Effect of Oxygen on the Evaporation Rate of Lead from Liquid Copper under Reduced Pressure

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Previously, the present authors have investigated the effects of temperature and pressure on the evaporation rates of Pb and Zn from liquid copper under reduced pressure. Oxygen does easily contaminate molten metal during high temperature processing and is known as a strong surface active element. In this study, the effect of oxygen on the evaporation rate of Pb from liquid copper was discussed at 1 473 K and 1.3 kPa. The rate constant was supposed to be slower with oxygen content due to lowering the interfacial chemical reaction rate. However, the rate constant increased with oxygen content in the present experiment. Assuming that the acceleration of vaporization is due to the volatile lead oxide, the rate equation was derived for the evaporation of lead oxide together with that of metallic Pb. As a result of the analysis for the present experiment, it was found that Pb evaporated from copper melt containing higher oxygen in the form of PbO. The presence of PbO in the vapor phase was confirmed by the mass spectroscopy. The rate mechanism of vaporization of Sn and Cu from liquid steel containing oxygen have also been discussed.

KEY WORDS: copper scrap; tramp element; reduced pressure; oxygen; evaporation rate constant; surface tension; mass transfer; lead oxide; rate determining step.

1. Introduction

The efficient reuse technology of so-called ‘base-metal’ should be urgently developed on the viewpoint of the energy saving, depletion tendency of valuable resources and reduction of environmental loading. Since copper and iron, which are the most representative ‘base-metal’, are used in relatively high purity state as the final products and the amounts of their products are huge, copper and iron scraps are expected as new artificial resources. However, the contamination by the tramp element in the remelting process of the scraps becomes a problem for the recycling as high purity resources, so that the development of the efficient removal technology of the tramp elements in the remelted base-metal scrap is being expected. For the upgrading of base-metal scrap from the level of 99% to 99.9 or 99.99%, inert gas injection or vacuum treatment has economical and technological potential with respect to the elimination of volatile impurities from molten base-metal if vapor pressures of the impurities are much higher than that of the solvent.

As a research on the vacuum treatment or the inert gas blowing for crude base-metal, the evaporation behavior of the tramp elements in molten steel has been reported by many investigators. Ward and coworker first investigated the kinetics of Mn evaporation from inductively stirred liquid iron under vacuum. They reported that evaporation rate of Mn was the first order with respect to its concentration in liquid iron and the measured first order rate constant agreed with the free evaporation rate constant. Ohno and Ishida and Fischer and Janke also studied the evaporation rates of Cr, Cu, Sn and S from liquid iron under vacuum and found the evaporation rate constant of each element agreed with the free evaporation rate constant. Hino et al. observed the evaporation rate of Zn from liquid iron by impinging Ar on the surface of melt. The evaporation rate of Zn was mostly limited by liquid phase mass transfer, and they suggested that tens ppm of Zn could remain in liquid iron during typical operation period for refining in spite of high vapor pressure of Zn if initial Zn content in steel scrap was as high as hundreds ppm. Ito et al. demonstrated that Sn in liquid Fe–C–S alloy could be removed by the evaporation of SnS under the reduced pressure. Li et al. studied the evaporation rates of Pb and Zn from liquid Fe–4 mass%C alloy at 1 873 K under 10 kPa to 5 MPa of Ar pressure. The evaporation rates of Pb and Zn were found to be the first order with respect to their concentrations in liquid iron, and Li et al. concluded that the rates were controlled by the mass transfer processes in liquid and gas phases. Chen et al. investigated the effects of pressure and temperature on the evaporation rate of Cu from liquid high carbon steel under the reduced pressure of approximately 100 Pa. Recently, Savov and Janke measured the evaporation rate constants of both Cu and Sn from scrap-based iron melts.

As for the evaporation kinetics of tramp elements in copper scraps, some researches have been made. Harris and his coworkers measured the removal rates of As, Bi, Pb and Sb under reduced pressure. Ozberk and Guthrie also studied the evaporation removal kinetics of Pb from molten copper. They have indicated that the evaporation rates of As and Sb from copper melt were very slow.
due to low vapor pressure and activity coefficient in liquid copper. Therefore, it would be difficult to remove them from copper melt by vacuum refining.

The present authors have also studied the evaporation kinetics of Pb and Zn in liquid copper in their previous work.\(^1\) They discussed effects of temperature and pressure on the evaporation rates. It was found that the removal rates of these impurities were controlled by the mass transfer in the gas phase on the most of experimental conditions except for some cases at 1 693 K and below 1 kPa.

Copper scrap contains significant amount of oxygen that easily dissolves into copper from an oxide layer. Additionally, remelting of copper scrap is generally performed in air and copper has relatively large oxygen solubility (approximately 2 mass% at CuO saturation at 1 473 K\(^1\)). Since oxygen in molten metal is known to act as a strong surface active element, the dissolved oxygen possibly retards the evaporation kinetics in the practical remelting process of copper scrap. On the other hand, Hiraga et al.\(^1\) reported that the evaporation rates of Cu and Sn from liquid iron under reduced pressure became faster at high oxygen content while oxygen was supposed to retard the evaporation rate because of its surface active nature. They deduced that such enhanced effect of oxygen would be due to vaporization of sub-oxide such as CuO and SnO at higher oxygen content. Ozberk and Guthrie\(^1\) observed the positive effect of oxygen rather than retardation on the vaporization of both Bi and Pb in molten copper under reduced pressure.

