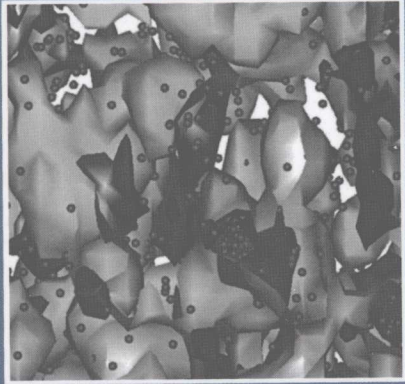


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Phase transformations in steels

Volume 2: Diffusionless transformations,
high strength steels, modelling and
advanced analytical techniques

Edited by Elena Pereloma and David V. Edmonds

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A new and comprehensive book on phase transformations in steels is both timely and welcome. It is gratifying near the beginning of a new, technology-dominated, century to see a group of experts and well accomplished researchers, some of whom have devoted major parts of their professional activities to this area, as well as a group of younger researchers and steel users, all willing to assemble together a new two-volume publication on steels.

Strikingly, unlike many other groups of important metallic materials, it is the onset of transformations in steels resulting from the various thermal and mechanical treatments that make steels so special. This is possible mainly because of the unique properties of iron (Fe) which exhibits three different simple crystal structures; bcc, fcc and bcc again, as temperature rises. Even more unique is the fact that contrary to the usually observed order of the sequence of phase changes observed with temperature, the gamma phase at higher temperatures, is the 'more open' phase than the bcc alpha phase, and hence more able to absorb substantial amounts of alloying element additions. As a result, on quenching or cooling, and other heat treatments, all kinds of phase transformations can take place, and their understanding, manipulation, and utilization constitutes the essence of the importance that steels have exhibited in the past in the development of civilizations and related technologies.

The various chapters bring nicely up to date the vast assembled knowledge of steel transformations in the literature: from the more basic aspects (thermodynamics, diffusion, kinetics, etc.), through the more particular transformation features (nucleation and growth, bainite, martensite, massive, shape memory, etc.), to some aspects of the more recent and advanced analytical possibilities (synchrotron, atom probe, etc.).

Perhaps it is fitting also to mention that the bewildering role of magnetism in iron is the basis of much of this behavior. It is well documented that the ferromagnetic transition in the bcc-Fe phase makes the bcc phases more stable at lower temperatures than the fcc-gamma phase, but still too few people realize that it is the anti-ferromagnetic transition in the gamma phase at temperatures near 0 K that makes the crystalline closed-packed (therefore

‘wrong’) gamma phase return to stability on heating. Without these unusual features of iron, phase transformations in steels would not take place and the enormous versatility and benefits of steels in the progress of society would be lost.

It may also be time to admit that the ferromagnetic alpha phase has actually a bc-tetragonal symmetry due to the magnetic moments, if the more modern standards of phase definition are adopted, and so the bcc (and paramagnetic) beta phase which has been banished from the iron phase diagrams since the 1920s should be rightfully restored to its original position.

Undoubtedly, research on transformations in steels will continue in the future, as more sophisticated heat treatments are devised and more advanced techniques are brought into use to study the results, particularly at the micro and nano scales. The present book is likely to serve here as a good basis for future advances.

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Steel has been available as a high tonnage engineering material for nearly two centuries. During this time it has had a very creditable track record and one which is crucial to engineering progress, especially in providing the infrastructure in underdeveloped and developing parts of the world, which still dwarf in size and population the more developed nations. This is why the volume of steel production continues to increase, leading to the continual need to consider more economic ways of manufacturing using steel in order to minimise energy consumption and preserve natural resources.

Despite commendable efforts by scientists and engineers to understand fully the processing-microstructure-property relationships in steels, these continue to present new challenges to researchers because of the complexity of the phase transformation reactions and the wide spectrum of microstructures and properties achievable. Thus, an important theme and objective of this book is to follow the development of our understanding of phase transformations in iron alloys and steels through to the development of modern commercial steels, and in particular to highlight the clear connection between phase transformation studies, no matter how isolated and remote they may seem at the outset, to the emergence of new steels with enhanced engineering properties.

