Effects of convection on physical vapor transport of Hg\(_2\)Cl\(_2\) in the presence of Kr - Part I: under microgravity environments

Yong Keun Lee and Geug-Tae Kim*†

Graduate School of NID Fusion Technology, Seoul National University of Science and Technology, Seoul 139-743, Korea
*Department of Nano-Bio Chemical Engineering, Hannam University, Taejon 305-811, Korea

(Received November 29, 2012)
(Revised January 2, 2013)
(Accepted January 18, 2013)

Abstract Special attention in the role of convection in vapor crystal growth has been paid since some single crystals under microgravity environments less than 1 g\(_0\) exhibits a diffusive-convection mode and much uniformity in front of the crystal regions than a normal gravity acceleration of 1 g\(_0\). The total molar fluxes show asymmetrical patterns in interfacial distribution, which indicates the occurrence of either one single or more than one convective cell. As the gravitational level decreases form 1 g\(_0\) down to 1.0 × 10\(^{-4}\) g\(_0\), the intensity of convection, indicative of the maximum molar fluxes, is reduced significantly for ∆T = 30 K and 90 K. The total molar fluxes decay first order exponentially with the partial pressure of component B, P\(_B\) (Torr) for 20 Torr ≤ P\(_B\) ≤ 300 Torr, and two gravity accelerations of g\(_y\) = 1 g\(_0\) and 0.1 g\(_0\).

Key words Mercurous chloride, Convection, Microgravity

1. Introduction

Physical vapor transport (PVT) has become an important crystal growth process for a variety of acousto-optic materials. Of particular importance is the use of PVT for materials processing experiments in high gravity environments, which would provide a better and thorough understanding of transport phenomena occurring in the vapor phase and crystal growth phenomena. Until now many theoretical studies and quantitative experiments on transport phenomena in PVT have been extensively investigated. Most important theoretical works were achieved by Rosenberger et al. [1-6] and, recently extended for transition to chaos flow fields in specialty materials of mercurous chloride in applications of microgravity experiments by Duval [7-12]. They have addressed the underlying phenomena in the PVT processes on the relative importance and influencing parameters of diffusion-advection, thermal and/or solutal convection on mass transport. Our recent studies [13-17] are for PVT processes of specialty materials such as mercurous halides under normal and microgravity environments to investigate the role of convection on the mass transport rate and its transition from diffusion-dominated to circulatory convection-dominated regimes in relation to total pressure, temperatures of source and crystal ends, aspect ratio (transport length-to-width), wall temperature profiles, molecular weights.

It is the purpose of this paper to study the essence of convection covering the various gravity accelerations in the PVT processes of Hg\(_2\)Cl\(_2\) crystal growth system. For this theoretical analysis of the PVT processes, a two-dimensional model is in horizontally oriented, cylindrical, closed ampoules in a two-zone furnace system. A mixture of Hg\(_2\)Cl\(_2\) vapor and impurity of Krypton (Kr) will be considered under microgravity environments.

2. The Model

Mercurous chloride (Hg\(_2\)Cl\(_2\)) materials are important for applications in acousto-optic and opto-electronic devices such as Bragg cells, X-ray detectors operating at ambient temperature [11]. The equimolar Hg\(_2\)Cl\(_2\) compound decomposes to two liquids at a temperature near 525°C where the vapor pressure is above 20 atm [18]. Because of this decomposition and high vapor pressure, Hg\(_2\)Cl\(_2\) cannot be solidified as a single crystal directly from the stoichiometric melt. However, very similar to the mercurous bromide [19], mercurous chloride exhibits sufficiently high vapor pressure at low temperatures so that these crystals are usually grown by the physical vapor transport (PVT) in closed silica glass ampoules.