As above-mentioned, two opposite effects of oxygen are recognized for the vaporization kinetics of impurities from molten iron or copper, and the quantitative discussion on this mechanism is quite insufficient. The present work, therefore, aims to reveal the effect of oxygen on the evaporation rate of Pb from liquid copper under reduced pressure at 1 473 K.

2. Experimental

2.1. Apparatus and Materials

Experimental details are essentially the same as that explained in our earlier work.\(^1\) An induction furnace (10 kW, 200 kHz) was used for the melting of copper. A high purity Al\(_2\)O\(_3\) crucible (24 mm i.d. and 92 mm in depth) was used to hold approximately 180 g of copper. A graphite ring of 25 mm in height was set around the lower part of Al\(_2\)O\(_3\) crucible. Temperature of the melt was monitored by an infrared radiation pyrometer through a prism attached on the top of gas inlet tube. The pyrometer was calibrated with the melting points of pure copper.

2.2. Experimental Procedure

After purging the inside of the quartz reaction tube with pure Ar or Ar–H\(_2\) gas mixture, the copper was heated by the induction furnace under purified Ar or Ar–H\(_2\) stream. Then the copper was melted and temperature was kept at 1 473 K. The gas mixture was switched to pure Ar and a given amount of Pb droplets (99.99%) was added into the metal bath. In the most of the experimental runs, initial Pb content was adjusted in the range from 0.5 to 1.2 mass%. The evaporation reaction of Pb was started by evacuating inside of the reaction tube with a rotary pump. This period was assumed as starting time for Pb evaporation (\(t=0\)). Inner pressure was measured by digital manometer and controlled at the constant pressure of 1.3 kPa. After given period, Ar was introduced in the reaction tube to recover the inner pressure to an atmospheric pressure for an instant, and then 5 g of sample for chemical analysis was sucked by a silica tube. Inside of reaction tube was evacuated again up to the original pressure, and then this procedure was repeated to continue the experiment. Such sampling procedure was completed within 120 sec. Pb and oxygen contents in the sample were determined by Induction Coupled Plasma Emission Spectroscopy (ICP) and the inert gas fusion oxygen analyzer (LECO), respectively. The results of oxygen analysis were calibrated by the two kinds of standard sample (254±4 ppm, 687±6 ppm).

3. Evaporation Rate Equations

The authors have found that lead evaporates from liquid copper in the form of monatomic metallic vapor at low oxygen content.\(^1\) In this case, evaporation reaction was expressed by Eq. (1), and the rate was given by Eq. (2) as the first order reaction with respect to Pb content in metal.

\[
Pb(l, \text{ in liquid copper}) = Pb(g) \quad \text{.........(1)}
\]

\[
-ln \left[ \frac{\% \text{ Pb}}{\% \text{ Pb}_0} \right] = k_{\text{at(Pb in Cu)}} \frac{A}{V} t \quad \text{.........(2)}
\]

The evaporation process of impurity from molten metal can be divided into three steps such as liquid phase mass transfer, interfacial reaction including free evaporation and gas phase mass transfer. Since the rate constant of each step can be expressed by the first order reaction with respect to impurity content in metal,\(^1\) the following relation can be derived.

\[
\frac{1}{k_{\text{at(Pb in Cu)}}} = \frac{1}{k_{\text{g(Pb in Cu)}}} + \frac{1}{k_{\text{el(Pb in Cu)}}} + \frac{1}{k_{\text{g(Pb in Cu)}}} \quad \text{.........(3)}
\]

In above equation, \(k_{\text{g(Pb in Cu)}}\) was found to be 3.0×10\(^{-4}\) (m\(^2\)·s\(^{-1}\)) in our previous work.\(^1\) The rate constant of free evaporation on the bear surface of liquid metal can be given by the Hertz–Knudsen–Langmuir's equation.\(^1\)

\[
k_{\text{el(Pb in Cu)}} = \frac{M_{\text{Cu}} p_{\text{Cu}}^\gamma P_{\text{Pb}}^\rho}{\rho_{\text{Cu}} \gamma R T} \quad \text{.........(4)}
\]

Effect of oxygen as a strong surface active element on the free evaporation rate constant can be formulated by assuming Langmuir’s ideal adsorption isotherm.

\[
k_{\text{el(Pb in Cu)}} = k_{\text{el(Pb in Cu)}}(1 - \theta_0) \quad \text{.........(5)}
\]
Combination of Eqs. (5) and (6) gives the rate constant of free evaporation at higher oxygen content.

\[ K_{O_{Cu}} \cdot a_{O} = \frac{\theta_{O}}{1-\theta_{O}} \]  
\[ k_{e(Pb in Cu)} = \frac{k_{e(Pb in Cu)}}{1 + K_{O_{Cu}} \cdot a_{O}} \]

