CZOCHRALSKI GROWTH OF OXIDE CRYSTALS: NUMERICAL SIMULATION AND EXPERIMENTS

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Abstract

A mathematical model that explores the basic transport phenomena in a Czochralski process, their interaction and influence on the growth of high quality oxide crystals is presented. Rare earth garnets YAG and Nd-doped YAG are considered as representative oxide materials for the purpose of modeling and numerical simulation. The model proposed is evolutionary in time, and axisymmetric in space. All three velocity components enter the calculations, and in this respect, the model is posed in $2\frac{1}{2}$ dimensions.

The computational domain consists of the melt in the crucible, the crystal growing out of it, the seed rod, the gas phase and the enclosure. The conservation equations for mass, momentum and energy for all the three phases are jointly represented with the provision to account for abrupt changes in transport properties across the zonal boundaries. The zonal boundaries between two phases, for example, the phase-change interface move under the influence of flow and temperature fields and in turn can affect the transport behavior in the adjoining regions. The interfaces are followed by assigning a fixed grid line to them, and the interface movement is calculated using auxiliary equations that govern the interface dynamics. Grids are regenerated with every new location of the interface using a numerically derived coordinate transformation.

Assuming that the solid and liquid phases are separated by a sharp interface, the location and shape of the solidification front is obtained by the local energy balance between the heat fluxes in the crystal and melt along with the release of latent heat of fusion. The gas-melt interface is obtained by a force balance among the pressure forces, viscous forces, surface tension forces and centrifugal forces. The force balance accounts for thermocapillary (Marangoni) flow at the free surface. In addition, gas phase convection is taken to originate from the temperature difference between the melt surface and the enclosure, and not because of the surface velocity of the melt.

No-slip boundary conditions are used along all the solid surfaces. The crucible wall is assumed to be at a uniform temperature, while the temperature of the heat shield enclosing the crystal decreases linearly along the height until it reaches a low temperature at the top surface. The boundary pressures are derived from the internal pressure field, at the end of the overall computation. Owing to crystal pulling, there is an axial component of velocity at the melt-crystal interface. This is ignored in the boundary conditions because the pulling rate (which is around 1 mm/hour in YAG) is very small compared to other velocity components. The boundary conditions for the angular momentum equation at the melt-crystal interface is prescribed in terms of rotational Reynolds number of the crystal

The motion of Nd particles in the YAG melt is modeled using the dilute solution approximation. The segregation coefficient that determines the amount of Nd particles that enter the crystal from the melt, is assumed to be a constant for all time. Thus, it is independent of the local velocity and temperature gradients, the growth rate of the crystal and other operating conditions. Diffusion of Nd particles in the grown crystal has been neglected, since the appropriate time scale of diffusion is very large when compared to the time taken to empty the crucible by crystal growth.

Oxide crystals are not opaque to infrared radiation. In many instances, radiation losses from the bulk of the crystal and melt are quite large. Also the scattering of radiation by Nd in the YAG solution is expected to be significant during the growth of Nd:YAG crystals. The heat flux due to internal absorption, emission and scattering in the Czochralski domain is calculated by solving the Radiative Intensity Equation (RTE) simultaneously and iteratively along with the conservation of energy equation. The Czochralski domain is considered to be an isotropically scattering gray medium. The radiative properties are assumed to be independent of wavelength and temperature. The boundary surfaces are taken as diffusely emitting and reflecting opaque surfaces.

Results have been obtained for conditions under which the thermal boundary conditions do not change with time, the diameter of the growing crystal is a constant, but the pull velocity is a temporal variable that responds to the flow and thermal fields in the Czochralski process. Quantities of interest are the shape of the melt-crystal interface, the variation of pull velocity with time, consequences of bulk radiation and dopant transport. In addition, the onset of unsteadiness in the melt has been investigated.

