1. Introduction

Among various liquid–solid separation processes whose application to purification of semisolid metals was laid emphasis on, the fractional melting, F.M., process was reported as one of the most effective methods. For example, “for a “yield” of refined solid of 0.4 of the original sample and a partition ratio, \(k\) of 0.1, the process achieves a refining ratio of as low as 10\(^{-2}\), 1,000 times lower than isothermal separation and comparable to that obtained by multi-pass zone refining.”\(^1\)

The purification through the fractional melting involves heating an alloy within its liquid–solid region while simultaneously draining the liquid from the solid. Also, the efficiency of the fractional melting process was known to depend on the heating rate and the amount of liquid separated from the solid–liquid mixture, so called “cake”. That is, if heating is sufficiently slow that complete diffusion is obtained in the solid and separation between the solid and the liquid attained perfectly, the most effective results could be achieved. The degree of the separation was expressed by the “wetness,” \(W\) which refers to the fraction of the liquid remaining in the cake, solid–liquid mixture, \(m_l/m_c\) \((m_l:\) mass of liquid in the cake, \(m_c:\) total mass of the cake).\(^1\)

The effect of wetness on purification and comparison of fractional melting with zone refining were shown in Fig. 1. As shown in the figure, only 5% of the remained liquid reduced as much as one order of the refining ratio at the refined solid of 0.4 of the original sample.

Lux and Flemings accomplished the purification through the heating rate of 100°C/h (1.67°C/min) and applying a compressive force of 2,900 psi (20 MPa) for separating the liquid from the cake. A “wetness” of 0.07 as well as the commercialization of the process, therefore, was achieved even by about 2 MPa. However the effect of two major parameters of the process, that is the pressure and heating rate on the process efficiency had not been understood quantitatively. The purposes of the current research were to investigate the effects of the pressure on the liquid–solid separation behaviors and therefore the refining ratios. The effect of the heating rate on the degree of the purification was also studied.

2. Experimental Apparatus and Procedure

The experimental apparatus is shown schematically in...
The quartz (or pyrex) tube filled with an inorganic oil (i.e., silicone oil) was placed in a heating rate controllable cylindrical furnace. The “L” shape specimen holder of which two ends were made by stainless steel mesh was placed in the middle of the quartz tube and connected to a motor.

When the temperature reached the solid–liquid region during the heating process, the motor is switched on and the sample starts to rotate. The liquid ejected from the solid–liquid mixture by the centrifugal force, collects at the bottom of the tube in ejected order. Since the lower part of the tube was maintained at ambient temperature, the liquid droplets solidified instantly as they settled down. The liquid and the solid droplets did not agglomerate because of the intervention of the silicon oil. The droplets, therefore, were isolated from each other and maintained their inherence of the ejected liquid phase. The functions of the silicon oil in the process were the “cleaning action” (diluting and washing out the liquid) of the solid–liquid mixture in the filter as well as the isolating the droplets from each other. Instead of inorganic oil, salts were used for high melting temperature metals. The refining ratio could be mainly varied by the heating rate and by the rotating speed. The heating rate could be controlled down to 0.1°C/min, while the rotating speed was up to 3 000 rpm. The exact experimental details have been presented in elsewhere.

The Sn–2%Pb alloy system which was prepared from melting the elements of 99.99 wt% purity in an evacuated quartz tube was selected to study the refining behaviors in the modified fractional melting process.

### 3. Results and Discussion

In the present F.M. process, the refining ratio depends on partition ratio, cake wetness, fraction of solid and extent of the diffusion in the solid. In this investigation, the effects of experimental variables such as a heating rate and rotation speed on the cake wetness and the extent of the diffusion in the solid were studied. The rotation speed mainly affects the cake wetness, while the heating rate affects solute diffusion. The variations of the refining ratio due to rpm and heating rate change were shown in Fig. 3. The refining ratio, $C_C/C_S$, decreases as the fraction of the solid decreases.

Figure 3(a) shows refining ratio changes with the changes in RPM. As shown in the figure, the refining ratio for $0.8f_S$ is about 0.1 for 3 000 rpm, while 0.3 for 2 000 rpm. It appears that this is due to the increasing centrifugal force which promotes removal of liquid in the cake. That is, the liquid drains more easily from the cake, when the rotation speed is higher and when the centrifugal force was larger. The effects of heating rate were shown in Fig. 3(b). The decrease in the refining ratio with decrease in the heating rate would be expected as a result of increasing of solid diffusion. As shown in the figure, there is the difference in refining ratio by 3 times at $0.8f_S$.

As mentioned above, the successful performance of refining is largely dependent on the slow heating rate for complete diffusion in the solid, and the high centrifugal force for completely removing the liquid in the cake. The quantitative analysis using the wetness suggested by Lux and Flemings were also superimposed in the figure. That is, the present process with the rpm of 3 000 and the heating rate of 0.1°C/min was as effective as the wetness of 0.02. However, it appears that the constant value of the wetness does not agree well with the experimental results. In other words, wetness is not a constant value during the present F.M. process but rather variable with a solid fraction.

