물리증착에서 지방산 분포의 측정

정수영, 김영한*, Keisuke Fukui[1], Kouji Maeda[1]
동아대학교 화학공학과
[1]일본 효고현립대학 기계・시스템공학과
(yhkim@mail.donga.ac.kr*)

Measurement of Fatty Acid Distribution in PVD

Su Yeong Jeong, Young Han Kim*, Keisuke Fukui[1], Kouji Maeda[1]
Department of Chemical Engineering, Dong-A University
[1]Department of Mechanical and System Engineering, University of Hyogo
(yhkim@mail.donga.ac.kr*)

1.Instruction

PVD (Physical Vapor Deposition) is a fine technique to form a crystalline phase of high purity from a melt of mixture under vacuum, whereas melt crystallization is a mass purification technique for metals and organic compounds. We have reported that the separation performance of the PVD, and compared the performance with the melt crystallization by measuringt he growth rate of solid phase in the PVD using a quartz crystal resonator [1].

In this work, we reported the separation capacity of the PVD from the several fatty acid melts having different compositions of lauric and myristic acids. The growth rate of deposit was correlated with melt temperature, and the composition of lauric acid in the deposit and the distribution coefficient of lauric acid were correlated with the growth rate of deposit using the distribution coefficient model [2, 3].

2.Experiment

Material used in this work was binary fatty acid mixtures consisting of lauric acid and myristic acid. The fatty acid vapor was prepared from binary melt in a flask heated at a given temperature with a mantle heater. The cold quartz crystal resonator was placed on the top of the flask, and the temperature of the cold resonator, T_c, was kept at a constant temperature between 283 K and 288 K using circulating water temperature-controlled with a thermostat. The binary vapor was deposited on the cold resonator, while the evacuation pressure, P^{ex}, was maintained ata pressure of 2.5 Pa.

The resonator has a base frequency of 8 MHz, and detects a mass loading of 1.0 ng per 1 Hz of frequency variation [4]. The composition of lauric acid in the melt was adjusted in the range of 0.19 – 0.75 as a operating variable. The melt temperature was varied between 353 K and 473 K as another operating variable.

3.Results and Discussion

3.1 Deposition rate and growth rate of deposit

Fig.1 shows the deposition rate of fatty acids as a function of melt temperature. The melt temperature increases the deposition rate almost linearly, even though the vapor pressure, the driving force of the PVD, is exponentially raised with the elevation of melt temperature.

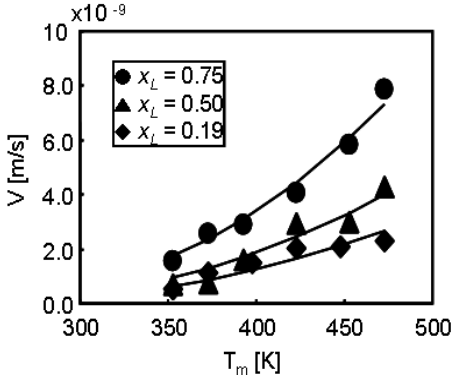

Fig.1 Growth rate of deposits as a function of melt temperature.

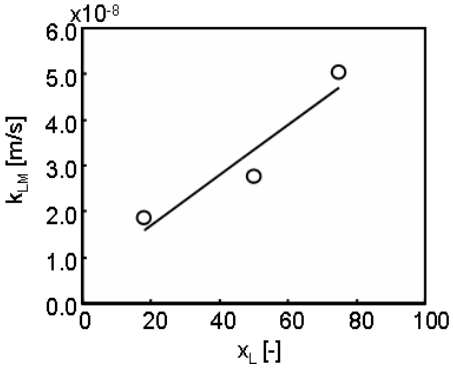

Fig.2 Mass transfer coefficient as a function of melt composition

As the composition of lauric acid rises, the deposition rate also grows. The rate increase with the temperature elevation is more apparent at the higher melt composition of lauric acid. The growth rate of solid deposit, V, is computed from the deposition rate, G, as follows.

$$V = G / \rho_s \tag{1}$$

where r_s is the density of solid phase, 0.9 g/mL. Fig.2 shows the growth rate of deposits as a function of melt temperature. We correlated the following equation for the growth rate of deposits because the driving force of PVD is the vapor pressure of melt

$$V = K_{LM} \exp\left(\frac{A}{T_m}\right), A = \Delta H / R = -2000[K] \tag{2}$$

When the energy parameter, A, is set and the mass transfer coefficient, K_{LM}, is a function of the composition of lauric acid in melt because the composition affects the growth rate. Fig.3 shows the effect of the composition of lauric acid in melt on the mass transfer coefficient. It is obvious that mass transfer of lauric acid is faster than that of myristic acid due to higher volatility.