Unlike many other metals, the combination of several characteristics, such as magnetism, allotropic phase changes and the different solubility and diffusion behaviour of interstitial and substitutional elements, makes iron-based alloys unique and is responsible for a diversity of phase transformations. The first chapter of this book provides a historical perspective on the first pioneering attempts to gain insight into the complexity of these reactions. All aspects of phase transformations (thermodynamics, diffusion, kinetics and crystal structure) must be properly understood in order to develop a complete picture of the transformation reactions in steels. Thus it was deemed necessary to devote the first section of the book to the fundamental principles of thermodynamics, diffusion and kinetics, and in addition, owing to its growing importance in helping to understand transformations, the phase boundary interface separating parent and product, now much more amenable to observation and analysis using the increased power of modern metallographic instrumentation, as well as modelling.

Starting from the earliest studies on phase transformations in steels, a large number of theories and definitions have emerged leading to continual debates amongst researchers. Only with the development of more advanced experimental capabilities have some of these issues been satisfactorily resolved while others still provoke conflicting opinions. This book aims to represent the current status of knowledge on steel phase transformations whilst also highlighting the challenges facing future researchers in this field.

As mentioned in the Foreword, and demonstrating how the Fe-C system continues to generate important issues, magnetism plays an important role in the phase transformations of iron and steels due to the ferromagnetic and anti-ferromagnetic transitions that take place. Thus it is suggested that paramagnetic beta phase should be restored to the Fe-C phase diagram.

The most important transformations in steels, and the area where almost all research has been concentrated, are those which result in the final microstructure and properties. These involve decomposition of the high temperature γ -phase, austenite, which takes place on cooling and, dependent upon steel alloying and cooling conditions and also whether mechanical working occurs, could follow different paths resulting in a large diversity of lower temperature phase types and their mixtures. These phase transformations could be classified based upon microstructure, thermodynamics or mechanisms and in the present book the phase transformations are classified according to their mechanism. In this scheme the phase transformations in steels are customarily divided into two major groups, which are named according to whether long-range diffusion of atoms occurs or not, namely diffusional or non-diffusional (diffusionless). Each type of phase transformation is then characterised by a set of specific features, including but not limited to composition, crystal structure, shape change and carbon mobility.

It is generally accepted that the formation mechanisms of proeutectoid grain boundary allotriomorphs (of α -ferrite and cementite) and pearlite are diffusional. These reactions take place within the higher temperature region of the low temperature phase field with slow kinetics and generally do not require significant undercooling below the $\gamma \rightarrow \alpha$ transition temperature. In contrast, the formation of martensite with a structure change but composition inherited from parent austenite occurs by a diffusionless transformation at rapid cooling and/or large undercoolings. In-depth presentations of the current state of phase transformation theory for the former type of reactions are given in Volume 1, Part II, whereas the latter is addressed in Volume 2, Part I. These constitute the more traditional microstructures which have long been studied; Henry Clifton Sorby, for example, first identified pearlite around the middle of the 19th century. Moreover, they have long provided the properties of the high-tonnage carbon and alloy steels used in construction and many engineering applications. Nevertheless, as described in these sections, significant progress has been made in understanding their

formation, both for ferrite/pearlite and for basic martensite, in the latter case the *phenomenological theory of martensite crystallography* and, more recently, the proposals deriving from interface mechanics embodied in the so-called *topological model*, which attempt to describe the mechanistic aspects of the transformation. This demonstrates the rich variety of transformations in iron-based alloys, especially when one also adds the shape memory effect, which is of immense interest and commercialisation in non-ferrous systems.