In the present work, \( K_{O_{Cu}} \) was calculated from the surface tension of liquid Cu–O alloy as a function of \( P_{O_{2}} \) reported by Gallois and Lupis \(^{19} \) and Gibbs free energy change of oxygen dissolution into liquid copper after Kemori et al. \(^{20} \), which was used to convert the oxygen partial pressure to the activity of oxygen in liquid copper with Eq. (8).

\[ \sigma - \sigma_{O} = -RT \ln(1 + K_{O_{Cu}}a_{O}) \]  

Finally, the value of \( K_{O_{Cu}} \) was obtained as \( K_{O_{Cu}}=3 \text{ 740} \) at 1473 K. Then, \( k_{e(Pb in Cu)} \) can be calculated by substituting Eq. (4) into Eq. (7). The calculated \( k_{e(Pb in Cu)} \) and apparent rate constant are presented in Fig. 1 as a function of oxygen content in liquid copper together with the previous observed value \(^{19} \) at [mass%O]=0.0016. \( K'_{e(Pb in Cu)} \), \( k_{e(Pb in Cu)} \) and \( k_{e(Pb in Cu)} \) are also shown in Fig. 1. As it is indicated in Fig.1, the overall rate constant of metallic Pb evaporation becomes possibly slower with increase of oxygen content if the rate constant of free evaporation as monatomic Pb vapor is retarded by oxygen adsorption. If this assumption is true, oxygen contamination of remelted copper scrap should be prevented for the efficient removal of Pb by evaporation. However, as mentioned later, the rate increased at higher oxygen content in liquid copper in the present work.

\[ k_{e(Pb in Cu)} = \frac{k_{e(Pb in Cu)}}{1 + K_{O_{Cu}} \cdot a_{O}} \]

4. Results and Discussion

4.1. Variation of Pb Content with Time

Figure 2 represents the variation of Pb content in liquid copper with time at 1473 K and 1.3 kPa. Oxygen content in Fig. 2 is the average value during each heat. Pb content decreases definitely with time, e.g., Pb content becomes approximately half after 1 h exposure under reduced pressure at oxygen content of 1.4 mass%. Figure 3 is the re-plot of the results shown in Fig. 2 according to Eq. (2). Linear relations are found in each run. It indicates that the Pb evaporation is the first order reaction with respect to Pb content in liquid copper on the present experimental condition. The rate constant corresponds to from the slope of each linear relation.

\[ \text{Fig. 1. Effect of oxygen on the rate constant of lead evaporation in liquid copper at 1473 K and 1.3 kPa.} \]

\[ \text{Fig. 2. Variation of lead content in liquid copper with time at 1473 K and 1.3 kPa.} \]

\[ \text{Fig. 3. First-order plots for vaporization of lead from liquid copper at 1473 K and 1.3 kPa.} \]
might be a volatilization of lead sub-oxide at higher oxygen content.

4.2. Estimation of Evaporated Lead Oxide Species

If we assumed that Pb evaporated from liquid copper in the volatile oxide form of PbO$_x$ at higher oxygen content, its reaction and equilibrium constant can be represented as:

\[ \text{Pb} \text{(l, in liquid copper)} + x\text{O} \text{(in liquid copper)} \rightarrow \text{PbO}_x \text{(g)} \]

\[ K_g = \frac{P_{\text{PbO}_x}}{a_{\text{Pb}} \cdot a_{\text{O}}} = \frac{P_{\text{PbO}_x}}{a_{\text{Pb}} \cdot X_{\text{PbO}_x} \cdot a_{\text{O}}} \]  

\[ \text{Pb} \text{(l, in liquid copper)} + x\text{O} \text{(in liquid copper)} \rightarrow \text{PbO}_x \text{(g)} \]  

Rearrangement of Eq. (10) yields vapor pressure of PbO$_x$ as Eq. (11).

\[ P_{\text{PbO}_x} = Y_{\text{Pb}} \cdot X_{\text{PbO}_x} \cdot a_{\text{O}} \cdot K_g \]  

Equilibrium vapor pressure of PbO$_x$ and metallic Pb can be calculated from the data source of Kubaschewski and Alcock and the free energy of formation of respective oxides.

\[ \text{Pb} \text{(l, in liquid copper)} + x\text{O} \text{(in liquid copper)} \rightarrow \text{PbO}_x \text{(g)} \]

\[ \Delta G_{12}^{\circ} = 139835 - 107.30T \text{ (J \cdot mol}^{-1}) \]  

\[ \Delta G_{14}^{\circ} = -253860 + 287.61T \text{ (J \cdot mol}^{-1}) \]  

\[ \Delta G_{16}^{\circ} = 293450 - 13.36T \text{ (J \cdot mol}^{-1}) \]

The calculated equilibrium vapor pressure of each species is shown in Fig. 5 as a function of oxygen content in liquid copper at 1 473 K and 1 403 K, where vapor pressure is calculated at constant Pb content of 0.2 mass%. The equilibrium vapor pressure of metallic Pb is 6.8 Pa at 1 473 K. Among lead oxides, the vapor pressure of PbO is at least 7 to 12 orders of magnitude greater than that of Pb$_2$O$_3$ and PbO$_2$ at 1 473 K. The equilibrium vapor pressures of lead oxides become larger with increasing oxygen content and that of PbO is equivalent to that of metallic Pb in the vicinity of 0.004 mass% of oxygen at 1 473 K. It is deduced from Fig. 5 that PbO is probable vapor species at high oxygen content in liquid copper among PbO, Pb$_2$O$_3$ and PbO$_2$ while reliable thermodynamic information on the vapor of Pb$_3$O$_4$ or other lead oxide is not available.