Steady state analysis of convection in the melt reveals the extent of interaction of the individual transport mechanisms and their influence on the overall flow pattern and temperature distribution. Buoyant convection in a YAG melt produces melt-crystal interfaces that are convex into the melt. When the crystal is given a rotation, the centrifugal forces drive a clockwise roll that counteracts the thermally driven flow. Thus, when a critical rotation rate is exceeded, the interface shape changes from convex to flat, and subsequently becomes concave. The critical rotation rate has been identified as a function of the radius ratio and aspect ratio. When thermocapillarity at the free surface of the melt is included in the model, the Marangoni convection is found to enhance the circulation due to buoyancy-driven convection. The superposition of these two flow mechanisms leads to deeply convex melt-crystal interface. Under these circumstances, the effect of rotation is seen to be less prominent.

Unsteadiness in the YAG melt is observed at high Grashof numbers. The introduction of crystal rotation at high Grashof numbers is found to change the periodic oscillations to aperiodic high amplitude fluctuations. Chaotic patterns, as defined on a phase plot, appear at higher rotation rates. Unsteadiness at low Grashof numbers but high rotation rates was not observed in this work. In addition, Marangoni convection was also seen to have only a limited influence on the unsteady patterns.

Steady state simulation has been carried out for the full Czochralski domain including the melt, crystal and gas within the enclosure. The study reveals the possibility of superheating of the crystal beyond its melting point, thus leading to the grown crystal returning to the melt. Similarly, the possibility of subcooling of the melt below the melting point of YAG at locations away from the crystal edge has been indicated.

The numerical code has been modified to simulate continuous growth of a YAG crystal under quasi-steady conditions, by taking into account the increase in crystal height and a reduction in the melt volume. The maximum length of the crystal that can be grown using pull velocity control is established for different stages of crystal growth.

Absorption in the crystal increases thermal losses from the melt, steepens temperature gradients and is found to create deeply convex melt-crystal interface towards the melt. Absorption in the melt diminishes the intensity of natural convection flow. The bulk of the melt is found to become cooler with an increase in the absorption coefficient. The pull velocity required to maintain constant diameter crystal is higher when absorption in the crystal and the melt are taken into account. Scattering is found to have an opposite influence on the melt-crystal interface, strength of natural convection and pull velocity.

The solutal transport model predicts axial and radial segregation of Nd in the grown (Nd:YAG) crystal. Both radial and axial segregation are quite large at the initial stages of growth. The enrichment of the melt with the solute rejected by the crystal homogenizes the distributions in the crystal at later times.

Experiments using liquid crystal thermography have been conducted to study the interaction between buoyancy and crystal rotation, as well as for validating the computer codes. The experimental images show a cold plume descending along the axis of the beaker in the limit of pure buoyancy. The thickness of the plume reduces as the beaker wall temperature is increased. Complete axisymmetry is observed in the images when crystal rotation is absent. With crystal rotation, the cold plume is pushed radially along the crystal wall. At moderate rotation rates, convection patterns lose their symmetry and the flow appears to be chaotic. Symmetry is seen to be restored once again at a higher rotation rate. Isotherms seen in the experiments match reasonably well with the numerically generated isotherms simulated on a comparable geometry and set of boundary conditions.

Chapter 1

Introduction

1.1 Background of Czochralski Method

Techniques that grow crystals from the melt can be classified into two main categories: 1. confined crystal growth systems and 2. meniscus-controlled crystal growth systems. In confined crystal growth, both crystal and melt are confined within a solid container. In meniscus controlled crystal growth, there is a three-phase boundary line at which crystal, melt and the gaseous phases coexist. Czochralski technique, falls in this category.

The Czochralski technique originated from the pioneering work of J. Czochralski [1] in 1917 who pulled single crystalline wires of low melting point metals from the melt in order to determine the maximum speeds at which these could be crystallized. The work of Czochralski did not become widely known until 1951. As a technique for growing single crystals of useful size and perfection, Czochralski method was developed by Teal and Little in 1951 [2], who grew single crystals of Germanium (Ge), 203 mm long and 19 mm diameter. Since then, its application has been extended to the growth, first to silicon and then to a wide range of compound semiconductors, oxides and hallides.