### 3.1. Quantitative Analysis

From the quantitative analysis of the F.M. process, the refining occurs by the partition between the high concentrated

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**Fig. 2.** Schematic diagram of the Fractional melting apparatus.
1. motor 2. furnace 3. pyrex tube 4. silicone oil (or salt) 5. filter 6. thermocouples 7. stainless rod

**Fig. 3.** Effects of RPM and heating rate on the refining ratio.
The partition ratio of the Sn–2%Pb is taken to be 0.0656.
liquid phase and the relatively pure solid in the mixed region. If the partition was perfect, the value of the wetness in the cake would be 0 and the concentration of the cake was expressed by the equilibrium partition coefficient \( k = C_S/C_L \). Therefore, the highest refining result could be expected.

If there was not a complete partition, however, the concentration of the cake, \( C_C \), could not follow the equilibrium soliudus line because the cake contained partly the unseparated liquid, though still the concentration of the separated liquid could be estimated by the equilibrium liquiuds line (Fig. 4).

Therefore, a new refining partition coefficient between the cake and the liquid, was needed and suggested by \( k' = C_C/C_L \). The loci of the \( C_C \), could be regarded as the effective soliudus line which the real refining ratio could be estimated from. The effects of the processing variables such as a rotating speed and a heating rate on the effective refining partition ratio, \( k' \), thus, might explain the refining behaviors of the present F.M. process more completely.

In Fig. 4, the fraction of cake, \( f_c \), and the fraction of the liquid, \( f_L \), can be obtained from the “leverage rule”:

\[
f_c = \frac{C_L - C_o}{C_L - C_C}, \quad f_L = f'_L + f''_L = \frac{C_o - C_s}{C_L - C_s}
\]

By the each definition:

\[
C_s = kC_l, \quad W = \frac{f'_L}{f_c}, \quad f''_L + f_c = 1
\]

Therefore, the relationship between new parameter, \( k' \) and the existing \( W \) is given by:

\[
k' = k + W(1-k) \quad (1)
\]

It was also noted that \( k' \) increased from \( k \) to 1 as the wetness increased. The change of \( k'/k \) according to RPM and heating rate at 0.75 \( f_c \) is shown in Fig. 5.

In this figure, it is shown that \( k' \) which obtained from experimental results is larger than \( k \) by 1.5–2 times, because of both limited diffusion extent and the non-zero values of the wetness. The new suggested value, \( k' \) consists of \( k \) and wetness, and indicates the efficiency of refining process. The effects of a heating rate and a rpm (or a centrifugal force) on a refining partition coefficient, \( k' \) and thus a refining ratio were intended to analyze quantitatively.

3.2. Effect of Centrifugal Force

In order to understand an effect of centrifugal force on the separation, the amount of ejected liquid was measured according to the pressure. The relationship between the mass of liquid removed from the cake, \( m_L \) and applied pressure is shown in Fig. 6; a sample used in this case is the Sn–2%Pb alloy, 15 g at 220°C. It is observed that \( m_L \) increases linearly with pressure.

When sample is heated into the liquid–solid range, if the wetness is not 0, the fraction of the liquid, \( f_L \) consists of \( f'_L \) which remains in the cake, and \( f''_L \) which is removed from the cake. The fraction of the cake, \( f_c \), therefore, is composed of the fraction of solid, \( f_s \), and \( f'_L \). These relationships are described by the equations:

\[
f'_L + f''_L = f_L \quad (2)
\]

\[
f'_L + f''_L = f_c \quad (3)
\]

The increment of \( f''_L \) was equal to the decrement of \( f'_L \), for a constant \( f_c \), and also proportional to the applied pressure (Fig. 6) and total amount of \( f'_L \).

\[
df''_L = -df'_L \quad (4)
\]

\[
df''_L = \alpha df' \quad (5)
\]

Here, \( \alpha \) is a proportional constant and can be determined from the experimental data. Substitute of Eq. (4) into Eq.
(5) and integrate between the limits \( f'_L = f_L \) at \( P=0 \) and \( f'_L = f_L \) at \( P=P \) yields

\[
f'_L = f_L \exp(-\alpha P)
\]

Then, the wetness should be rewritten as:

\[
W = \frac{f'_c}{f_c} = \frac{f'_C}{f_C} = \frac{f_L \exp(-\alpha P)}{f_L \exp(-\alpha P) + f_S}
\]

\[
= \exp(-\alpha P) \frac{\frac{f_S}{f'_L}}{\exp(-\alpha P) + \frac{1-C_0/C_L}{C_0/C_L - k}}
\]

When the effect of centrifugal force is considered for wetness, it also affects refining partition coefficient \( k' \), then from Eq. (1) \( k' \) is defined as:

\[
k' = k + W(1-k)
\]

\[
= k + \frac{\exp(-\alpha P)}{\exp(-\alpha P) + \frac{1-C_0/C_L}{C_0/C_L - k}} (1-k)
\]

Where the pressure can be calculated from the centrifugal force exerting on the filter.

\[
P = \frac{F}{A} = \frac{mf_d a}{A} = \frac{mf_d r^2 \omega^2}{A} = \frac{mf_d r^2 (2\pi f)^2}{A} = \frac{mf_d r^2 \pi^2 R^2}{A}
\]

\[
\frac{C_C}{C_0} = \frac{b}{k_0} f_C^{(1-n)/b}
\]

Substituting Eq. (1), therefore, the coefficient \( b \) could be expressed:

\[
b = (k' - k)(k + 1) + k
\]

This equation would be useful in predicting the refining ratio according to various rotating speeds. The refining ratios obtained in the experiments with 2 000, 3 000 rpm are in good agreement with the value predicted by Eq. (10), as shown in Fig. 7.