Consider a rectangular enclosure of height H and transport length L, shown in Fig. 1. The source is main-
tained at a temperature $T_s$, while the growing crystal is at a temperature $T_c$ with $T_s > T_c$. PVT of the transported component $A$ ($\text{Hg}_2\text{Cl}_2$) occurs inevitably, due to presence of impurities, with the presence of a component $B$ (Kr). The interfaces are assumed to be flat for simplicity. The finite normal velocities at the interfaces can be expressed by Stefan flow deduced from the one-dimensional diffusion-limited model [20], which would provide the coupling between the fluid dynamics and species calculations. On the other hand, the tangential component of the mass average velocity of the vapor at the interfaces vanishes. Thermodynamic equilibria are assumed at the interfaces so that the mass fractions at the interfaces are kept constant at $\omega_{A,s}$ and $\omega_{A,c}$. On the vertical non-reacting walls appropriate velocity boundary conditions are no-slip, the normal concentration gradients are zero, and wall temperatures are imposed as nonlinear temperature gradients. The density is assumed to be a function of both temperature and concentration. The ideal gas law and Dalton’s law of partial pressures are used. The transport of fluid within a rectangular PVT crystal growth reactor is governed by a system of elliptic, coupled conservation equations for mass (continuity), momentum, energy and species (diffusion) can be represented by the generic equations, Eq. (1) through (4) [21] with their appropriate boundary conditions, Eq. (5) through (7). Let $u_x$, $u_y$ denote the velocity components along the $x$- and $y$-coordinates in the $x$, $y$ rectangular coordinate, and let $T$, $\omega_A$, $p$ denote the temperature, mass fraction of species $A$ ($\text{Hg}_2\text{Cl}_2$) and pressure, respectively, where the superscript of * denotes the dimensionless [13-17]. The linear temperature profiles at wall boundary conditions only are considered.

$$\nabla^* \cdot \nabla^* T^* = 0, \quad (1)$$

$$\nabla^* \cdot \nabla^* \omega^* = - \nabla^* p^* + Pr \cdot \text{Ar} \nabla^2 \omega^* - \frac{Ra \cdot Pr}{\text{Ar} \cdot T^*} \cdot e_y, \quad (2)$$

$$\nabla^* \cdot \nabla^* \omega^* = \frac{\text{Ar} \nabla^2 \omega^*}{Le} \quad (4)$$

On the walls ($0 < x^* < L$, $y^* = 0$ and 1):

$$u^*(x^*, 0) = u^*(x^*, 1) = v^*(y^*, 0) = v^*(y^*, 1) = 0, \quad (5)$$

$$T^*(x^*, 0) = T^*(x^*, 1) = \frac{T - T_c}{T_s - T_c} \quad (6)$$

On the source ($x^* = 0$, $0 < y^* < 1$):

$$u^*(0, y^*) = 0, \quad v^*(0, y^*) = 0, \quad T^*(0, y^*) = 1, \quad \omega_A^*(0, y^*) = 1. \quad (7)$$

On the crystal ($x^* = L/H$, $0 < y^* < 1$):

$$u^*(L/H, y^*) = 0, \quad v^*(L/H, y^*) = 0, \quad T^*(L/H, y^*) = 0, \quad \omega_A^*(L/H, y^*) = 0. \quad (8)$$

The vapor pressure [10] $p_A$ of $\text{Hg}_2\text{Cl}_2$ (in the unit of Pascal) can be evaluated from the following formula as a function of temperature: in which $a = 29.75$, $b = 11767.1$.

3. Results and Discussion

The six dimensionless parameters, namely Gr, Ar, Pr, Le, C, Pe, and thermo-physical properties for the operating conditions of this study are considered in this study. Because the molecular weight of a noble element (Kr) is not equal to that of the crystal component ($\text{Hg}_2\text{Cl}_2$) during the physical vapor transport, both solutal and/or thermal effects should be considered in this study.

