Kinetic Phase Diagrams: Nonequilibrium Phase Transitions

(Studies in Modern Thermodynamics)

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Description:
The present theoretical and experimental knowledge of the time evolution of a system during solidification, not only in equilibrium, but also in nonequilibrium conditions, is summarized in this book. Such knowledge is of fundamental importance for the determination of the constitution of materials or of the technological conditions necessary to prepare materials with a desired structure. Emphasizing the importance of kinetic phase diagrams, the authors focus the attention of the reader on the problems connected with nonequilibrium conditions, that are encountered during real phase transformations. A critical review of phenomenological and statistical theories of phase transformations and of mass and heat transport enables the reader to determine the range of applicability of concrete models for the description of the evolution of a given system. The book is supplemented with several less-known methods and results of phase characterization, including a detailed account of the Soviet school of T.A. Cherepanova which is not well known in the West. The text covers in details the modern research area of glasses, their theory and preparation. Includes also description of methods of thermal analysis and its application to description of glass crystallization and formation.
KINETIC PHASE DIAGRAMS
NONEQUILIBRIUM PHASE TRANSITIONS

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PREFACE

Modern technology is based largely on materials such as semiconductors, ferrites, magnetic garnets, solid state lasers, superconductors, materials for microelectronics and optoelectronics etc. Many of these materials are prepared with metastable constitution and structure. The theory and the experimental investigation of the conditions of preparation of appropriate materials represents a very large field. Different approaches to these problems are scattered over a large number of specialized journals and books. For a broad and fundamental study of the metastable phase formation and solidification under nonequilibrium conditions these sources require a prohibitive amount of supplementary reading. Consequently, overspecialization is widespread and a disturbing gap has developed between the theory and everyday laboratory practice.

In our book we try to summarize present theoretical and experimental knowledge of the description of the time evolution of the system during solidification not only in equilibrium but also in nonequilibrium conditions. This is of fundamental importance for the determination of the constitution of materials or for the determination of the technological conditions if we wish to prepare materials with a desired structure. Emphasizing the importance of kinetic phase diagrams, the authors can turn the attention of the readers to the problems connected with nonequilibrium conditions, which we encounter during real phase transformation.

In this book we introduce the physical foundations of the description of the state of the systems, of the conditions of the equilibrium coexistence of phases and of the kinetics of the phase transformation.

The critical review of phenomenological and statistical theories of the phase transformation and of the mass and heat transport enables us to determine the range of applicability of concrete models for the description of the evolution of the system. The book is complemented with several less-known methods and results of the phase characterization.

Our text is directed to research workers in materials science, chemical engineering and processing of different materials. The book also covers the modern research area of glasses and their preparation. It will be useful for a postgraduate study in the field of advanced thermodynamics, and useful to physical chemists, chemists and physicists, who are interested in the theory of phase transformation kinetics and who require an introduction to the foundations of material processes and an understanding of the processes which take place during preparation of new materials.

The text was prepared by a team of authors from the Institute of Physics, Czechoslovak Academy of Sciences in Prague and from
the Institute of Inorganic Chemistry, Slovak Academy of Sciences in Bratislava.

I am indebted not only to the authors' team but also to J.Nadrchal, J.Rogalewicz, J.Nádhera, V.Rozhoňová and P.Demel for their assistance during typing of the manuscript. I wish to thank I.Gregora for his help with language correction and J.Hajnovičová for her translation of Chapter 1.

I hope that this book will contribute to the understanding of the difficult problems of the new phase formation and we will be delighted if our book helps in the development of the technology and the improvement of the properties of important new materials.

Prague, Czechoslovakia
July 1990

Zdeněk Chvoj
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CONCLUSIONS

In the opening chapters of our book several technologies were introduced which are used to produce materials in a metastable state and for which the change of temperature is characteristic. If we can construct a theory of these processes, we must be able to predict the structure and constitution of the new phase on the basis of knowledge of the parent material and the boundary and initial conditions which determine the technology. A broad aim of these theories is to predict the technology and the parent material if we set the properties of the resulting material. If we follow this aim, our theory must cover all processes which are connected with the phase transformation.

In the foregoing chapters we have considered the nonequilibrium state, non-stationary solidification processes. These processes represent not only laser technologies, surface material modification by electron or ion beams, or rapid cooling but even the classical technologies of crystal growth (Bridgman method, zone melting, growth from the vapour or Czochralski method, etc.) when the constitution and the quality of crystals (which can be improved and controlled) depend on external conditions.

Thus the requirement of a systematic study (theoretical and experimental) of the processes of preparation of new materials urgently emerges. This study has in fact two aspects. On one hand, we need a deeper knowledge of these processes, of their dynamics and a deeper understanding of the influence of external fields, which would lead to the optimization of these processes. On the other hand, technological applications call for the preparation of advantageous crystals and materials which possess the desired physical properties.

