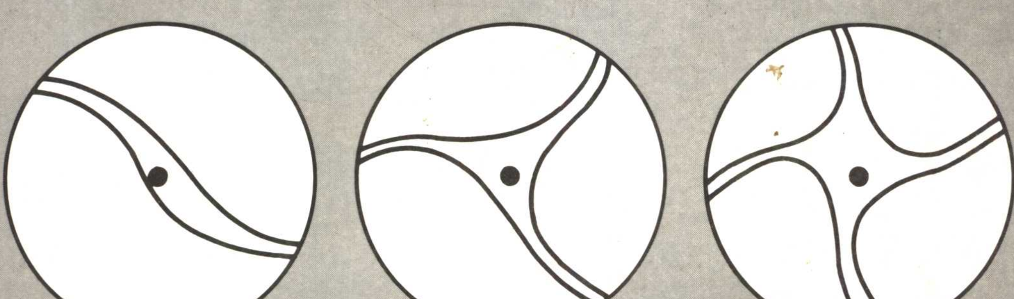
preparation and properties of solid state materials

volume 3

III-V alloys, convective instabilities, and nucleation



edited by
WILLIAM R. WILCOX
and
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Preparation and Properties of Solid State Materials

VOLUME 3

III-V Alloys, Convective Instabilities, and Nucleation

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Preparation and Properties of Solid State Materials

Volume 3

III-V Alloys, Convective Instabilities, and Nucleation

PREPARATION AND PROPERTIES OF SOLID STATE MATERIALS

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Volume 1 / Aspects of Crystal Growth, *edited by Robert A. Lefever*

Volume 2 / Chemical Vapor Transport, Secondary Nucleation, and Mass Transfer in Crystal Growth, *edited by William R. Wilcox*

Volume 3 / III-V Alloys, Convective Instabilities, and Nucleation, *edited by William R. Wilcox and Robert A. Lefever*

Additional volumes in preparation

INTRODUCTION TO THE SERIES

This series consists of reviews on important topics in preparation of solids and the influence of preparative conditions on properties. It was initiated as a result of a favorable response to a questionnaire distributed about ten years ago, supported by discussions with those engaged in the synthesis of solid state materials. The need for review and interpretation of recent advances became increasingly apparent as the primary journal literature continued to expand, with relevant papers dispersed throughout this literature.

Future volumes are planned which will contain reviews on temperature control, automatic diameter control, heat transfer, interface properties, morphological stability, graphite, silicon, integrated optics, chemical vapor transport, chalcogenides, eutectic solidification, space processing, transition metal oxyfluorides, $(SN)_x$, and perovskites, etc. While most of the topics considered to date are principally of interest in growth of single crystals, it is hoped that future reviews will deal with preparation of polycrystalline and amorphous materials.

Future volumes should appear at approximately annual intervals. Prospective authors are invited to contact the editor.

PREFACE

The goal of this advances series continues to be provision of timely reviews on special topics in preparation of materials, and the dependence of properties on preparative conditions. This volume deals with recent developments in convective phenomena in crystal growth, heterogeneous nucleation, and preparation of III-V alloy semiconductors with emphasis on ternary phase equilibria. It should therefore be of interest to chemical engineers, chemists, physicists and materials scientists.

We are grateful to Mrs. Lefever for her valuable assistance in preparation of the final copy for reproduction.

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PREPARATION AND PROPERTIES
OF SOLID STATE MATERIALS

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A Review of the Preparation of Single Crystals by Fused Melt Electrolysis and Some General Properties
--W. KUNNMANN

The Role of Mass Transfer in Crystallization Processes
--W. R. WILCOX

Exploratory Flux Crystal Growth--A. B. CHASE

Volume 2

Secondary Nucleation--JOSEPH ESTRIN

A Model of Vapor Transport and Its Interplay with Surface Reactions--DAVID BATTAT, MARC M. FAKTOR, and IAN GARRETT

