# **REFRACTORY MATERIALS**

A SERIES OF MONOGRAPHS

VOLUME 6-III



# PHASE DIAGRAMS

# **Materials Science and Technology**

**VOLUME III** 

The Use of Phase Diagrams in Electronic Materials and Glass Technology

# **REFRACTORY MATERIALS**

#### A SERIES OF MONOGRAPHS

John L. Margrave, Editor DEPARTMENT OF CHEMISTRY RICE UNIVERSITY, HOUSTON, TEXAS

- VOLUME 1. L. R. MCCREIGHT, H. W. RAUCH, SR., and W. H. SUTTON Ceramic and Graphite Fibers and Whiskers A Survey of the Technology
- VOLUME 2. Edmund K. Storms The Refractory Carbides
- VOLUME 3. H. W. RAUCH, SR., W. H. SUTTON, and L. R. MCCREIGHT Ceramic Fibers and Fibrous Composite Materials
- VOLUME 4. LARRY KAUFMAN and HAROLD BERNSTEIN Computer Calculation of Phase Diagrams With Special Reference to Refractory Metals
- VOLUME 5. ALLEN M. ALPER, Editor High Temperature Oxides (In Four Parts)
- VOLUME 6. ALLEN M. ALPER, Editor Phase Diagrams: Materials Science and Technology (In Three Volumes)

In Preparation

LOUIS E. TOTH Transition Metal Carbides and Nitrides

# PHASE DIAGRAMS MATERIALS SCIENCE AND TECHNOLOGY

# Edited by ALLEN M. ALPER

Chemical and Metallurgical Division Sylvania Electric Products Inc. Subsidiary of General Telephone and Electronics Towanda, Pennsylvania

**VOLUME III** 

The Use of Phase Diagrams in Electronic Materials and Glass Technology



ACADEMIC PRESS

1970

New York and London

Copyright © 1970, by Academic Press, Inc. All rights reserved no part of this book may be reproduced in any form, by photostat, microfilm, retrieval system, or any other means, without written permission from the publishers.

ACADEMIC PRESS, INC. 111 Fifth Avenue, New York, New York 10003

United Kingdom Edition published by ACADEMIC PRESS, INC. (LONDON) LTD. Berkeley Square House, London W1X 6BA

LIBRARY OF CONGRESS CATALOG CARD NUMBER: 78-97487

PRINTED IN THE UNITED STATES OF AMERICA

#### DEDICATED TO

## Professor Rustum Roy

for the pioneering work he has done in the field of phase equilibrium and materials science.

## Contents

List of Contributors	xi
Foreword	xiii
Preface	xv
Contents of Other Volumes	xvii

#### I. The Use of Phase Diagrams in Crystal Growth

#### J. W. Nielsen and R. R. Monchamp

I.	Introduction	2
II.	Crystal-Growth Techniques	3
III.	Growth from the Melt	19
IV.	Growth from High-Temperature Solutions	30
V.	Growth from the Vapor	41
VI.	Crystal Growth with Scant Information	45
VII.	Summary and Recommendations	49
	References	50

#### II. The Use of the Phase Diagram in Investigations of the Properties of Compound Semiconductors

#### M. B. Panish

I.	Introduction	53
II.	Binary Semiconductor Systems	54
III.	Ternary Systems	67
IV.	Crystalline Solid Solution Systems	84
	References	84

#### III. Superconductivity and Phase Diagrams

#### V. F. Zackay, M. F. Merriam, and K. M. Ralls

I.	Introduction	87
II.	Phase Diagram of the Superconducting State	91
III.	Superconductivity and the Determination of Phase Diagrams	93
	References	100

#### IV. Rapidly Quenched (Splat-Cooled) Metastable Alloy Phases; Their Phase-Diagram Representation, Preparation Methods, Occurrence, and Properties

#### B. C. Giessen and R. H. Willens

I.	Introduction	104
II.	Phase-Diagram Represention of Metastable Alloy Phases	105
III.	Experimental Preparation of Metastable Phases by	
	Rapid Quenching (Splat Cooling)	118
IV.	Alloy Constitution Changes by Rapid Quenching	122
<b>V</b> .	Properties of Splat-Cooled Metastable Alloy Phases	133
	References	139

#### V. Liquid Immiscibility in Oxide Systems

#### Ernest M. Levin

I.	Introduction	144
II.	Thermodynamic Considerations	145
III.	Courses of Crystallization and Phase Composition	149
IV.	Structural Interpretation	159
<b>V</b> .	Immiscibility and Compound Formation	177
VI.	Superduty Silica Brick	181
VII.	Metastable Liquid Immiscibility and Microphase Separation	184
	References	233

### VI. The Use of Phase Diagrams in Dissolution Studies

#### A. R. Cooper

I.	Introduction	237
II.	Mechanism for Dissolution	238
III.	Binary Solutions	241
IV.	Multicomponent Systems	245
V.	Effect of Strain Energy	249
VI.	Conclusions	250
	References	250