Fig. 2 shows the interfacial distributions of total molar flux (moles cm$^{-2}$s$^{-1}$) of $\text{Hg}_2\text{Cl}_2$ for two gravity accelerations ($1g_0$, $0.1g_0$, where $1g_0 = 981$ cm s$^{-2}$), based on $\Delta T = 90$ K (350°C $\rightarrow$ 260°C), $P_B = 20$ Torr, $Ar = 5.0$, $Pr = 0.8$, $Le = 0.95$, $Gr_f = 2.9 \times 10^6$, $Gr_c = 2.6 \times 10^6$, $Pe = 4.5$, $C_v = 1.0$. The horizontal orientations and the linear temperature profiles at walls are considered in this case. Here,
the subscript of 0 denotes the normal gravity acceleration of 981 cm $\cdot$ s$^{-2}$. With decreasing the gravitational acceleration from 1 g$_0$ down to 0.1 g$_0$, the total molar flux for 0.1 g$_0$ is reduced by a factor of 0.57, in comparison with 1 g$_0$. As depicted in Fig. 2, similar to the earlier results of Markham, Greenwell and Rosenberger [2], one sees that the convective flow can cause significant non-uniformities in the total molar flux, with the specific distribution revealing dominance of solutal convection. Even though not shown here, the single convection cell flows towards the growing interface in the lower half of the growth ampoule, thus better supplying this part of the interface with vapor supersaturated in component A. Note that if there is thermal convection alone, with the left part of the ampoule warmer than the right part, an oppositely rotating roll would appear and, thus, result in enhancing the growth of crystal in the upper half of the interface [2]. As shown in Fig. 2, the interfacial distributions of total molar flux shows asymmetrical with respect to y = 1.0 cm, which indicates the presence of asymmetrical convection. Therefore, the asymmetrical convection cell in front of the crystal interface indicates three dimensional flow structures. It is also obvious that from the point of view of the uniformity, the total molar flux along the interfacial positions at g$_y$ = 0.1 g$_0$ exhibits to have a relatively flat structure compared to that at g$_y$ = 1 g$_0$. It indicates a factor of ten reduction in the gravitational level is enough to suppress convective effects on the crystal growth flux.

Fig. 3 shows interfacial distributions of total molar flux (moles cm$^{-2}$ s$^{-1}$) of Hg$_2$Cl$_2$ for two gravity accelerations (1g$_0$, 0.1g$_0$, where 1g$_0$ = 981 cm $\cdot$ s$^{-2}$), based on $\Delta T$ = 30 K (350$^\circ$C $\rightarrow$ 320$^\circ$C), P$_b$ = 20 Torr, Ar = 5.0, Pr = 0.8, Le = 0.45, G$_t$ = 3.9 $\times$ 10$^4$, G$_s$ = 5.4 $\times$ 10$^5$, Pe = 3.2, C$_r$ = 1.04.

In PVT processes, the temperature difference between source and crystal is one of the major parameters as well as a driving force for the mass transport. Under otherwise unchanged process conditions, decreasing the temperature difference for Ar = 5 gives similar results to Fig. 2. This suggests that in a 0.1g$_0$ of gravity environment the total molar fluxes would be increased by using smaller aspect ratio ampoules (Fig. 4) or larger temperature differences between source and crystal (Fig. 2), without the drawback of increased convection that would result from these measures on ground experiments. Compared with Figs. 2 and 3, it is clear that the effects of thermally buoyancy driven convection are important even in reduced gravity environments. The maximum total molar flux at $\Delta T$ = 90 K reaches at 1.57 moles cm$^{-2}$ s$^{-1}$, and the maximum flux of 1.18 moles cm$^{-2}$ s$^{-1}$ is obtained at $\Delta T$ = 30 K. When the temperature difference is de-
creased from 350°C by a factor of 0.33, the corresponding maximum molar flux is also decreased from 1.57 moles cm\(^{-2}\)s\(^{-1}\) by a factor of 0.75.

Fig. 4 shows interfacial distributions of total molar flux (moles cm\(^{-2}\)s\(^{-1}\)) of Hg\(_2\)Cl\(_2\) for two gravity accelerations (1g\(_0\), 0.1g\(_0\), where 1g\(_0\) = 981 cm s\(^{-2}\)) under the same conditions except for Ar = 2 as Fig. 2. The temperature difference between source and crystal remain unchanged and the source temperature of 350°C is fixed so that the effects of thermo-physical properties due to the variations in temperature could be negligible. Note that in actual crystal experiments of Hg\(_2\)Cl\(_2\), the typical source and crystal temperature correspond to 320°C and 290°C, respectively. It is interesting that the maximum total molar fluxes appear near the bottom of the ampoule with decreasing the aspect ratio (transport length-to-width) from Ar = 5 down to 2. In other words, the width is increased from y = 2 cm to 5 cm. As shown in Fig. 2, the maximum total molar fluxes occur near at the y = 0.5 cm for gravity accelerations under consideration in this study. Fig. 4 shows the total molar flux decreases linearly in accordance with interfacial position. In addition, the maximum total molar flux for normal gravity level is greater than that for 0.1g\(_0\) by a factor of 2. But, the total molar flux is likely to converge to some flux close to 0.55. This suggests the effect of side wall suppresses the convective flow and is greater for normal gravity level than the level of gravity acceleration with a factor of ten reduction.