Although significant advances have been made in developing a basic understanding of the nucleation and growth processes, and in validation of various theories, questions still remain due to the limitations of even the most powerful experimental techniques and the complexities of multiphase microstructures forming under a variety of conditions, generally at elevated temperatures. Examples include: elucidating the exact path for carbon diffusion; determining the embryo structure, location and evolution; measuring the effect of so-called 'solute drag' on interface migration; determining the diffusivities and binding energies of elements in multi-component systems; accurately measuring interfacial and strain energies; providing explanations on the differences between the predicted rates of diffusion of substitutional elements at low temperatures and the observed solute clustering. Proving again the complexity, even previously well-accepted ideal cases of partitioning of alloying elements under local equilibrium (LE) or paraequilibrium (PE) conditions for diffusional transformations are now challenged by assumption of negligible partitioning of substitutional elements under local equilibrium (NP-LE).

However, the issues most difficult to resolve, not unexpectedly, have been related to the intermediate products formed between the classical diffusional (e.g. ferrite/pearlite) and diffusionless (e.g. martensite) ones. A variety of morphologies of these products including Widmanstätten ferrite, upper bainite, lower bainite and carbide-free bainite, as well as granular bainite and the so-called 'acicular ferrite microstructures', are considered to exhibit a mixture of characteristics familiar to both classes of transformation, which has fuelled continuous debate regarding the exact formation mechanisms. Perhaps the main discord concerned with the fundamentals of the reaction mechanism has been related to the nature of the bainite transformation (Volume 1, Part III), which essentially reduces to the behaviour and location of carbon during the formation of the bainitic ferrite crystals. As mentioned above, better resolution of such questions might evolve from real-time measurement of carbon concentrations in parent austenite and product ferrite during transformation at elevated temperatures.

Nevertheless, there have been significant positive advances in these phase transformation studies. In this quest for greater understanding of the bainite reaction mechanism, experimental steels have been developed which contain untransformed austenite, useful for studying features of the transformation

mechanism, but which have subsequently been shown can impart valuable properties to a new generation of formable high strength steels for automotive use that has eventually led to commercialisation, e.g. transformation induced plasticity (TRIP) steels. Chapters on these new steels can be found in Volume 2, Part II, alongside comparative chapters on the new twinning induced plasticity (TWIP) steels and high alloyed maraging steels.

Almost all modern high-volume metal production processes are continuous, involving continuous cooling, often associated with mechanical forming, such that complex dynamic changes are more often the norm and sometimes even difficult to simulate in a laboratory environment. Thus, near-equilibrium microstructures are not always the ones which could lead to commercial success. Consequently, given the different industrial processes required in the production of steel in all its various forms, which are continually being updated or modified, a section dealing with parameters involved in transformation other than temperature was considered necessary. External factors, such as deformation, heating rate or application of electromagnetic field could either accelerate or retard the phase transformations depending upon the chosen set of conditions (Volume 1, Part IV). Although a significant body of evidence has been accumulated over time on the effects of these parameters, the underlying mechanisms are not yet fully understood. The phenomenon of restoration of prior austenite morphology and orientation at slow or fast heating rates and absence of it at intermediate heating rates continues to puzzle physical metallurgists. The explanations put forward for this structural inheritance also lack direct and comprehensive experimental evidence.

Many of the significant advances to our understanding of phase transformations in the evolution of steel microstructure during the last 50 years would not have been possible without the parallel development of higher resolution microscopes and related techniques. In the last two decades significant advances have been made in many characterisation techniques (Volume 2, Part IV) and microstructure observations have moved from only *ex-situ* to also *in-situ* ones. It is now possible using *in-situ* transmission electron microscopy, neutron and synchrotron scattering or electron backscattering diffraction coupled with energy dispersive X-ray spectroscopy, to observe the progress of phase transformations not only on heating or cooling, but under external load too. Recent leaps in the development of atom probes and aberration corrected transmission electron microscopes enable the collection of compositional and crystallographic information with atomic resolutions (<0.1 nm). The ability to gather microanalytical data at high resolutions has become increasingly important with the realisation that relatively low bulk concentrations of alloying elements can have disproportionately large effects on transformation behaviour. The exact structure of grain and interphase boundaries and solute segregation to them can now be revealed more clearly.