A Generalized Treatment of Mass Transfer in Crystal Growth--WILLIAM R. WILCOX

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Chapter 1

THERMAL CONVECTION INSTABILITIES RELEVANT TO CRYSTAL GROWTH FROM LIQUIDS

J. R. Carruthers

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Murray Hill, New Jersey 07974

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I. INTRODUCTION

In order to grow large bulk crystals, it is necessary to avoid heterogeneous nucleation and to control the position, general shape, and local morphology of the growth interface. These objectives are achieved through the use of heat and mass flows. However, the gradients of temperature and composition required to drive these flows produce variations in the properties of the fluid medium from which the crystal grows. The most important property which changes is density. In the presence of a gravitational field, a density gradient will always cause fluid motion to occur when the gradient is not aligned in a direction parallel to gravity, as will be described later. Such fluid flow is called natural convection and may give rise to several phenomena which adversely influence crystal growth.

1. *GEOMETRY OF FLOW PATTERNS*

   a. Isotherms or isoconcentrates in the system adopt shapes influenced by the flow patterns so that the growth interfaces will be subject to similar spatial variations.

   b. The thermal center of symmetry may be displaced from the geometrical or rotational center of symmetry so that, in Czochralski growth, crystal rotation would produce growth-rate variations.

   c. The radial temperature gradient may go to zero at some radial position other than the thermal center of symmetry in Czochralski growth, making diameter control difficult at these radial positions.

   d. The fluid flow adjacent to the growth interface influences mass transfer and segregation processes, and therefore makes compositional control of the growing crystal difficult.

2. *FLOW TRANSIENTS*

   a. Under certain conditions, natural convection flows may become unstable and generate local variations of temperature and/or composition which will cause the growing crystal to develop inhomogeneous compositional distributions usually in the form of compositional striations parallel to the growth interface.

   b. Accelerations and decelerations in the growth rate associated with temperature fluctuations may give rise to nonequilibrium segregation behavior if the instantaneous growth velocity is too fast in any system possessing interfacial absorption phenomena.

These phenomena have all been well documented in crystal growth literature and excellent accounts have been given for growth from melts by Hurle [1], Brice [2], and Jakeman and Hurle [3], and for growth from fluxes by White and Wood [4].

At this stage in our understanding of crystal-growth dynamics, the special nature of natural convection flows in geometries and boundary conditions of relevance to crystal growth is not generally appreciated. In this chapter, the relevant fluid dynamics literature is reviewed with respect to the factors influencing thermal convection flow stability, the forms of unstable flow, and the control of thermal convection. The nomenclature used here will follow that of Ostrach in his treatise on laminar flows with body forces [5]. It is first necessary to recognize the distinction between the two general types of forces exerted on a fluid element; surface and body forces. Surface forces produce fluid motion in such a way that the net sum of the forces on all fluid elements is equal to the force on the bounding surface alone. Body forces, on the other hand, arise from action at a distance (e.g., from gravitational, rotational, electric, and magnetic fields) so that the reaction to these forces occurs outside the system under consideration and the magnitude of body forces depends on the properties of the medium (e.g., mass density, electrical conductivity, or magnetic permeability). Consequently body forces are effective throughout the interior of the fluid body.

Fluid motions caused entirely by the action of a gravity field are usually called natural flows, in contrast to forced flows brought about by surface forces. If natural flow is not constrained to a finite region by boundaries, it is often referred to as free convection. Only partially and completely confined natural convection will be considered here. The orientation of the heating and/or cooling surfaces with respect to the vertical direction of gravity is very important in thermal convection flows. When these surfaces are horizontal, the fluid density gradients produced are aligned in the same direction as gravity. When the density of such vertical graients increases upward, the fluid is gravitationally unstable although, as will be seen, a critical density gradient is required to initiate flow. On the other hand when the heating and/or cooling surfaces are not vertical, the density gradients produced in the fluid possess horizontal components which will always cause a fluid motion known as shear flow to occur. As will be shown in this chapter, such shear flows are basically stable in the sense that there is no time-dependent flow behavior until relatively high driving forces are reached (temperature differences), and in fact the vertical density gradients generated in the liquid are gravitationally stable. However, fluid flows generated by vertically upward heat flows are usually unsteady (time varying). The influence of confining boundaries on thermal convection flows has been recently reviewed by Ostrach [6] with an emphasis on the characteristics of the fully established shear flows rather than the instability problems.