In order to identify the vapor species of lead oxide, a Knudsen cell type mass spectroscopy was also used in the present work. The details of the mass spectrometer and procedure have been described elsewhere. This device consisted of Knudsen cell, the ionization source, a scanning part for the magnetic field and the ionic detector. The cell was heated with radiation of tantalum and temperature was measured by two sets of Pt–13%Rh/Pt thermocouples. There was a shutter between Knudsen cell and the ionization source for the measurement of background. The cell shape was cylinder of 9 mm I.D. and 7 mm in height. The pressure inside the Knudsen cell was the order of 10$^{-4}$ Pa and ionization energy was 20 eV. Because of the limit of heating power of this equipment, the temperature was below approximately 1 400 K. The composition of the sample used in the mass spectrometry was initially 1.5 mass% Pb and 1.5 mass% O while it was reduced to 0.2 mass% Pb after the experiment due to the vapor loss during the mass spectrometry which was performed in very low pressure of 10$^{-4}$ Pa. Figure 6 shows the relationship between the relative ion current intensity and mass number observed at 1 403 K. Since the detectable mass number was limited below 400 in this mass spectrometer, the presence of Pb$_3$O$_4$ (mass number: 460–462) and Pb$_2$O$_3$ (682–684) in the vapor could not be observed. Mass peaks of PbO (206–208) were, however, clearly detected together with those of metallic Pb and those of PbO$_2$ (238–240) were not observed in the pre-
sent condition. Therefore, it was deduced from Figs. 5 and 6 that PbO would be the most probable vapor species at higher oxygen content.

4.3. Rate Equation for the Evaporation of PbO

If the major vapor species is assumed as PbO at higher oxygen content in liquid copper, free evaporation or gas phase mass transfer of PbO will control the overall rate of Pb evaporation as same as the evaporation of metallic Pb. The former rate constant can be given by the following equation.

$$\frac{1}{k_{\text{overall(Pb in Cu)}}} = \frac{1}{k_{\text{g(PbO in Cu)}}} + \frac{1}{k_{\text{g(Pb in Cu)}}}$$

(24)

The calculated free evaporation rate constant $k_{\text{g(PbO in Cu)}}$ is presented in Fig. 4. The value of $k_{\text{g(PbO in Cu)}}$ is approximately two order of magnitude greater than the observed first order rate constant. This means that the resistance of free evaporation of PbO is negligible and the rate of Pb evaporation is possibly controlled by the gas phase mass transfer of PbO at higher oxygen content on the present experimental condition.

The rate of gas phase mass transfer of PbO is given by Eq. (19).

$$N_{\text{PbO}} = \frac{\gamma_{\text{p}}}{RT} \frac{1}{k_{\text{g(PbO in Cu)}}} \ln \frac{P_{\text{PbO}}^s}{P_{\text{PbO}}^b}$$

(19)

Where, superscripts ‘s’ and ‘b’ mean the value at gas–liquid interface and that in the gas bulk, respectively. Equation (19) can be approximated as Eq. (20) if $P_{\text{PbO}}^b$ is negligibly small due to the low total pressure and $P_{\text{PbO}}^s << P_{\text{PbO}}^b$.

$$N_{\text{PbO}} = k_{\text{g(PbO in Cu)}} \frac{1}{RT} P_{\text{PbO}}^s$$

(20)

Substitution of Eq. (11) to Eq. (20) on the condition of $x=1$ results in Eq. (21), where $P_{\text{PbO}}^s$ in Eq. (20) is equal to $P_{\text{PbO}}$ in Eq. (11).

$$N_{\text{PbO}} = k_{\text{g(PbO in Cu)}} \frac{1}{RT} \gamma_{\text{p}} \cdot X_{\text{p}} \cdot \alpha_{\text{O}} \cdot K_{\text{g}}$$

(21)

As shown in Eq. (21), molar flux of PbO in the gas phase is a function of both oxygen and Pb content in liquid copper. Since the atomic weight ratio of Pb and oxygen is small ($M_{\text{O}}/M_{\text{Pb}} = 0.077$) and no remarkable change of oxygen content was observed on the present experimental conditions, oxygen activity in Eq. (21) could be treated as a constant value as the first approximation. Based on such assumption, the rate equation for the evaporation of PbO given by Eq. (21) is simplified as Eq. (22).

