Note

Estimation of the Evaporation Rate of Copper and Tin from Molten Iron–Silicon Alloy

Hideki ONO-NAKAZATO, Kenji TAGUCHI and
Tateo USUI

Department of Materials Science and Processing, Graduate
School of Engineering, Osaka University, Yamadaoka, Suita,
Osaka 565-0871 Japan.

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1. Introduction

Most of ferrous scraps include tramp elements, such as Cu and Sn, which cause adverse effects on the mechanical properties of steel products, if their content exceeds a certain level. However, the refining techniques of those elements in molten steel are not necessarily established, and the removal of the tramp elements is one of the most important problems in recycling the ferrous scraps. The vaporization processes are considered to be suitable for the efficient elimination of Cu and Sn from iron alloys, and many studies have been conducted on the vaporization of Cu and Sn from iron melts. In order to promote the vaporization, the addition of silicon, which has a strong affinity with iron, is considered to be effective, because the activity coefficients of Cu and Sn in molten iron can be expected to increase. Two studies were previously reported on the effect of silicon on the vaporization rates of Cu and Sn in molten iron.^{1,2)} However, those results are not much in accord with each other. In particular, the effect of Si on the vaporization rate of Cu shows a different dependency on the Si content. On the other hand, it is possible to evaluate the effect of silicon on the vaporization rate thermodynamically. The activity data at least for Si–Cu and Si–Sn binary system are required for the evaluation. However, the activity data for such silicon alloys have been limited, and the evaluation has not been conducted enough. In the present study, the effect of silicon on the vaporization rates of Cu and Sn in Fe–Si alloy is thermodynamically examined based on the activity coefficients of the Si–Cu and Si–Sn binary alloys, which are reported recently,^{3,4)} and the correlations with the two previous studies are discussed.

2. Vapor Pressure of Cu and Sn in Molten Fe–Si Alloy

The activity coefficient of M (Cu or Sn) in Fe–Si–M alloy can be estimated from the activity coefficients of M in Fe–M and Si–M binary alloys by the regular-solution model in a ternary system^{5,6)} as follows:

$$\ln \gamma_{M(\text{Fe-Si-M})} = \ln \gamma_{M(\text{Fe-M})} \cdot \frac{X_{\text{Fe}}}{X_{\text{Fe}} + X_{\text{Si}}} + \ln \gamma_{M(\text{Si-M})} \cdot \frac{X_{\text{Si}}}{X_{\text{Fe}} + X_{\text{Si}}} - \frac{\Delta H_{(\text{Fe-Si})}^M}{RT} \dots (1)$$

where $\Delta H_{(\text{Fe-Si})}^M$ denotes the enthalpy change of mixing for Fe–Si alloy (J/mol), R the gas constant ($=8.314\text{J}/(\text{mol} \cdot \text{K})$), T the temperature (K), X_i the mole fraction of component i , and $\gamma_{M(\text{A-B-M})}$ the activity coefficient of M in A–(B)–M alloy. **Table 1** shows the activity coefficient of M in Fe–M or Si–M alloy at 1 873 K, which is used in the present study. In **Table 1**, the activity coefficient of Cu in Si, $\gamma_{\text{Cu}(\text{Si-Cu})}$, was calculated from that of Si in Cu³⁾ by Gibbs–Duhem equation.⁹⁾ The enthalpy change of mixing for Fe–Si alloy, $\Delta H_{(\text{Fe-Si})}^M$, is shown in **Table 2**.^{10,11)} The activity coefficient of M in Fe–Si–M alloy at 1 873 K can be calculated by substituting the data given in **Tables 1** and **2** into Eq. (1), and the results are also shown in **Table 2**. The activity of M in Fe–Si–M alloy, a_M , is represented by

$$a_M = \gamma_{M(\text{Fe-Si-M})} X_M = \frac{P_M}{P_M^\circ} \dots (2)$$

where P_M° and P_M denote the vapor pressures of pure M¹⁰⁾ and M in Fe–Si–M alloy (Pa), respectively. The dependence of the vapor pressure of M in Fe–Si–0.5mass%M alloy on the silicon content was investigated, and the results are shown in **Fig. 1**. It is found that the vapor pressures of Cu and Sn in Fe–Si–M alloys show maximum values at about 15 and 35 mass% Si, respectively.

3. Effect of Si on the Vaporization Rate of Cu and Sn

The vaporization reaction of M in Fe–Si alloy is expressed by

$$\underline{M}(\text{mass\%, in Fe-Si alloy}) = \underline{M}(\text{g}) \quad (\text{M: Cu or Sn}) \dots (3)$$

If free evaporation controls the overall rate, the evaporation rate equation can be described as follows:^{12,13)}

Table 1. The activity coefficient of M (Cu or Sn) in Fe–M or Si–M alloy at 1 873 K.