1.2 Fundamentals of Czochralski Growth

The conventional Czochralski method is a *batch process* in which a single crystal is grown from the melt in a crucible, as shown in Figure 1.1. Czochralski processes for individual applications differ in terms of details, but the central idea has remained unchanged. The growth process comprises of the following steps: The crucible is initially charged with the polycrystalline material from which the single crystal is to be grown. Thermal energy is supplied by a heater surrounding the crucible thereby raising the temperature transfer and lead to an improvement in the growth conditions in a Czochralski process. The transport properties of the melt are the primary factors affecting the quality of grown crystals. These properties of melt are themselves determined by a broad and inter-dependent matrix of variables that include crystal rotation, crucible rotation, pull velocity, crucible temperature, gas pressure, and orientation. Thus, state-of-the-art crystal growth requires algorithms that model the physical phenomena by incorporating all parameters of interest. In addition, these simulations can form the basis of optimizing the process parameters, and evolve guidelines for future designs.

1.6 Scope of the Present Work

The motivation behind the present work is to explore in detail the basic transport processes in a Czochralski process, the interaction among the transport processes and their influence on the growth of high quality YAG and Nd:YAG crystals. With this objective, a mathematical model incorporating all the three phases of the Czochralski environment is developed. The model incorporates fluid flow, heat and mass transfer mechanisms in the melt, the crystal and the gas phase in the enclosure. Since YAG and Nd:YAG crystal are semi-transparent, a model to account for absorption, emission and scattering in the crystal as well as the melt phase has been adopted. The mathematical model also incorporates the macroscopic segregation of Nd in YAG. The melt-crystal interface shape and its changes during the growth of YAG and Nd:YAG crystals is an important factor that determines crystal quality. Special emphasis has been given to understand the interface movement throughout the work. The pull velocity and its change due to various transport mechanisms are carefully analyzed. A model flow visualization experiment using LCT as a sensor and water as the fluid medium has been conducted to study the interaction between buoyancy and forced convection.

1.7 Organization of the work

The present work has been organized in the following manner:

1. Chapter 2 is a review of the published literature on various aspects of transport phenomena in the Czochralski process. The growth of oxides in general and YAG and Nd:YAG in particular have been discussed. A detailed review of mathematical models proposed by various researchers is covered in this chapter.

2. Chapter 3 describes the mathematical formulation used in the present work for modeling the individual Czochralski growth processes, including fluid flow, heat transfer, radiative exchanges, solutal transport and phase change.

3. Chapter 4 presents numerical methodologies used for solving the partial and integro-differential equations arising from the mathematical model.

4. In Chapter 5, results from the numerical simulation of steady state flow and heat transfer in the YAG and Silicon melt are reported. The effect of various flow mechanisms in the melt and their influence on the melt-crystal interface are discussed.

5. Results pertaining to the onset of unsteadiness in melt flow are discussed in Chapter 6. The aim of this chapter is to understand the unsteady flow structures in a YAG melt and to obtain the range of parameters that define a steady flow regime.

6. Chapter 7 presents numerical results for the full Czochralski apparatus, with the components clearly identified[4]. The influence of gas convection, conduction in the crystal and radiative exchange between the exposed surfaces under continuous growth conditions are examined in this chapter.

7. The importance of internal absorption, emission and scattering on flow, heat transfer and pull velocity during growth of YAG and Nd:YAG crystals is presented in Chapter 8.

8. Chapter 9 discusses macroscopic transport of Nd particles in YAG. The dopant distribution, particularly the radial and axial segregation due to melt flow are described in this chapter.

9. Flow visualization experiments using LCT as a tool and water as the working medium are described in Chapter 10. The interaction between free and forced convection seen in experiments has been compared against the numerical simulator.

10. Conclusions drawn from the present study are summarized in Chapter 11.

[4]It is an example of system simulation.

Chapter 2

Literature Survey

2.1 Introduction

Theoretical and experimental research in the field of Czochralski growth of semiconductors have mostly been to understand the flow modes in buoyant convection, and to develop methods to restrain time dependence, three dimensionality and turbulence in the melt. Application of magnetic field [9] has been found to be an attractive method for limiting flow in semiconductors.

Of recent origin is the large scale utility of transparent oxide crystals in optics including lasers, windows, scintillators, along with nonlinear and passive optical devices. The Prandtl number for most of the oxide melts is high (around 10). Thus, the probability of the melt becoming time dependent, three dimensional and turbulent is less, when compared to semiconductors. On the other hand the coupling between the flow and heat transfer is significantly strong in case of oxide melt. Also, oxide crystals, as in semi conductors, require stringent control in their material structure, so that appropriate electrical, mechanical and optical properties are obtained.

