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Falling film melt crystallization (II): Model to simulate the dynamic sweating using fractal porous media theory

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HIGHLIGHTS

- Dynamic sweating was simulated with the fractal porous media theory.
- A characteristic factor φ was introduced to modify the model with a good agreement.
- The structure and permeability variation of crystal layer during sweating was explained with the model.
- A model system of FFMC is expected to establish and wildly used in industrial crystallization.

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ABSTRACT

This paper describes the model development of dynamic sweating in falling film melt crystallization (FFMC) using fractal porous media theory. The crystal layer has the characteristics of a fractal porous medium. An overall mass balance is applied to determine the structural and characteristic parameters of the crystal layer. Two ideal hypothetical models are adopted to describe the dynamic change of flow rate in sweating under sweating conditions. The characteristic factor φ is introduced to modify the model to describe the real process. The model is validated by experiment, and the simulated result agrees well with the experimental result. The model is then exploited to understand sweating behavior and the structure and permeability variations of the crystal layer in FFMC. More significantly, the sweating model is also an important part of the model system of the overall FFMC process.

1. Introduction

Sweating is defined as a temperature-induced purification step based on a partial melting of crystals or crystal layers by heating the cooled surface closely up to the melting point of the pure component (Ulrich and Bierwirth, 1995). As a consequence, the impurities adhering to the crystal surface and those contained in the pores of the crystal layer melt and are then discharged under the influence of gravity (Myerson, 2002). Sweating has received increasing amounts of attention as an effective technology for hyperpure material manufacturing (Jung et al., 2008), wastewater recovery (Veesler et al., 2010) and seawater desalination (Rich et al., 2012).

Wangnick and Ulrich (1994) focused on the sweating behavior and the impact factors of a solid-layer-type crystallization process. They described the purification efficiencies of each step using a dimensional analysis of the influencing parameters, which gave rise to a discussion on the separation effect of melt crystallization.

The purity of the product was reported to be determined by the growth rate and the sweating conditions (Poschmann and Ulrich, 1996). To obtain a given product, research on the stage number was carried out, which facilitates research into the optimized melt crystallization strategy for industrial applications (Ulrich and Neumann, 1997). König and Schreiner (2001) explored the purification potential of melt crystallization with sweating processes, which led to a high-purity product. This development inspired researchers to investigate sweating as an effective purification process when fine control was unapproachable in the crystal layer growth process. The purifying effect of

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sweating was influenced by the crystal layer growth conditions and the inclusion in the crystal layer (Kim and Ulrich, 2002a, 2002b).

At the beginning of sweating, the impure liquid phase comprises the majority of the sweating liquid. The impure liquid phase will be transported out of the crystal layer under the temperature gradient. When the temperature is close to the melt point of the pure component, an increasing number of pure crystals melt, which leads to a reduction of the product. Therefore, it is necessary to develop a dynamic model for the sweating of melt crystallization that describes the sweating behavior and predicts the separation effect. There are various driving forces (temperature gradient, tension differences) of sweating liquid discharge, complex crystal–liquid phase surfaces and intricate pore distributions of the crystal layer. There is also a phase transition (crystal–melt–liquid) during the dynamic sweating. Thus, the application of multi-field theory is required to build the dynamic model.

Yu (2008), Shou et al. (2010) and Cai and Yu (2011) reported that the seepage of fluid in porous media was strongly influenced by the structural and characteristic parameters of the porous medium. A model to simulate the seepage process in porous media with constant driving force and no phase transition was also developed by Xu et al. (2008) and Yun et al. (2009), which offered a fundamental basis for further theoretical and experimental research.

In the work of Jiang et al. (2011), an existing fractal porous media model was applied to simulate the structure of the crystal pillar formed in static melt crystallization for hyperpure phosphoric acid separation. The model simulated the liquid discharge process with satisfactory results. Fractal porous media theory was deemed appropriate to describe the structure of the crystal layer in melt crystallization.

Some early experiments were carried out on the dynamic sweating of falling film melt crystallization (FFMC) by Jiang et al. (2012a). The results showed that the average melt discharge rate increased with the overall average superheating degree. The structural parameters of the crystal layer also affected the sweating.

As reported in the authors' former work (Jiang et al., 2012b), the thickness of the crystal layer along the crystallizer can be obtained by the existing model with known operational conditions. The impure liquid entrapment and the formation of a branched-porous (B–P) structure occur inevitably in FFMC. Therefore, it is crucial to investigate the structural and characteristic parameters of the crystal layer.