M	$\gamma_{M(\text{Fe-M})}$	$\gamma_{M(\text{Si-M})}$
Cu	9.49 ⁷⁾	0.16 ³⁾
Sn	2.8 ⁸⁾	5.68 ⁴⁾

Table 2. The enthalpy change of mixing for Fe–Si alloys and the activity coefficients of M (Cu or Sn) in Fe–Si–M alloys at 1 873 K.

X_{Fe}	X_{Si}	$\Delta H_{\text{Fe-Si}}^M$ (J/mol)	$\gamma_{\text{Cu}(\text{Fe-Si-Cu})}$	$\gamma_{\text{Sn}(\text{Fe-Si-Sn})}$
1	0	0	9.49	2.80
0.9	0.1	–12500	14.1	6.73
0.8	0.2	–22600	17.9	13.8
0.6	0.4	–35200	17.8	35.5
0.5	0.5	–37700	13.9	44.8
0.4	0.6	–36800	8.76	45.5
0.2	0.8	–23000	1.60	21.6
0.1	0.9	–11300	0.500	10.9
0	1	0	0.161	5.68

$$\frac{d[\text{mass}\% \text{ M}]}{dt} = -\frac{A}{V} \cdot k_{\text{M, id}} \cdot [\text{mass}\% \text{ M}] \quad \text{.....(4)}$$

$$k_{\text{M, id}} = 4.43 \times 10^4 \cdot \frac{\sqrt{M_{\text{M}}/T}}{\exp(\Delta G_{(3)}^{\circ}/RT) \cdot \rho_{\text{Fe-Si}}} \quad \text{(for dilute solution)(5)}$$

where A denotes the reaction area (m^2), $\Delta G_{(3)}^{\circ}$ the standard Gibbs energy for Eq. (3) (J/mol), $k_{\text{M, id}}$ the free evaporation rate constant of M in Fe-Si-M alloy (m/s), M_{M} the atomic weight of M (kg/mol), V the metal volume (m^3) and $\rho_{\text{Fe-Si}}$ the density of Fe-Si alloy (kg/m^3).¹⁰ The standard Gibbs energy for Eq. (3) can be derived by combining the standard Gibbs energies for Eqs. (6)⁹ and (7)^{7,14} as follows:

$$\underline{\text{M}}(\text{mass}\%, \text{ in Fe-Si alloy}) = \text{M(l)} \quad \text{.....(6)}$$

$$\text{M(l)} = \text{M(g)} \quad \text{.....(7)}$$

$$\Delta G_{(3)}^{\circ} = \Delta G_{(6)}^{\circ} + \Delta G_{(7)}^{\circ} \\ = RT \ln \left(\frac{100 \cdot M_{\text{M}}}{\gamma_{\text{M(Fe-Si-M)}} \cdot M_{\text{Fe-Si}}} \right) + \Delta G_{(7)}^{\circ} \quad \text{.....(8)}$$

The free evaporation rate constant of M in Fe-Si-M alloy was calculated by Eq. (5) at 1873 K, and the $k_{\text{M, id}}$ values are plotted against the silicon content in **Fig. 2**. The dependence of $k_{\text{M, id}}$ on the silicon content is similar to that of the vapor pressure in Fig. 1, and it is found that each evaporation rate constant takes a maximum value at a fixed Si content, at which Cu or Sn is expected to be removed efficiently. By the silicon addition, the rate constant of Cu becomes about twice as larger as that for pure iron. On the other hand, the rate constant of Sn increases by about 16 times, and silicon is considered to be more effective for the removal of Sn. This mainly originates in much larger activity coefficient of Sn in Si than that of Cu in Si, as shown in Table 1.

The evaporation rate of M (Cu or Sn) in Fe-Si alloy was investigated by Morales *et al.*¹⁾ and by Esimai²⁾ based on a

Fig. 1. The vapor pressures of M (Cu or Sn) in Fe-Si-0.5mass%M alloys at 1873 K.

levitation technique. Each experimental condition is summarized in **Table 3**. Morales *et al.* estimated the evaporation rate constant of M, k_{M} (m/s), on the basis of Eqs. (9) and (10) under the assumption that the gaseous mass transfer of M is a rate-limiting step.