Comparing the Fig. 7 with the Fig. 3, it appears that the parameter \( k' \) instead of \( W \) explains well the present experimental results. The change of the cake concentration due to a rotation speed was shown in Fig. 8. As the rotation speed increased the concentration of the cake became close to that of equilibrium. The dotted line, therefore, could be considered the effective solidus line which the refining ratio could be estimated from.

### 3.3. Effect of Heating Rate

For the case which does not take the applied pressure into account, but rather considers only the effect of the heating rate on purification, DTA (Differential Thermal Analysis) is used. From the DTA thermograms, the real fraction of the solid and the liquid in the solid–liquid mixture region could be estimated. Therefore, the shift of the solidus curve and the shape of the effective phase diagram was also estimated based on the heating rate. Under a constant heating rate of 5°C/min and 20°C/min, the relationships between the shapes of the melting curves and the shapes of the DTA curves of the Pb–2%Sn alloy are investigated. A mathematical model proposed by Chen and Huang is used for converting the DTA curves into melting curves.

The variations of the fraction of the solid due to a heating rate change in the solid–liquid mixture region were shown in the Fig. 9.

The equilibrium curve was drawn by the lever rule in the phase diagram. Since the equilibrium curve represents the change of the fraction of solid in the equilibrium phase diagram, it shows the smallest amount of \( f_S \) at the same temperature, or the lowest temperature at the equivalent \( f_S \).
The shift of the effective solidus line in the phase diagram due to the heating rate is shown in Fig. 10. In this figure, it appears that the effective solidus line moves into the mushy zone because the diffusion in the solid occurs slowly during the melting. Since the diffusion increases as the heating rate decreases, as well as the temperature increases, the differences between the equilibrium solidus curve and the effective curve were reduced.

For quantitative analysis of this effect, the “effective partition coefficient due to the heating rate, \(k_0\)” which means real partition coefficient according to the heating rate, is suggested. From the experimental data, the ratio of \(k_0/k\) are shown in Fig. 11. The results of 0.1°C/min and 0.5°C/min are obtained by the F.M. and those of 5°C/min and 20°C/min are obtained by the DTA curves.

Experimental plots of the \(k_0/k\) versus heating rate give straight lines in the logarithmic scale. Because \(k_0/k\) at the heating rate of 0 (isothermal condition) is 1, \(k_0/k\) may be expressed as:

\[
k_0/k = k + \varepsilon k \log \left( \frac{dT}{dt} + 1 \right)
\]

where \(\varepsilon\) is the slope of the straight line and about 0.363. Equation (12) is a useful means of predicting the relation between heating rate and purification. It is also noted that \(k_0/k\) is the value at least bigger than \(k\) and increases as heating rate increases.

The effective partition coefficient, \(k’\) which is used before to understand the effects of the centrifugal force (or rpm) in the present F.M. process, could be also used to analyze those of the heating rate. If both the variables are assumed to be independent of each other, the \(k’\) can be expressed that:

\[
k’ = k + (\text{effect of force}) + (\text{effect of heating rate})
\]

\[
= k + \frac{\exp(-\alpha P) - C_0/C_L}{\exp(\alpha P) - 1} \left(1 - k\right) + 0.363k \log \left( \frac{dT}{dt} + 1 \right)
\]

...........................(13)

Equation (13) indicates the actual partition coefficient according to a centrifugal force and a heating rate, and is a useful means of predicting the relationship between these processing variables and purification.

4. Conclusion

The refining behaviors in the modified F.M. process was quantitatively analyzed. The effects of both two major processing variables such as a heating rate and a rotating speed, were considered through the change of effective partition coefficient \(k’\). Combining the results of the calculation with those of experiments, the following findings were obtained:

1. The purification by the F.M. is a strong function of wetness and heating rate. In order to analyze relationship quantitatively between these processing variables and the purification behaviors, the “effective refining partition coefficient \(k’\)”, \(k’\) is proposed. This value means the ratio of effective solidus related to the wetness and a heating rate to equilibrium liquidus.

2. The results of quantitative analysis for \(k’\) give:

\[
k’ = k + (\text{effect of force}) + (\text{effect of heating rate})
\]

\[
= k + \frac{\exp(-\alpha P) - C_0/C_L}{\exp(\alpha P) - 1} \left(1 - k\right) + 0.363k \log \left( \frac{dT}{dt} + 1 \right)
\]

where the effective refining partition coefficient \(k’\) could be reduced by increasing a centrifugal force or decreasing a heating rate.

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