The improved resolution limit is especially valuable with the increased trend towards production of steels with ultrafine and nano-sized grains and precipitates. Perhaps it should be mentioned that more and more use of 3D techniques in addition to more customarily utilised 2D provides invaluable information on the morphology and distribution of various phases and their crystallography, which helps to fine-tune existing theories and indicates the route for other experiments. But whilst researchers should remain vigilant to artefacts related to each technique and continue to analyse data diligently, these newly developed techniques will allow gathering of the essential information for advancement or validation of existing theories and models, as well as provide the necessary input data for rapidly developing modelling methodologies.

However, we must remain mindful that these instruments and their applications, as will be evident from this section in the book, have become extremely specialised and expensive, and are not widely available, and consequently much of the metallographic work on commercial steel microstructures is still conducted at much lower resolutions by more conventional microscopy. This emphasises the need for consistent descriptions and classifications of microstructure and transformation behaviours across the length scales. As far as has been possible, we have tried to maintain a similar nomenclature throughout the book.

The major new inclusion in this book derives from probably the most significant and totally new topic or field of activity in phase transformations to emerge during the latter part of the main period covered, namely phase transformations modelling. A full section (Volume 2, Part III) has been devoted to this fairly embryonic but rapidly growing field, including all of the well-known approaches: first principles, phase field, molecular dynamics, neural networks. The models provide qualitative and semi-quantitative insight into phase transformations. Some good examples of the preliminary applications to ferrous transformations will be found, some of which have already produced useful advances whilst others are meeting the extensive challenges arising from the complexity of the subject. The hope exists that eventually steels may be designed from first principles taking into account the complexities of phase change associated with those of processing on a large scale, so often difficult to reproduce accurately in the laboratory, or alternatively to study during commercial production. However, it is clear that despite the progress made, the lack of reliable experimental data for input into the models hinders their development. For first principles models reliable experimental data are needed for validation of the potentials. As mentioned previously, quantitative interfacial and strain energy data, data on diffusivities and nucleation, are urgently required to further advance modelling and the theories of ferrous phase transformations.

Finally, the success of applying the knowledge of phase transformations to design of advanced high strength steels should be acknowledged (Volume 2 Part II). This part begins with a chapter on high strength low alloy (HSLA) or microalloyed steels which have probably been the category of steels that have seen the most resource-intensive development during the latter part of the period covered by this book, and still do, driven mainly by the ever more stringent engineering requirements for steels needed in the recovery and transmission of oil and gas. In the quest for greater strength and toughness combined with weldability, extensive data and understanding have been accumulated on the influence of alloying and controlled deformation processing and cooling on the phase transformation and precipitation reactions.

The pathway from the development of quenched and tempered steels and HSLA steels to dual phase, transformation-induced plasticity, nanostructured bainitic ('Nanobain'), twinning-induced plasticity and quenched and partitioned steels is marked by gradual increase in complexity of processing schedules and the microstructures formed. In the latter steels, the direct application of phase transformation sequences in the design of processing schedules led to either significant strength advantage or desirable combinations of high strength/high ductility in formable steels. These manipulations of steel microstructures also enable the achievement of cost savings due to leaner steel compositions and consequently the reduced use of natural resources, coupled with socio-economic benefits.

This project would not have been possible without support from Woodhead Publishing staff and the enthusiasm and co-operation of authors and co-authors in joining us in this task – which apart from confirming our inception of the idea, has made it a more worthwhile and also an enjoyable activity over the last two years. Our authors must also be congratulated on their efforts to produce comprehensive overviews of the topics, including fair and balanced treatments of various theories and models where appropriate. There can be no doubt that it has been an immense task and we can attest to the considerable work which has gone into the production of the manuscript for this book. It will always be a snapshot of where we have reached in this discipline by the year of publication, but it will also we hope, and because of the quality of the chapters provided, stand as a useful source for reference, advanced teaching and learning for a long time to come. In particular, it is hoped that this book will inspire a young generation of scientists and engineers to further advance the knowledge on phase transformations in steels, which remains a fascinating and significant field to explore.

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