The most important aspects of crystal-growth configurations with regard to thermal convection are the confined nature of the fluid flows and the presence of both adverse vertical as well as nonvertical heat flows. In order to understand the more complex problems involved in crystal growth however, simple natural convection configurations and boundary conditions will be discussed first.

Other phenomena which interact with thermal convection flows occur in crystal growth situations. These include density gradients due to compositional differences (thermosolutal convection), surface tension gradients along free surfaces giving rise to surface-driven flows (Marangoni convection), imposed variations in the boundary temperature or position (as may occur at growth interfaces), the presence of other modes of heat transfer in the liquid, and the presence of externally applied body-force fields other than gravity (such as magnetic, rotational, or electric fields and field gradients). These subjects will be dealt with separately in the remainder of this chapter.

This chapter will not deal with the turbulent regimes of thermal convection but will examine the conditions for and forms of the first instabilities appearing as time-dependent flows and associated temperature fluctuations. The effects of absolute pressure on thermal convection will also not be dealt with here, because attention will be directed almost exclusively to the case of liquids where such effects are small. Consequently, very little will be said about hydrothermal and vapor-growth systems where thermal convection flows provide most or all of the mass transport. Such systems usually display turbulent thermal convection at elevated pressures. An excellent account of thermal convection in vapor crystal growth has recently been published by Curtis and Dismukes [7].

II. REVIEW OF THE EFFECTS OF CONTAINER GEOMETRY AND ORIENTATION ON THERMAL CONVECTION STABILITY

The nature and extent of the bounding surfaces are of primary importance in determining the flow patterns developed by thermal convection. The case of free convection, which is not dealt with here, is concerned with the flow generated at a single surface immersed in a fluid of infinite dimensions and different temperature. The next *degree* of fluid confinement is provided by the presence of a second bounding surface, parallel to the first but at a different temperature. These surfaces may still be infinite in lateral extent (semi-infinite). Such a configuration is the starting point for this chapter and there are two additional aspects which must be considered; the orientation of the surfaces with respect to the vertical direction of gravity and the orientation of the heat flow directions with respect to the vertical direction of gravity. These two aspects are shown in Table 1 which is a tabulation of literature references pertinent to such thermal convection problems. The last degree of spatial fluid confinement is to remove the lateral semi-infinite extent criterion and move the lateral boundaries into positions so that

TABLE 1

Literature References for Thermal Convection in Containers of Various Geometries and Orientations with Respect to Gravity and for Different Heat Flow Directions

	Semi-infinite					
	Plates			Cylinders		
Heat flow	Horizontal	Vertical	Variable	Horizontal	Vertical	Variable
Side heating	--	15,16	--	23-25	--	--
Bottom heating	8-14	15-19	16,20	24	17,19,21	--
2-dimensional heating	22	15	--	24,25	--	--
3-dimensional heating	--	--	--	--	--	--

	Finite				
	Boxes		Cylinders		
Heat flow	One side parallel to g	Variable	Horizontal	Vertical	Variable
Side heating	26-37	65-70	--	--	--
Bottom heating	38-48	65-70	--	72-82	72-82
2-dimensional heating	49-64	--	71,105-119	83-104	--
3-dimensional heating	--	--	--	--	--

the spacing between them is comparable with the distance between the boundaries across which heat flows are occurring. The literature references pertinent to such completely confined thermal convection flows are shown on the right-hand side of Table 1 for different container orientations and heat flow directions with respect to the vertical direction of gravity.

Although studies of thermal convection between semi-infinite plates and cylinders have no direct application to crystal-growth geometries, they serve as starting points for thermal convection studies in the fluid dynamics literature and therefore must be understood first. The studies of finite containers have a direct bearing on crystal growth and in fact most of the published work has been performed in relation