$$-\ln \left( \frac{[\% \text{ Pb}]}{[\% \text{ Pb}_0]} \right) = k_{\text{g(PbO in Cu)}} \frac{A}{V}$$

(22)

Where, $k_{\text{g(PbO in Cu)}}$ denote the apparent gas phase mass transfer coefficient of PbO defined as Eq. (23).

$$k_{\text{g(PbO in Cu)}} = \frac{M_{\text{Cu}} k_{\text{g(PbO in Cu)}} V \gamma_{\text{p}} \cdot X_{\text{p}} \cdot \alpha_{\text{O}} \cdot K_{\text{g}}}{\rho_{\text{Cu}} RT}$$

(23)

If Pb would evaporate from molten copper in the form of PbO together with metallic Pb, the competitive rate mechanism can be assumed. As pointed out in our previous paper, the mass transfer coefficient in the liquid phase is much larger than the overall rate constants observed in the present work. In this case, overall evaporation rate constant of Pb from liquid copper under reduced pressure is given as;

$$k_{\text{overall(Pb in Cu)}} = k_{\text{g(Pb in Cu)}} + k_{\text{g(PbO in Cu)}}$$

(24)

Among rate constants in Eq. (24), $k_{\text{g(PbO in Cu)}}$ is observed by the experiment and $k_{\text{g(Pb in Cu)}}$ could be calculated by Eqs. (3), (4), (7), $k_{\text{g(PbO in Cu)}}$ and $k_{\text{g(Pb in Cu)}}$. Therefore, the value of $k_{\text{g(PbO in Cu)}}$ can be evaluated. Logarithm of Eq. (23) yields the following relation.

$$\log k_{\text{g(PbO in Cu)}} = \log \alpha_{\text{O}} + \log \frac{M_{\text{Cu}} k_{\text{g(PbO in Cu)}} V \gamma_{\text{p}} \cdot X_{\text{p}} \cdot \alpha_{\text{O}} \cdot K_{\text{g}}}{\rho_{\text{Cu}} RT}$$

(25)

Since the interaction between Pb and oxygen would be small within the Pb concentration range in the present work, the activity coefficient of Pb in liquid copper is reasonably assumed as a constant value. Therefore, the plots of $\log k_{\text{g(PbO in Cu)}}$ against log $\alpha_{\text{O}}$ would yield the linear relation and the slope of this straight line should be unity, which corresponds a stoichiometry of volatile lead oxide. The result is represented in Fig. 7, where the slope is 1.16, which is very close to unity as expected. This confirms again that a stoichiometry of volatile lead oxide is PbO and Pb would be removed as PbO rather than metallic Pb at higher oxygen content. From the present experiment, the value of the gas phase mass transfer of PbO, $k_{\text{g(PbO in Cu)}}$ is evaluated as 3.4 (m·s$^{-1}$) at 1473 K and 1.3 Pa by Eq. (23).
4.4. Rate Determining Process of Pb Evaporation

The rate constant of each step is illustrated in Fig. 4 as a function of oxygen content in liquid copper. It is seen that the calculated overall rate constant (thick solid line) agrees well with the observed ones. Therefore, the following rate mechanism can be revealed: When oxygen content is lower than 0.01 mass%, Pb evaporation is limited by the gas phase mass transfer of metallic Pb. If oxygen content is in the range of 0.01 to 0.1 mass%, the rate is controlled by gas phase mass transfer and free evaporation of metallic Pb. More addition of oxygen into liquid copper results in the increase of contribution of gas phase mass transfer of PbO and the overall evaporation rate is essentially governed by the free evaporation of Pb together with the gas phase mass transfer of PbO in the oxygen concentration range from 0.1 to 0.6 mass%. If oxygen content is higher than 0.6 mass%, the rate would be limited by the gas phase mass transfer of PbO.

Ozberk and Guthrie\textsuperscript{14}) observed the effect of oxygen on the evaporation rate of Pb from liquid copper at $W_{Cu} = 34\, kg$, $A/V = 7\, m^{-1}$, $t = 120\, min$, 1523 K and 13.3 Pa. Their observed rate constants are also plotted in Fig. 4 for the comparison. Though the numbers of their observed data points are very limited, oxygen exhibited positive effect rather than retardation on the elimination of both Bi and Pb in molten copper under reduced pressure.

It is concluded from the above-mentioned discussion that oxygen contamination would not be a serious problem for the removal of Pb from liquid copper under reduced pressure due to the contribution of the evaporation of PbO at high oxygen content.

4.5. Effect of Oxygen on the Evaporation Rates of Sn and Cu from Liquid Iron

Hiraga et al.\textsuperscript{17}) studied the evaporation rates of Sn and Cu from liquid iron–oxygen alloy under reduced pressure from 13.3 to 532 Pa at 1923 K. They found that the evaporation rates, $R_i$, of Sn and Cu became faster at higher concentration range of oxygen as shown in Fig. 8 for Sn and Fig. 9 for Cu. $R_i$ was defined by the following equation.

\begin{equation}
R_i = -\frac{V}{A} \frac{d[M]}{dt} = k_{overall}(t)\text{[%]} \frac{d}{dt} \text{[%]} \quad \text{or} \quad k_{overall}^{2nd} \text{[%]}^2
\end{equation}

Fig. 7. Effect of activity of oxygen in liquid copper on the mass transfer coefficient of lead oxide in the gas phase at 1473 K and 1.3 kPa.