Greenwell et al. [1] showed that small non-uniformities in growth rates can occur even in the absence of gravity and are associated with the recirculation of the inert gas. This was also true in numerical calculations as can be seen in Figs. 2 through 5. Even for situations of purely diffusive transport the growth rate was not strictly uniform, with growth being greater near the center than the edges. However, these growth rate variations were very small and within tolerable limits, unlike the large variations resulting from convective contributions.

Fig. 5 shows effects of partial pressure of component B, P\(_B\) (Torr) on the total molar flux of Hg\(_2\)Cl\(_2\) in terms of moles cm\(^{-2}\)s\(^{-1}\) for various partial pressures of component B, P\(_B\) (Torr), 20 ≤ P\(_B\) ≤ 300, based on ΔT = 90 K (350°C → 260°C), Ar = 5.
$P_B = 100$ Torr, decrease slowly until at $P_B = 300$ Torr. At both $g_y = 1g_0$ and $0.1 g_0$, the decrease in the total molar flux appears relatively small for $200 \text{ Torr} \leq P_B \leq 300$ Torr, and the corresponding regression profile is nearly flat. Moreover, as the $P_B$ is increased from $20$ Torr to $300$ Torr, i.e., by a factor of $15$, and the total molar flux for $g_y = 1g_0$ is decreased from $2.26 \times 10^{-5}$ down to $0.89 \times 10^{-5}$ moles cm$^{-2}$s$^{-1}$ by a factor of $0.39$, and for $g_y = 0.1g_0$, from $1.7 \times 10^{-5}$ to $0.49 \times 10^{-5}$ moles cm$^{-2}$s$^{-1}$ by a factor of $0.29$, respectively. Consequently, with decreasing the gravitational acceleration from $1g_0$ down to $0.1g_0$, the factor of reduction in molar flux is $0.74$, which reflects reduction in the effects of convection. Moreover, the gaps between the total molar flux for $g_y = 1g_0$ and $0.1g_0$ is smaller for the range of $20$ Torr $\leq P_B \leq 50$ Torr, and then, become larger $50$ Torr $\leq P_B \leq 100$ Torr and, for the range of $P_B$ more than $100$ Torr, appears invariant. The effect of gravity acceleration is likely to affect in the main the total molar flux rather than the effect of a convective parameter of partial pressure of component B, $P_B$.

Fig. 6 shows the interfacial distributions of total molar flux (moles cm$^{-2}$s$^{-1}$) of Hg$_2$Cl$_2$ for two gravity accelerations ($1g_0$, $0.1g_0$, where $1g_0 = 981$ cm s$^{-2}$), based on $\Delta T = 90 \text{ K (350}^\circ\text{C} \rightarrow 260^\circ\text{C})$, $P_B = 300$ Torr, $Ar = 5$. The operation parameters for $g_y = 1g_0$ in Fig. 5 are as follows: $Ar = 0$, $Pr = 0.75$, $Le = 1.28$, $Gr_t = 5.2 \times 10^4$, $Gr_i = 3.8 \times 10^5$, $Pe = 9$, $C_v = 1.1$. As shown in Fig. 6, like the cases of $P_B = 20$ Torr, i.e., as shown in Fig. 2, the maximum molar flux for two gravitational accelerations appear at the neighborhood of $y = 0.5$ cm, and the molar fluxes versus the interfacial positions show asymmetrical against the position of $y = 1.0$ cm. The molar fluxes for two different gravities of $1$ and $0.1g_0$, converge at the neighborhood of $0.2$, while for the cases of $P_B = 20$ Torr, the molar fluxes approach the value of $0.8 \times 10^{-5}$ moles cm$^{-2}$s$^{-1}$ near at $y = 2.0$ cm. This result indicates that the convection for $P_B = 20$ Torr is likely to be more predominant near at $y = 2.0$ cm than for $P_B = 200$ Torr. In comparisons of Figs. 2 and 6, an increase in the partial pressure of component B, $P_B$ from 20 to 200 Torr suppresses the convective effects. The maximum molar flux for $P_B = 20$ Torr and $1g_0$ is greater than for $P_B = 200$ by a factor of 2.45, while for the gravity level of $0.1g_0$ in Fig. 6, the maximum molar flux for $P_B = 20$ Torr is greater than for $P_B = 200$ Torr by a factor of 3.54. Also, the difference between the maximum and the minimum molar flux for $P_B = 20$ Torr and $1g_0$ is greater than for $P_B = 200$ Torr by a factor of 2.2, which implies the mass transport by the diffusion is strong to enough to cause more significant non-uniformities with increasing the partial pressure of component B, $P_B$.