The quality of the grown crystal, in particular the formation of defects is dependent on the shape of the melt-crystal interface. The shape of this interface is strongly dependent on the thermal field near the interface. The thermal field near the interface is governed by flow and heat transfer in the melt and the gaseous phase surrounding the crystal, and heat transfer in the crystal. Most of the research on the growth of oxide crystals has thus far focused on understanding the flow and heat transfer in the melt and its influence on the melt-crystal interface.

Oxide crystals are not opaque to infrared radiation, and are classified as *semi-*

Chapter 3

Mathematical Formulation of Equations Governing Transport Phenomena in a Czochralski Process

3.1 Introduction

The physico-chemical hydrodynamics of a Czochralski process involves fluid flow, heat transfer and change of phase of liquid to solid. Fluid flow problems involving phase change phenomena are characterized by internal boundaries that demarcate regions with different physical and chemical properties. Across the interfaces, compositions, phases, material properties and flow structures can have an abrupt variation. The interfaces move under the influence of flow and temperature fields. Their position and velocity can affect the transport behavior in the adjoining regions. Thus, not only are the transport of momentum, heat and mass inter-dependent, the formation, evaluation and dynamics of interfaces also play a major role in defining the behavior of the process. The correct representation of interfacial dynamics jointly with the physico-chemical transport processes is central to modeling crystal growth in a Czochralski system [26, 69].

The present study is focused on the growth of single crystals of YAG and Nd:YAG (Neodymium-doped Yttrium Aluminum Garnet). These oxide crystals are not opaque to infrared radiation. The semitransparency of these crystals needs special attention while developing the model. A second point of concern during the growth of a doped crystals is the homogeneous distribution of the dopant in the host. The model should address the issue of dopant segregation and distribution in the melt. These aspects are discussed in detail in the following section.

Chapter 4

Numerical Solution of the Governing Differential Equations

4.1 Introduction

The Czochralski crystal growth process involves fluid flow, heat and mass transfer, phase change, radiative transfer and deformable surfaces. Several numerical techniques have been proposed for tracking complex interfaces. These schemes can be broadly classified under two categories [77]:

(a) Volume tracking (Eulerian) method,

(b) Surface tracking (Lagrangian) method.

The Eulerian method differs fundamentally from the Lagrangian in that the interface is not defined explicitly or tracked but is reconstructed at every step. The most commonly seen methods in this category are based on the volume-of-fluid and enthalpy-porosity approaches. In the Eulerian method, the boundary conditions are incorporated in the governing equations through appropriate source terms. The Lagrangian (namely, the interface tracking method) on the other hand, maintains the interface as a discontinuity and explicitly tracks its movement. The interface is tracked as an $(n-1)$ dimensional entity in an n-dimensional Euclidean space. The most commonly method used in the Lagrangian approach uses coordinate transformation with body-fitting grids. Thus, the interface is a surface of discontinuity, that appears prominently in the numerical calculations. Grids are generated adaptively as a function of time, so that the interfaces are continuously tracked. The Lagrangian approach has been adopted in the present work. The interfaces are followed by assigning a fixed grid line to them, and the interface movement is calculated using auxiliary equations that govern the interface dynamics. Grids

Chapter 5

Comparative Study of Melt Convection in YAG and Silicon

5.1 Introduction

Melt flow in a Czochralski process is a superposition of buoyancy-driven convection, thermocapillarity and forced convection due to crystal rotation. These are respectively parameterized by Grashof number, Marangoni number and Reynolds number. By applying numerical simulation, it is possible to systematically investigate the influence of one physical phenomenon at a time. For example, crystal rotation and buoyancy effects can be excluded in order to investigate the convection phenomena due to thermocapillarity alone[1].

Of the three non-dimensional parameters referred above, (namely Grashof, Reynolds and Marangoni numbers) one is varied at a time while keeping the other two fixed. In this manner, one can observe the effect of individual phenomenon on melt flow and the shape of the melt-crystal interface. The dimensionless height of the crucible and the crystal diameter are additional parameters in numerical simulation. The effects of physical and geometric parameters on pull velocity required for the growth of a constant diameter crystal are also discussed.