Fig. 8. Effect of initial oxygen content on the evaporation rate of tin from liquid steel at 1923 K.

Fig. 9. Effect of initial oxygen content on the evaporation rate of copper from liquid steel at 1923 K.
where, \( k_2^{\text{nd}} \) is the second-order rate constant of \( i \) in liquid \( j \). For the calculation, initial Sn and Cu contents were fixed at 0.4 mass\% which was the typical experimental condition of Hiraga et al. As shown in Figs. 8 and 9, higher oxygen content in liquid iron definitely enhances the evaporation rates of Sn and Cu. Though Hiraga et al. suggested the possibility of formation of Sn and Cu sub-oxides, they did not make quantitative discussion on such rate mechanism. Therefore, their results are also re-analyzed in view of competitive evaporation of metallic and sub-oxide of Sn and Cu in the present work.

The equilibrium vapor pressures of tin and copper oxides are first calculated by the available thermodynamic information. Sn(l, in liquid iron) + O(in liquid iron) = SnO(g) \( \Delta G_{27}^\circ = 107 \text{ J} \cdot \text{mol}^{-1} \) \( \text{(27)} \)

Cu(l, in liquid iron) + O(in liquid iron) = CuO(g) \( \Delta G_{29}^\circ = 320 \text{ J} \cdot \text{mol}^{-1} \) \( \text{(29)} \)

Other volatile oxides of Sn and Cu are not available in the literature. The estimated values of equilibrium vapor pressure are demonstrated in Fig. 10. For Sn, vapor pressure of SnO over liquid Fe–Sn–O alloy exhibits relatively large value, and those of metallic Sn and SnO become equivalent at 0.01 mass\% of oxygen. When oxygen content increases beyond this critical value, vapor pressure of SnO is greater than that of metallic Sn. It implies that SnO would be a major vapor species at higher oxygen content than 0.01 mass\%. This may be a reason of faster evaporation rate of Sn at higher oxygen content in Hiraga et al.’s experiment. Hiraga et al. also confirmed the presence of SnO in the vapor phase by mass spectrometry.

Figure 11 represents the effect of total pressure on the rate of Sn evaporation from liquid iron at \([\%O]=0.0016\) and 0.074. Free evaporation rate constants of Sn and SnO can be calculated by the similar equation with Eqs. (4), (7) and (18). For the calculation of \( k_{\text{Sn in Fe}} \), the adsorption coefficient of oxygen on the surface of liquid iron, \( K_{\text{Fe}}^{\text{O}} = 140 \), is referred from the paper by Jimbo and Cramb. The calculated values of \( k_{\text{Sn in Fe}} \) and \( k_{\text{SnO in Fe}} \) at oxygen content of 0.074 mass\% are \( 3.6 \times 10^{-6} \) and \( 2.1 \times 10^{-4} \text{ (m} \cdot \text{s}^{-1}) \), respectively, and \( k_{\text{Sn in Fe}} \) at \([\%O]=0.0016\) is \( 1.3 \times 10^{-5} \text{ (m} \cdot \text{s}^{-1}) \). These values are presented in Fig. 11. At \([\%O]=0.0016\) (Fig. 11(a)), the evaporation of SnO would be negligible as it is indicated from Fig. 10. Since the liquid phase mass transfer was negligible in Hiraga et al.’s experiment, the rate is deduced to be controlled by gas phase mass transfer or free evaporation of Sn. If the former is predominant, the overall rate should be in proportion to the reciprocal of total pressure, and if the latter limits the rate, it should be independent of the pressure. Actually, the rate constants were in proportion to \( P^{-1} \) at higher pressure but tended to approach that of free evaporation at lower pressure as shown in Fig. 11(a). At \([\%O]=0.074\) (Fig. 11(b)), the evaporation of SnO could occur in addition to that of Sn. In this case, gas phase mass transfer and free evaporation of SnO should also be taken into account. As shown in Fig. 11(b), the observed rate was very close to that of free evaporation of Sn at higher pressure, but became faster with decreasing pressure and tended to approach to the free evaporation rate of SnO. As a summary, the evaporation rate of Sn are controlled by both of the free evaporation of Sn and the gas phase transfer of SnO at the lower oxygen content (\([\%O]=0.0016\)), and by the gas phase mass transfer of Sn and SnO at the higher oxygen content (\([\%O]=0.074\)). Mutual resistance of each process depends on total pressure and oxygen content in metal as shown in Fig. 11. Since \( k_{\text{Sn in Fe}} \) and \( k_{\text{SnO in Fe}} \) are now known values and the gas phase
mass transfer coefficient is in proportional to $P^{-1}$, the following relation is given.