3.2 Composition of lauric acid in deposits and distribution coefficient of lauric acid between vapor and deposit phases

Fig.4 shows that the composition of lauric acid in deposits is slightly raised when the melt temperature increases for different compositions of lauric acid in melts. The deposits have more lauric acid when the melt composition of lauric acid is 0.5 or higher. It indicates that myristic acid resublimates selectively. Consequently, the depoits of either lauric acid rich or myristic acid rich can be obtained from the PVD by adjusting the melt temperature and the

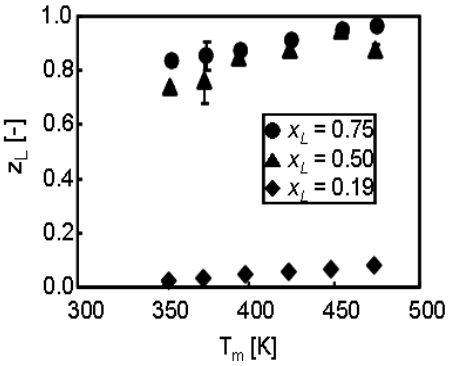

Fig.3 Composition of lauric acid in the deposits vs. melt temperature

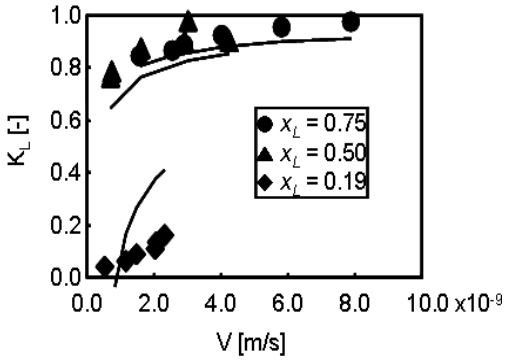

Fig.4 Distribution coefficient of lauric acid as a function of growth rate

composition of lauric acid in melt as operating variables. Note that the vapor phase composition of lauric acid lowers with temperature increase at a constant pressure. Probably the composition of lauric acid in the vapor phase was higher at the raised temperature. Here, the distribution coefficient of lauric acid, K_L, was computed as the ratio of the composition of lauric acid in deposits, z_L, to that in vapor phase, y_L.

$$K_L = \frac{z_L}{y_L} \tag{3}$$

We assumed the compositions of lauric acid in vapor phase, y_L, in equilibrium with the melts having the compositions of 0.19, 0.50 and 0.75 of lauric acid were 0.5, 0.97 and 0.99, respectively. Fig.5 shows the distribution coefficient of lauric acid as a function of the growth rate. The distribution coefficient for the melt having lauric acid composition of 0.19 is very good for the separation, but the distribution coefficients for those of the composition of 0.5 and 0.75 are not. The non-equilibrium distribution coefficient, k_L, can be a function of the growth rate as the following equation.

$$k_L = 1 - (1 - k_0)\sqrt{\frac{1 - \exp(-V_{min}/k_{m0})}{1 - \exp(-V/k_{m0})}} \tag{4}$$

where k_0 is the equilibrium distribution coefficient and is equal to zero for non-equilibrium. Therefore, the only correlating parameters are $V_{\min}$ and k_{m0}. In the recent study [1], the distribution coefficient of lauric acid for the PVD was very small compared with that for the melt crystallization[1,3]. The distribution coefficient is very sensitive to the growth rate, and the distribution coefficient drastically increases when the growth rate approaches to a specific growth rate. The growth rate is denoted as the minimum growth rate, $V_{\min}$, at which the segregation of impurity occurs. The distribution coefficients obtained in this study are large because the growth rates are also large. The minimum equilibrium distribution coefficient, k_{m0}, was fixed at 0.001 m/s in this study, and the minimum growth rate, V_{min}, was thought to be a function of the lauric acid composition in the melt.

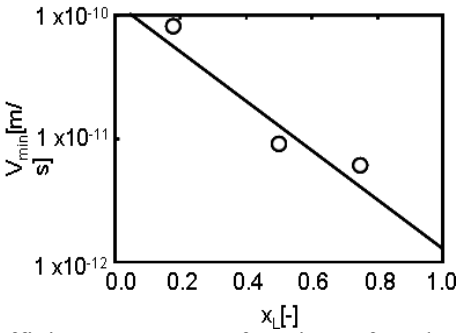

Fig.5 Coefficient V_{min} as a function of melt composition

4. Conclusion

The PVD of fatty acid mixtures was performed at different compositions of lauric acid in melt. The deposition rate and the growth rate of deposits were increased with the elevations of melt temperature and the melt composition of lauric acid. The growth rate of deposits was correlated as a function of the melt temperature and the melt composition. The deposits from the melt composition of 0.19 of lauric acid contains less than 10 % of lauric acid though the vapor composition is about 50 %. On the contrary, the deposits from the melt compositions of 0.5 and 0.75 have much higher composition of lauric acid. The distribution coefficient for the PVD was correlated as a function of growth rate and the melt composition of lauric acid.

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