Depending on the thermophysical properties, different materials would require their own specific growth conditions. Hence it is essential to study the transport phenomena in the melt for individual materials. With this objective, the transport phenomena in the melt of low Prandtl number silicon is compared with high Prandtl number YAG in

[1]Such a physical situation can arise in a microgravity experiment where the force of buoyancy is almost negligible. In this respect, microgravity is an ideal laboratory for the study of Marangoni flow.

Chapter 6

Simulation of Unsteady Flow and Transport in a Czochralski Process

Velocity and temperature fluctuations encountered in the Czochralski crucible have been identified as one of the factors leading to inhomogeneities in the grown crystal [52]. These fluctuations can cause the crystallization front to melt and resolidify alternately with time, and lead to variation of impurity concentration in the crystal. These variations are visible in experiments as growth striations.

The Czochralski growth of oxide crystals involves high temperatures, and the options available for controlling unsteady fluctuations are limited. It is more important to know limits on the excess temperature and crystal rpm beyond which flow (and temperature) fluctuations would be set up in the melt. Against this background, the presently a systematic investigation is carried out to evaluate the effects of Grashof number, Reynolds number, crystal radius (Rr) and crucible aspect ratio (Ar) on the flow oscillations.

6.1 Code Validation

To ascertain the accuracy and temporal resolution of the present unsteady simulation, the code has been validated against published data. An available benchmark is the work of Mohamad *et al.* [94] for two dimensional natural convection in a square cavity with differentially heated side walls. The simulation has been carried out at a Prandtl number of 0.02, typical of liquid metals. This is appropriate because convection in such melts have a greater tendency for unsteadiness, when compared to high Prandtl number liquids. The comparison with [94] is over a Grashof number range of $2{\times}10^5$ to $2{\times}10^6$.

Chapter 7

System Simulation of a Czochralksi Process

7.1 Introduction

A real-life Czochralski system has an enclosure, a gas phase, a growing crystal and a continuously diminishing melt level. It is understandable that the quality of crystals grown in a Czochralski process as well as the growth rate, are influenced by a combination of the following factors:

1. Heat transport by conduction in all the three phases (melt, crystal and gas);
2. Convection in the melt and gas phases;
3. Radiative exchange between various parts of the system.

The above mechanisms lend severity to mathematical analysis because of (1) an increase in the geometric complexity of the system as a whole, (2) rapid changes in material properties at material interfaces, and (3) the intrinsic coupling in transport phenomena among the three phases. A large number of geometric parameters and operating temperatures control transport phenomena in a complete Czochralski system. The list of parameters significant for the present analysis include the following: 1. Crucible wall temperature (T_w), 2. Crystal rotation rate ($\mathrm{Re}_{\mathrm{ct}}$), 3. Melt height (Ar), 4. Crystal height (Hr), and 5. Enclosure roof temperature (T_∞). In addition, the radiation properties of the melt, crystal and the enclosure surface also appear in the calculations.

In the present formulation, the pull velocity is calculated by requiring that the crystal diameter remains constant during the growth process. Hence it does not appear as an independent parameter. Pull velocity as a function of time is an output of the

Chapter 8

Role of Internal Radiation in a Czochralski Process

Crystals of YAG and Nd:YAG are grown from their molten state by the Czochralski technique. Oxide crystals are not opaque to infrared radiation. In many instances, radiation losses from the bulk of the crystal and melt are quite large. The scattering of radiation by dopants such as Nd particles can be significant during the growth process. The present study is a numerical simulation of flow and heat transfer during the growth of YAG and Nd:YAG crystals in a Czochralski process. The importance of radiation in the growth process has been examined in this chapter . The heat flux in the melt comprises of contributions from conduction, advection and radiation. The radiative portion of heat transfer comprises of internal absorption, emission and scattering. It has been calculated in the present work by solving the radiative transfer equation (RTE) simultaneously with the conservation of energy equation. The Czochralski domain is considered to be an isotropically scattering gray medium. The radiative properties are assumed to be independent of wavelength and temperature. The boundaries are taken as diffusely emitting and reflecting opaque surfaces. The results obtained in the present study clearly show that the losses calculated by including internal radiation are higher, when compared to surface radiation alone. In addition, the temperature distribution develops skewness with respect to the crystal axis and thereby influences the shape of the melt-crystal interface. Calculations incorporating the bulk radiation model also show the importance of enclosure conditions for controlling the crystal growth process.