# VII. Relationships between Phase Diagrams and the Structure of Glass-Forming Oxide Melts

#### E. F. Riebling

I.	Introduction	253
II.	Network Alteration in Silicate and Germanate Systems	259
III.	Conclusions	268
	References	269

#### CONTENTS

VIII.	Phase The C	Relations and Dilute Molten Salt Solutions— Cryoscopic Approach	
	<i>T</i>	R. Kozlowski	
	I.	Introduction	271
	II.	Theory	272
	III.	Cryoscopy in Molten Salts	285
	IV.	Comments on Experimental Procedures	302
	<b>V</b> .	Summary	304
		References	305
Аитнов	r Index		309
SUBJECT	INDEX		317

#### ix

### **List of Contributors**

Numbers in parentheses indicate the pages on which the authors' contributions begin.

- A. R. COOPER (237), Department of Metallurgy, Case Western Reserve University, Cleveland, Ohio
- B. C. GIESSEN (103), Department of Chemistry, Northeastern University, Boston, Massachusetts
- T. R. KOZLOWSKI (271), Research and Development Laboratories, Corning Glass Works, Corning, New York
- ERNEST M. LEVIN (143), National Bureau of Standards, Washington, D.C.
- M. F. MERRIAM (87), Department of Mineral Technology, College of Engineering, University of California, Berkeley, California
- R. R. MONCHAMP (1), Research Division, Raytheon Company, Waltham, Massachusetts
- J. W. NIELSEN (1), Bell Telephone Laboratories, Incorporated, Murray Hill, New Jersey
- M. B. PANISH (53), Bell Telephone Laboratories, Incorporated, Murray Hill, New Jersey
- K. M. RALLS (87), Department of Mechanical Engineering, University of Texas, Austin, Texas
- E. F. RIEBLING\* (253), Research and Development Laboratories, Corning Glass Works, Corning, New York
- R. H. WILLENS (103), Bell Telephone Laboratories, Murray Hill, New Jersey
- V. F. ZACKAY (87), Inorganic Materials Research Division, Lawrence Radiation Laboratory, Berkeley, California

<sup>\*</sup> Present address: Institute of Polymer Science, The University of Akron, Akron, Ohio.

#### Foreword

Perhaps no area of science is regarded as basic in so many disciplines as that concerned with phase transitions, phase diagrams, and the phase rule. Geologists, ceramists, physicists, metallurgists, material scientists, chemical engineers, and chemists all make wide use of phase separations and phase diagrams in developing and interpreting their fields. New techniques, new theories, computer methods, and an infinity of new materials have created many problems and opportunities which were not at all obvious to early researchers. Parodoxically, formal courses and modern, authoritative books have not been available to meet their needs.

Since it is the aim of this series to provide a set of modern reference volumes for various aspects of materials technology, and especially for refractory materials, it was logical for Dr. Allen Alper to undertake this new coverage of "Phase Diagrams: Materials Science and Technology" by bringing together research ideas and innovative approaches from diverse fields as presented by active contributors to the research literature. It is my feeling that this extensive and intensive treatment of phase diagrams and related phenomena will call attention to the many techniques and ideas which are available for use in the many materials-oriented disciplines.

JOHN L. MARGRAVE

### Preface

Many recent advances in materials science and technology have been made by scientists, engineers, and technologists who have used phase diagrams to solve materials problems. Many books have been written on the use of phase diagrams in the heat treatment of metals; however, the use of phase diagrams in other areas of materials science and technology has not been as thoroughly covered. Also, there have been numerous advances in this field in the last five years which have not appeared elsewhere than in this volume.

This volume deals with the use of phase diagrams in electronic materials and glass technology. Each article has been written by an authority in the field. The contents should be extremely useful to all scientists and engineers who are investigating and developing materials and to those who are using materials. It should also help in the education of materials science students.

The editor wishes to thank Professor John L. Margrave of Rice University and Dr. John H. Munier of Corning Glass Works. Thanks are also due to Corning Glass Works and Sylvania Electric Products Inc. for their assistance. Special thanks are given to all the authors who have contributed articles to this volume. The editor is particularly grateful for the many papers submitted by scientists of the Bell Telephone Company.

### **Contents of Other Volumes**

# Volume I: Theory, Principles, and Techniques of Phase Diagrams

- I. Thermodynamics of Phase Diagrams Y. K. Rao
- II. Computer Calculations of Refractory Metal Phase Diagrams Larry Kaufman and Harold Bernstein
- III. The Methods of Phase Equilibria Determination and Their Associated Problems

J. B. MacChesney and P. E. Rosenberg

- IV. Interpretation of Phase Diagrams H. C. Yeh
- V. The Use of Phase Diagrams in Solidification William A. Tiller
- VI. Phase Diagrams in High Pressure Research A. Jayaraman and Lewis H. Cohen
- VII. Metastable Phase Diagrams and Their Application to Glass-Forming Ceramic Systems

T. P. Seward, III