The theoretical description of these processes can be used not only in the basic research, but also in optimization of the materials technology, in the prediction of the properties, constitution and structure of the materials prepared by particular technologies, or, as the case may be, in the selection of suitable methods allowing the preparation of materials with desired properties.

It follows from the analysis presented in Chapters 8 - 11 and from the examples in Chapter 2 that a complex experimental study of these processes is always required. It is necessary to study the temperature and concentration distribution in the system, the existence and the composition of complexes and their changes with temperature, and all this during the whole solidification processes. It is necessary to know what metastable phases can arise under nonequilibrium conditions and to characterize these phases.

If we summarize the knowledge from the previous chapters, in which the results in these fields were discussed in detail, we can see that only
the Monte-Carlo calculations and the stochastic theory describe the whole problem in a sufficiently detailed way. Many theories of phase transformation deal with the equilibrium coexistence of phases, other theories consider the nonequilibrium conditions in the system; they assume that the temperature and the concentration in the system (which are mostly constant in time) are given. The theories which consider the transport in the system assume equilibrium conditions at the phase interface or a given temperature in the system. These theories solve only the partial problems which characterize the given technology. On the other hand, they are acceptable and very successful for some technologies. For example, we can consider the equilibrium conditions at the solidification front during slow cooling. In other cases, diffusion processes in the binary systems are decisive for the evolution of the system and other effects can be neglected.

The success of these theories is connected with the solution of particular technological problems. For example, it is very important to know the stability regions in the growth of eutectics of lamellar structure, or to determine the recrystallization rates of glasses using nucleation theories. The temperature distribution in the system influences the thermal stresses in the solid phase and thus it influences the distribution of defects. The kinetic phase diagrams advise us upon the formation of metastable phase. The distribution of defects and impurities in crystals is connected with the kinetic processes at the phase interface, etc.

However, if we work under extreme conditions of solidification, when metastable phases arise, it is evident that we cannot manage with the equilibrium conditions at the solidification front and we must consider the kinetics of the phase transformation besides the rapid changes of temperature and the constitution of the liquid phase. Thus it is necessary to bring both processes together in one theory. Further, it is necessary to realize that we do not satisfactorily use the steady-state approximation and it is necessary to consider the time-variable boundary conditions. The theory should be able to describe the nucleation and growth at the interface in a uniform way.

Now the question arises as to what theoretical description we can use in formulating the theory which fulfills our requirements. Because our processes are nonequilibrium processes, we should use the methods of nonequilibrium thermodynamics and the evolution theorem to determine the resulting structure (see refs.1-3). But we must be aware of the fact that this theorem holds if the boundary conditions are constant in time and hence it is advantageous to use it in the case of the steady-state processes, e.g. the arising of the dissipative structures (which is not the case of our variable boundary conditions) and the kinetic coefficients at the phase interface must be given by experiment.

For reasons which were discussed in Chapter 10, the Monte-Carlo calculations, the methods of molecular dynamics (we can calculate only the growth of several atomic layers), the method of density functional, the renormalization group or the field methods in the Landau-
Ginzburg approximation, and other theories where the kinetics of the phase transformation is not considered, are not suitable. Nor can we use the solution of Stefan's problem where the phase diagrams must be known. These theories must be generalized so that they fulfil our requirements.

Further it should be emphasized that we would be able to use statistical methods in describing the mentioned processes regarding the randomness of molecular processes of the phase transformation and regarding the existence and the influence of the thermodynamic fluctuations near the phase transformation point. The most general description would be the solution of the Liouville equation for the density matrix operator (or the solution of the generalized master equation - see ref. 4) within the framework of the quantum theory, where we must include the density matrix of the reservoir, the temperature of which is a function of time (see refs. 5,6). In the formalism of the Liouville equation we would be able to describe even the nonmarkovian processes. For obvious difficulties, this formalism has not been used to study the processes in which many effects must be taken into account.

The new method, which is based on the mathematical theory of stochastic processes and which fulfils our requirements appears promising. This theory enables us to describe the processes of nucleation and the growth at the solidification front within the framework of a single model.

From the mentioned theoretical and experimental results it follows that the study of the phase transformation kinetics under nonequilibrium conditions presents a rapidly developing branch of materials research, which is in limelight of studies by physicists and technologists. The effort to obtain new materials, more perfect or pure materials with new properties, leads us to more perfect determination and description of mentioned processes and to a deeper understanding of the course of phase transformation. A shortcoming of the present state of this branch is the nonsystematic experimental study of processes far from equilibrium or under time-dependent boundary conditions.

The development of the theory is in its initial stage. Even in spite of partial successes (kinetic phase diagrams, problems of the phase interface stability, etc.) calculations of the convection are complicated, the questions of the influence of external fields on the phase transformation and of the determination of the surface energy, kinetic coefficients etc., have not been solved. Nevertheless, the development of this field of study is promising and a closer contact between theory and experiment is required for the solution of the problems suggested in our book. It is necessary to devote attention to the characterization of materials and to the study of the phase transformation processes as well as to the study of the temperature fields in the system, which determine the overall processes.
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