$$R_{\text{overall(Sn in Fe)}} = k_{\text{overall(Sn in Fe)}}[\%\text{Sn}] = \frac{1}{1/k_{\text{g(Sn in Fe)}} + P/k_{\text{g(SnO in Fe)}}}$$
$$+ \frac{1}{1/k_{\text{g(SnO in Fe)}} + P/k_{\text{g(SnO in Fe)}}} \frac{[\%\text{Sn}]}{......(31)}$$

Where,

$$k'_{\text{g(Sn in Fe)}} = k''_{\text{g(Sn in Fe)}}/P \quad \text{(at a constant oxygen content)}$$
...........................................(32)

Apparent gas phase mass transfer coefficient, $k'_{\text{g(Sn in Fe)}}$ is inversely proportional to the total pressure, so that $k''_{\text{g(Sn in Fe)}}$ could be defined by Eq. (32) as a constant value independent of pressure. By fitting Eq. (31) for the observed values, $k'_{\text{g(Sn in Fe)}}$ and $k''_{\text{g(SnO in Fe)}}$ were evaluated as $1.08 \times 10^{-5}$ (Pa·m·s$^{-1}$) at $[\%\text{O}]=0.0016$ and $1.02 \times 10^{-5}$ (Pa·m·s$^{-1}$) at $[\%\text{O}]=0.074$, respectively. Solid lines in Fig. 11 denote the overall rate constant of Sn evaporation calculated by Eq. (31). Based on these rate parameters, $R_{\text{overall(Sn in Fe)}}$ can be calculated at any pressure and oxygen content. It is seen from Fig. 8 that the calculated overall rate fits the experimental values in the entire oxygen concentration range.

On the other hand, the equilibrium vapor pressure of CuO is much smaller than that of metallic Cu as shown in Fig. 10. If the faster Cu evaporation rate at higher oxygen content in Hiraga et al.'s experiment is caused by the vaporization of copper oxide, other volatile oxide of copper, such as Cu$_2$O, should be taken into account while no thermodynamic data is available in the literature except for CuO(g).

In the present work, the possibility of vaporization of Cu$_2$O, as Cu$_2$O, should be taken into account while no thermodynamic data is available in the literature except for CuO(g). Figure 12 shows the effect of total pressure on the evaporation rate of Cu from liquid iron at $[\%\text{O}]=0.0025$ and 0.125. Trend of the evaporation rate of Cu against pressure seems to be quite similar with that of Sn. Though the rate is approximately in proportional to $P^{-1}$ at $P>10^5$ Pa, it becomes to be independent of $P$ at lower pressure in both cases. Free evaporation rate of Cu at $[\%\text{O}]=0.0025$ is calculated in the above-mentioned manner as $k_{\text{g(Cu in Fe)}}=4.4 \times 10^{-5}$ (m·s$^{-1}$) and presented in Fig. 12(a). The observed Cu evaporation rate by Hiraga et al. at 13.3 Pa agrees well with $k_{\text{g(Cu in Fe)}}$. Therefore, the evaporation rate of Cu could be controlled by the free evaporation and the gas phase mass transfer of metallic Cu at lower oxygen content. From Fig. 12(a), $k_{\text{g(Cu in Fe)}}$ could be estimated as $7.1 \times 10^{-5}$ (m·s$^{-1}$) and $2.2 \times 10^{-3}$ (Pa·m·s$^{-1}$) at $[\%\text{O}]=0.125$ (Fig. 12(b)), respectively. Since CuO can not be considered as a volatile oxide species as discussed earlier, Cu$_2$O is assumed to be a major vapor species at higher oxygen content. In Fig. 12(b), the experimental plots tend to approach a constant value, which is much faster than the free evaporation rate of metallic Cu, at lower pressure. We assumed that this limiting rate is the free evaporation rate of Cu$_2$O, $R_{\text{g(Cu}_2\text{O in Fe)}}=1.9 \times 10^{-5}$ (m·s$^{-1}$) at $[\%\text{O}]=0.125$. On this assumption, the rate equation of Cu evaporation from molten steel would be the second-order with respect to $[\%\text{Cu}]$.

$$R_{\text{g(Cu}_2\text{O in Fe)}}=k_{\text{g(Cu}_2\text{O in Fe)}}[\%\text{Cu}]^2 = \frac{P/k_{\text{g(Cu}_2\text{O in Fe)}}}{1/k_{\text{g(Cu}_2\text{O in Fe)}}} \frac{[\%\text{Cu}]^2}{......(33)}$$

If the competitive vaporization of metallic Cu and Cu$_2$O is again assumed for the vaporization of Cu from liquid Fe–Cu–O alloy, the overall rate equation would be given by the sum of two rates.

$$R_{\text{overall(Cu in Fe)}} = R_{\text{g(Cu in Fe)}} + R_{\text{g(Cu}_2\text{O in Fe)}} = k_{\text{g(Cu in Fe)}}[\%\text{Cu}]+k_{\text{g(Cu}_2\text{O in Fe)}}[\%\text{Cu}]^2$$
$$= \frac{[\%\text{Cu}]}{P/k_{\text{g(Cu in Fe)}}+1/k_{\text{g(Cu}_2\text{O in Fe)}}}$$
$$+ \frac{[\%\text{Cu}]^2}{P/k_{\text{g(Cu}_2\text{O in Fe)}}+1/k_{\text{g(Cu}_2\text{O in Fe)}}} \frac{[\%\text{Cu}]^2}{......(34)}$$