Chapter 9

Solutal Transport of Nd Particles in Molten YAG

9.1 Introduction

Dopants are introduced in a controlled manner during the Czochralski growth of crystals to enhance their mechanical, thermal and optical properties. An example is Neodymium (Nd) that is added to YAG to alter its optical properties. The quality of the Nd:YAG crystal thus grown is determined by the degree of homogeneity of dopant distribution in the grown crystal. The inhomogeneity results from macroscopic as well as microscopic segregation of the dopant during growth. *Macrosegregation* is related to large-scale dopant transport in the melt. *Microsegregation,* generally referred to as striation, on the other hand, is introduced by the changes in growth conditions at a small length and/or time scale. The present chapter focuses on macrosegregation, particularly, the effect of melt flow on dopant transport.

During the growth process, there is a tendency for some of the solute particles to remain in the melt, while others prefer the solid, at the melt-crystal interface. Thus, it cannot be assumed that the layer of melt solidifying over a small time interval will transfer all the solute in the melt to the solid crystal. This phenomenon, namely, the rejection of some of the solute from the solidified crystal back to the melt causes the concentration of the dopant to increase in the melt with time. It is termed as *solute segregation.* The equilibrium segregation during the solidification of a binary system can be determined from the corresponding phase diagram. For a low solute concentration, the solidus and liquidus curves on the phase diagram can be considered as straight lines

Chapter 10

Experimental Study of Convection in Water using Liquid Crystal Thermography

10.1 Introduction

Numerical simulations provide direct insight into transport phenomena during Czochralski crystal growth. They help in optimizing the growth process with respect to the size and quality of the grown crystals, and the growth rate itself. Numerical simulation can, however, be unreliable if the thermophysical properties of the materials involved are not correctly specified. Intrinsic variability in radiative properties is also a source of error. The greatest uncertainty in simulation is related to the complexity of the transport process itself. For example, in a Czochralski process, fluid flow, all modes of heat transfer, mass transfer and interface movement are intricately coupled. Against this background, simplifying assumptions made regarding the geometry, the boundary conditions and relative importance of competing mechanisms become questionable. It is thus important to validate numerical solutions, not against other numerical results available in the literature alone, but against laboratory experiments, in which certain physical phenomena are localized and studied in detail. This approach is beneficial towards identifying complex flow structures and their sensitivity to small changes in the process parameters and boundary conditions.

In the present chapter, a validation of the numerical code against experiments in water is reported. The experiments reveal the interaction of buoyancy-driven convection in the crucible with crystal rotation. The crystal itself is passive, cold isothermal surface, while the crucible is a simple glass beaker.Steady state temperature distribution in the

Chapter 11

Conclusions and Scope for Future Work

11.1 Conclusions

A mathematical model that incorporates all the significant transport mechanisms in a Czochralski apparatus for the growth of YAG and Nd:YAG crystals is presented. The model is evolutionary in time, and axisymmetric in space. All three velocity components enter the calculations, and in this respect, the model is posed in $2\frac{1}{2}$ dimensions. Results have been obtained for conditions under which the thermal boundary conditions do not change with time, the diameter of the growing crystal is a constant, but the pull velocity is a temporal variable that responds to the flow and thermal fields in the Czochralski process. Quantities of interest are the shape of the melt-crystal interface, the variation of pull velocity with time, consequences of bulk radiation and dopant transport. In addition, the onset of unsteadiness in the melt has been investigated. The solutions of the governing system of partial differential equations and integro-differential equations have been numerically obtained. Experiments using liquid crystal thermography have been conducted to study the interaction between buoyancy and crystal rotation, as well as for validating the computer codes.

Major conclusions arrived at in the study are presented below.

Convection in the melt

Steady state analysis of convection in the melt reveals the extent of interaction of the individual transport mechanisms and their influence to the overall flow pattern and tem-