Fig. 7 shows the total molar flux of Hg$_2$Cl$_2$ in terms of moles cm$^{-3}$s$^{-1}$ as a function of gravity accelerations, $10^{-4} g_0 \leq g_y \leq 1g_0$, based on $P_B = 200$ Torr and $\Delta T = 90 \text{ K}$.
The convection mode is predominant over the diffusion mode for $10^{-1} \leq g_y \leq 1g_0$. The convection mode is transited into the diffusion mode at $g_y = 0.1g_0$. And, down to $g_y = 10^{-4}g_0$, the diffusion becomes predominant. As seen in Fig. 7, the total molar fluxes drop sharply for $10^{-1} \leq g_y \leq 1g_0$. This indicates the mass transport is diffusion-dominated under the microgravity environments less than $0.1g_0$. One can see that the effect of thermosolutal convection is first important and then decreases rapidly and eventually the mode of transport becomes largely diffusion.

Fig. 8 shows the interfacial distributions of total molar flux (moles cm$^{-2}$s$^{-1}$) of Hg$_2$Cl$_2$ for various molecular weight of component B, $M_B$, $2 \leq M_B \leq 400$, based on $Ar = 5$ Torr and $\Delta T = 90$ K. It is concluded that unless the two components have molecular weights very close to each other, the dominant mode of convection is likely to be solutal. It is emphasized that the effects of solutal convection are reflected through the density gradient and binary diffusivity coefficient. The maximum total molar fluxes occur in the neighborhood of $y = 0.5$ cm.

4. Conclusions

The convection transport in crystal growth of Hg$_2$Cl$_2$-Kr during the physical vapor transport appears to be predominant over the diffusive transport. Thus, for vapor growth near normal gravity acceleration levels less than $0.1g_0$ would be needed to suppress convection. Even under microgravity environments of $0.1g_0$, i.e., for the diffusion mode, the nonuniformites in front of the crystal regions appear. For the levels of gravitational acceleration from more than $0.1g_0$ up to $1g_0$, there are appropriate to ensure the mass transport by the means of diffusive-convection. The asymmetrical convection cell in front of the crystal interface indicates three dimensional flow structures. It is also obvious that from the point of view of the uniformity, the total molar flux along the interfacial positions at $g_y = 0.1g_0$ exhibits to have a relatively flat structure compared to that at $g_y = 1g_0$. For $2 \leq M_B \leq 50$, it is concluded that unless the two components have molecular weights very close to each other, the dominant mode of convection is likely to be solutal. For gravity accelerations less than $1.0 \times 10^{-4}g_0$, the total molar fluxes are nearly invariant for $\Delta T = 90$ K and $Ar = 5$. For the range of 20 Torr $\leq P_B \leq 100$ Torr, the molar fluxes drop significantly, and, for 100 Torr $\leq P_B \leq 300$ Torr, decreases slowly. The total molar fluxes decay first order exponentially with the partial pressure of component B, $P_B$ (Torr) for 20 Torr $\leq P_B \leq 300$ Torr, and two gravity accelerations of $g_y = 1g_0$ and $0.1g_0$.

Acknowledgement

This work was financially supported by the Hannam University under Grant No. 2012A021 (April 1, 2012 through March 31, 2013).

References

[1] D.W. Greenwell, B.L. Markham and F. Rosenberger,