Fractal and porous media theory will be applied to describe the dynamic sweating in FFMC in this paper, which is a more challenging and complicated endeavor than that for static melt crystallization. This paper will focus on how the crystal layer structure changes during the dynamic sweating. Some critical parameters based on the porous media theory will be proposed to investigate the impact of sweating on the structure of the crystal layer. In addition to comparing the simulative and experimental results of sweating, this paper also evaluates the separation efficiency of sweating. All of these results will contribute to proving that the dynamic sweating model has potential applications in dynamic simulations and separation effect evaluations.

2. Model development

2.1. Structural and characteristic parameters of the crystal layer as a fractal porous medium

2.1.1. Porous media structural parameters of the crystal layer

As reported by Jiang et al. (2011), the structure of the crystal layer formed in static melt crystallization was analyzed using fractal porous media theory. The mass balance for each step should be carried out first.

Mass balance for crystal layer growth:

$$m_F = m_{CL} + m_{ML}$$
$$m_F C_F = m_{CL} C_{CL} + m_{ML} C_{ML} \tag{1}$$

where m_F, m_{CL} and m_{ML} are the mass of the feed, crystal layer and mother liquid discharged from the crystallizer, respectively. C_F, C_{CL} and C_{ML} are the mass fraction of H_3PO_4 in each flow.

Mass balance for impure liquid phase entrapment:

$$m_{CL} = m_C + m_{LE}$$
$$m_{CL} C_{CL} = m_C C_C + m_{LE} C_{LE} \tag{2}$$

where m_C and m_{LE} are the mass of the crystal phase and the mass of impure liquid entrapped in the crystal layer, respectively. C_C and C_{LE} are the mass fraction of H_3PO_4 in each phase. C_{LE} is assumed to be the equilibrium concentration at the corresponding system temperature.

Mass balance for sweating liquid discharge:

During the sweating, the entrapped impure liquid phase will be transported out of the crystal layer from the open pore channels. Considering that some crystals will melt and discharge simultaneously, the sweating liquid is a mixture of the entrapped impure liquid and the melted crystal phase, which is

$$m_{Sw} = m'_C + m'_{LE}$$
$$m_{Sw} C_{Sw} = m'_C C_C + m'_{LE} C_{LE} \tag{3}$$

where m_{Sw}, m'_C and m'_{LE} are the mass of the sweating liquid, the melted crystal phase and the impure liquid phase discharge out of the crystal layer, correspondingly. C_{Sw}, C_C and C_{LE} are the mass fraction of H_3PO_4 in each phase. These three mass balances can be solved using experimental data.

According to the definition of porosity, the initial porosity of the crystal layer at the beginning of sweating (also the terminal porosity of the crystal layer at the end of the layer growth process) is

$$\phi_{ini} = \frac{V_P}{V_{CL}} = \frac{m_{LE}/\rho_{LE}}{m_C/\rho_C + m_{LE}/\rho_{LE}} \tag{4}$$

where ρ_{LE} and ρ_C are the densities of each phase, which can be obtained using known state temperature and mass fraction. As mentioned in authors' former work (Jiang et al., 2012b), the composition of the crystal layer was determined by the layer growth conditions. Therefore, the structural parameter ϕ_{ini} is not only the boundary condition of sweating but also the parameter that reflects the layer growth conditions (such as feed rate, feed mass fraction, cooling rate, etc.). ϕ_{ini} is introduced into the sweating model instead of the multi-operation conditions in crystal layer growth. This substitution will vastly simplify the sweating model, allowing the study to focus on how the sweating operation conditions influence the process.

The porosity of the crystal layer at the end of the sweating is

$$\phi_{Final} = \frac{V_P + \Delta V_P}{V_{CL}} = \frac{m_{LE}/\rho_{LE} + m'_C/\rho_C}{m_C/\rho_C + m_{LE}/\rho_{LE}}. \tag{5}$$

To simplify the developing model, the variation rate of the porosity a is assumed to be a constant,

$$\Delta\phi = \phi_{Final} - \phi_{ini} = at \tag{6}$$

where t is the sweating duration. The variation rate of the porosity a is thought to be a criterion for the stability of sweating under different operation conditions.

The effective porosity was defined as the ratio between the effective pore volume and the total volume of porous media. The effective pore volume is the connected volume in porous media,