$$\frac{d[\text{mass}\% \text{ M}]}{dt} = -\frac{A}{V} \cdot k_{\text{M}} \cdot [\text{mass}\% \text{ M}] \quad \text{.....(9)}$$

$$k_{\text{M}} = \frac{P_{\text{M}}^{\circ} \gamma_{\text{M(Fe-Si-M)}} M_{\text{Fe-Si}}}{RT \rho_{\text{Fe-Si}}} \cdot k_{\text{g}} \quad \text{.....(10)}$$

where k_{g} denotes the gaseous mass transfer coefficient of M (m/s). The dependence of the rate constant on the silicon content is shown in **Fig. 3**. On the other hand, the rate-limiting step of Cu or Sn evaporation was not discussed in Esimai's study, and the evaporation rate constant of copper or tin was calculated by applying Eqs. (9) and (10) to

Fig. 2. Effect of silicon on the free evaporation rate constants of M (Cu or Sn) in Fe-Si-0.5mass%M alloys at 1873 K.

Fig. 3. Effect of silicon on the evaporation rate constants of M (Cu or Sn) investigated by Morales *et al.* and by Esimai.

Table 3. Experimental conditions on the measurement of the evaporation rate of M (Cu or Sn) in Fe-Si-M alloy.

	Temperature (K)	He flow rate (cm^3/min)	Sample weight (g)	Initial content of M (mass%M)	
				Cu	Sn
Morales <i>et al.</i> ¹⁾	2073	250	0.8 ± 0.03	0.88 - 0.96	0.71 - 0.90
Esimai ²⁾	2100	300	approx. 1	1.0	1.0

Esimai's results in the present study. The results are also shown in Fig. 3. Here, in calculating the reaction area, A ($=\pi d^2$), the sphere equivalent diameter, d , was estimated from the sample volume. It is found from Fig. 3 that the evaporation rate constant of Sn increases as increasing the silicon content over the investigated Fe–Si composition range in both studies. On the other hand, the dependence of the evaporation rate constant of Cu on the silicon content is different from each other, in spite that a noticeable difference is not found in the experimental conditions between the two studies, as shown in Table 3. The evaporation rate constant of Cu by Esimai increases with increasing the silicon content, as well as the rate constant of Sn evaporation. On the other hand, the value by Morales *et al.* increases up to about 5 mass% Si, then decreases above 5 mass% Si. The rate constants of Cu and Sn evaporation by both Morales *et al.* and Esimai are over an order of magnitude smaller than the values estimated on the assumption of free evaporation. The following relationship can be derived from Eqs. (5), (8) and (10).

$$\frac{k_{M,id}}{k_M} = \frac{443 \cdot R \cdot \sqrt{\frac{T}{M_M}}}{\exp\left(\frac{\Delta G_{(7)}^\circ}{RT}\right) \cdot P_M^\circ} \cdot \frac{1}{k_g} = \text{const.} \quad \text{.....(11)}$$

The $k_{M,id}/k_M$ values are plotted against the silicon content in Fig. 4. The $k_{M,id}/k_M$ values are much larger than unity, namely 23 to 57 for copper and 7 to 32 for tin, because of the gaseous mass transfer of copper or tin. It is found that the $k_{M,id}/k_M$ values for the evaporation rate constant of Sn by Morales *et al.* are almost constant, which shows a good correlation with the values estimated in the present study. It is considered that the effect of Si on the evaporation rate of Sn can be explained by the regular solution model, using the available binary activity data. On the other hand, the

evaporation rate constant of Cu does not show a clear correlation with that estimated in the present study. In the present estimation of the effect of silicon on the evaporation of Cu, the activity coefficient of Cu in Si was estimated from that of Si in Cu³⁾ by Gibbs-Duhem equation, which may be a cause of such poor correlation. Accordingly, the evaporation rate constant of Cu may take a maximum value at lower silicon content than that estimated in the present study. Taking this fact into account with the results of the evaporation rate constant of Sn, the effect of silicon on the evaporation rate of M (Cu or Sn) by Morales *et al.* may be more valid than that by Esimai.

4. Conclusions

The effect of silicon on the evaporation rates of Cu and Sn in Fe–Si alloy has been estimated by applying a regular solution model, using the thermodynamic data of Si–Cu and Si–Sn alloys reported recently. The vapor pressures and the evaporation rate constants of Cu and Sn in Fe–Si alloy are evaluated, and it is found that they have maximum values at the fixed silicon contents. The effect of silicon on the rate enhancement of Sn evaporation is larger than that of Cu evaporation. From the correlations with the experimental studies in the literatures, the data by Morales *et al.* are considered to be more valid than those by Esimai.

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Fig. 4. Relationship between silicon content and the ratio of $k_{M,id}$ to k_M (M =Cu or Sn).