Therefore, $R_{\text{g(Cu in Fe)}}$ could be determined from Eq. (34) and Hiraga et al.'s experiment. At $[\%\text{O}]=0.125$, $k_{\text{g(Cu}_2\text{O in Fe)}}$ could be calculated as $5.2 \times 10^{-3}$ (Pa·m·s$^{-1}$). The solid lines in Fig.9 are overall evaporation rate of Cu calculated by Eq. (34). Figure 12(b) indicates that the evaporation rate of Cu can be well expressed as the sum of $R_{\text{g(Cu in Fe)}}$ and $R_{\text{g(Cu}_2\text{O in Fe)}}$ at high oxygen concentration range. As a conclusion, Hiraga et al.'s experimental results are reasonably explained by the competitive evaporation of metallic Cu.
and Cu₂O.

5. Conclusions

The effect of oxygen content on the evaporation rate of Pb from inductively stirred liquid copper at 1,473 K and 1.3 kPa has been studied. The following items have been concluded.

(1) The evaporation rate of Pb in liquid copper is expressed by the first order equation with respect to Pb content in liquid copper. Oxygen decreases the Pb evaporation rate due to retardation of free evaporation of Pb by the surface adsorption. However, the evaporation rate of Pb becomes faster with more increase of oxygen in liquid copper. The enhancement of Pb evaporation at higher oxygen content is due to the volatilization of PbO.

(2) The overall Pb evaporation rate is well explained by the competitive evaporation of PbO together with metallic Pb at higher oxygen content.

(3) Re-analysis is made for the effect of oxygen on the Pb evaporation rate in liquid copper. The overall Pb evaporation rate is well explained by the first order equation with respect to Pb content in liquid copper.

(4) For the vacuum treatment of crude copper or steel scrap, oxygen contamination would enhance the evaporation rate of Pb due to the retardation of free evaporation of Pb by the surface adsorption. However, the evaporation rate of Pb becomes faster with more increase of oxygen in liquid copper. The enhancement of Pb evaporation at higher oxygen content is due to the volatilization of PbO.

The effect of oxygen content on the evaporation rate of Pb from inductively stirred liquid copper at 1,473 K and 1.3 kPa has been studied. The following items have been concluded.

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Nomenclature

[% i]: Content of impurity i in liquid metal (mass%)
[% i]₀: Initial content of i in liquid metal (mass%)

\( k_{\text{app}} \): Apparent first order rate constant of ‘i’ in liquid \( j \) (m·s⁻¹)
\( A \): Gas–liquid interfacial area (m²)
\( V \): Volume of liquid metal (m³)

\( t \): Reaction time (s)

\( k_{\text{liq, app}} \): Liquid phase mass transfer coefficient of ‘i’ in liquid \( j \) (m·s⁻¹)
\( k_{\text{liq, eff}} \): Free evaporation rate constant of ‘i’ on the surface of liquid \( j \) (m·s⁻¹)

\( k_{\text{g, eff}} \): Gas phase mass transfer coefficient of ‘i’ (m·s⁻¹)

\( k_{\text{g, app}} \): Apparent gas phase mass transfer coefficient of ‘i’ (m·s⁻¹)

\( k_{\text{g, eff}} \): Free evaporation rate constant of ‘i’ on the surface of oxygen free liquid \( j \) (m·s⁻¹)

\( k_{\text{app}} \): Apparent second-order rate constant of ‘i’ in liquid \( j \).

(σ): Surface tension of liquid copper containing oxygen (N·m⁻¹)
\( \sigma _0 \): Surface tension of pure liquid copper (N·m⁻¹)

\( T \): Surface excess at oxygen saturation on liquid copper (mol·m⁻²)
\( M_i \): Atomic weight of ‘i’ (kg·mol⁻¹)
\( N_i \): Molar flux of ‘i’ in the gas phase (mol·m⁻²·s⁻¹)

\( \gamma _{\text{Pb}} \): Raoultian activity coefficient of Pb at infinite dilution in liquid copper (−)

\( P_{\text{PbO}} \): Vapor pressure of pure Pb (Pa)

\( P_{\text{PbO}} \): Vapor pressure of PbO in the gas–liquid interface (Pa)

\( P_r \): Total pressure (Pa)

\( \rho \): Density of ‘i’ (kg·m⁻³)

\( k_{\text{overall, app}} \): overall first order rate constant of ‘i’ in liquid \( j \) (m·s⁻¹)

\( \theta _0 \): Degree of surface coverage by absorbed oxygen (−)

\( K \): Adsorption equilibrium constant of oxygen on the surface of liquid \( j \) (−)

\( a_{\text{Li}} \): Activity of PbO in liquid copper in mass%


