructure. We have attempted to describe the state of knowledge as it appears to us in the years 1972–4, although limitations of space, time and expertise precluded every topic being described exhaustively, so that we are only too aware that there are likely to be important contributions that we have not included. These omissions should be seen as criticisms of ourselves and not of the scientists whose work we have not included; a major deliberate omission is that of the effect of surface or interface reactions (e.g. corrosion) on microstructure. In particular this volume reflects the regrettable but nearly universal tendency of English and American scientists to read mainly English language papers.

The approach adopted in the book has been to consider the instabilities that occur as classified by the form of potential free energy decrease that makes the existing microstructure unstable. This approach is discussed in some detail in the first chapter, and the subsequent chapters then deal in turn with each of the various types of free energy decrease.

The authors would like to acknowledge the important contributions made by numerous colleagues in Oxford, at Sussex, and elsewhere in helping us to formulate the ideas described in this book. We would like to give particular acknowledgement to Professor G.W. Greenwood who, in addition to his published work in this area, first suggested the form of approach adopted in this book, and to Professor R.W. Cahn for his initial stimulation of the project and his continued interest and encouragement. We are grateful to the many scientists who have given us permission to use their micrographs and in many cases have provided copies for publication and to the many publishers of scientific journals from which we have quoted for permission to reproduce figures and micrographs.

July 1975
Preface to the second edition

For the second edition, the objectives and the approach previously used have been maintained. In many areas the science base of the subject has shown little change since the first edition and here the text has only been modified by improved examples where available. In other areas the subject has advanced significantly and the text has been updated with the insights. Topics previously covered incompletely, notably the highly unstable microstructure produced initially by rapid solidification but subsequently by other processing routes, have been greatly expanded. Other significant developments that have taken place include the detailed experimental studies of homogeneous nucleation, the growth of Widmanstättten precipitates and precipitate coarsening, and the new insights into the nucleation of recrystallisation, and grain growth and its inhibition by second-phase particles. In other areas, despite the importance of the subject, progress has been disappointingly slow. As in the first edition, we have tried to indicate where there are unsolved problems. The first edition provided the authors with a rich supply of fruitful research topics and we hope that this was also true for our readers and will be equally true for the second edition. Microstructural stability of metallic (and other industrially important) materials remains a field of research with many scientific and potential engineering applications.

The authors are again grateful to Professor Robert Cahn FRS for his efforts to get this volume completed and his much-appreciated enthusiasm. We thank our many colleagues whose work and enthusiasm have stimulated our own efforts – these are fully referenced here. We are again grateful to many scientists and to the publishers of their research and scholarship for permission to use their
work and to reproduce their figures. We apologize to these people whose work we have overlooked or, worse, misunderstood, and would appreciate hearing of these and other mistakes. We look forward to seeing our ideas challenged by new research. If any studies are initiated by questions or misunderstandings in this volume we shall have succeeded in one of our tasks. We would be delighted to hear of any engineering successes helped by the ideas in this volume, even if the source was the original literature rather than our review. Our electronic and postal addresses are given below to facilitate any responses from readers of this book.

1997

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