Evaporation of Cu and Sn from Induction-stirred Iron-based Melts Treated at Reduced Pressure

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The evaporation of Cu and Sn from iron-based melts at reduced pressure has been investigated. The experimental work was carried out in a laboratory-scale vacuum induction melting (VIM) furnace. The effects of (1) chamber pressures of 1 to 100 Pa, (2) melt temperatures of 1,673 to 1,873 K, (3) different melt compositions and (4) two different stirring intensities of the metal bath on the evaporation rate of Cu and Sn, respectively, were studied. It was found that the evaporation of Cu represents a reaction of first order with respect to Cu content of the melt. The evaporation of Sn is represented by a first order rate law, too. Under the same experimental conditions, the evaporation rate of Cu exceeds that of Sn. The rate controlling steps of evaporation are discussed. The optimal conditions of vacuum refining iron melts with respect to Cu and Sn were determined. Recommendations for the design of new vacuum treatment equipment are also given.

KEY WORDS: scrap remelting; steel refining; volatile trace elements; copper and tin; evaporation; kinetics; vacuum.

1. Introduction

The main source of copper and tin in steel is recycled obsolete steel scrap. That is why, control and removal of copper and tin are necessary in order to preserve the steel recycling rate at the current high level without sacrificing of steel quality. Several approaches to reduce the Cu and Sn contents of steel have been proposed, namely, improvement of scrap sorting, dilution of contaminated charges by directly reduced iron, mechanical or chemical scrap pre-treatment aiming at impurity removal and pyrometallurgical melt refining.1,2) In steelmaking, refining with respect to common impurity elements usually occurs by selective oxidation. However the solute elements Cu and Sn are not oxidised preferentially to the base metal Fe. Due to this major difficulty, copper and tin cannot be removed from scrap-based iron melts by a conventional refining method.

Significant research efforts have been made to develop pyrometallurgical deco rerisation and detinning techniques. It was confirmed on a laboratory scale that copper can be removed by treatment with sulphide fluxes3–5) extraction into a liquid non-ferrous metal6) or selective adsorption on ceramic surfaces.7,8) It was demonstrated that tin can be eliminated by treatment with calcium-based slags9–11) as well as by extraction.12) These refining methods feature in most cases relatively low degrees of removal as well as insufficient refining rates. Moreover, the costs of refining are too high to make an industrial-scale application attractive.

A promising method of removal of Cu and Sn is the treatment of iron melts at reduced pressure of the gas phase. This method consists in the selective vapourisation of the impurity solute element, i.e., refining is based on the difference in the vapour pressures of iron and that of the impurity. One of the main advantages of this refining technique is that no harmful by-products, such as slag or dust, are generated. Recent studies confirmed on a laboratory scale that iron melts can be refined with respect to Cu and Sn by evaporation of the impurity elements in elemental state12–14) and in the form of volatile substances,15–19) respectively. The main factors controlling evaporation were identified and their effect on the kinetics of refining was studied. However, most of the experimental work was conducted on melts of small weight which were treated under particularly favourable conditions, such as extremely low pressures and high melt temperatures. That is why the obtained knowledge may have limited application with regard to possible large scale application of the vacuum refining process. Moreover, in many of the previous works the evaporation was investigated of either Cu or Sn but scrap is usually contaminated with both Cu and Sn. Therefore further comparative studies on the evaporation of both residual elements under experimental conditions closer to those in steelmaking practice are considered necessary.

The aim of the present study is to investigate the fundamentals of the evaporation of Cu and Sn in iron-based melts treated at reduced pressure. The effect of the main parameters of vacuum treatment on the evaporation rates of Cu and Sn is studied. The kinetics of refining is investigated with the ultimate aim to find possibilities of increasing the elimi-
nation rates of Cu and Sn in vacuum treated scrap-based iron melts.

2. Experimental Conditions

2.1. Experimental Set-up

Iron-based melts were treated at reduced pressures of the gas phase in a laboratory-scale vacuum induction melting (VIM) furnace which has a maximum power of 100 kW at a frequency of 3 kHz. The furnace was supplied by ALD Vacuum Technologies and is of the type VIM-12. Melting, alloying and sampling are performed under argon atmosphere. The induction coil and the crucible holding the charge are placed in a gas-tight cylindrical chamber which has a volume of approximately 3 m³ (Fig. 1). The reaction chamber is evacuated by two mechanical pumps and an oil-diffusion pump. Sampling and alloying are performed through a vacuum lock without breaking the vacuum in the reaction chamber. Most of the test runs were conducted on melts weighing approximately 20 kg. An alumina crucible with an inner diameter of 0.15 m was employed. The ratio of the free surface area to volume of the melt is approximately 6 m⁻². A summary of the experimental conditions is provided in Table 1.

2.2. Experimental Procedure

Blocks of ultra low carbon (ULC) steel, cast iron and stainless steel, respectively whose chemical composition is given in Table 2 were smelted under argon. After melt down, the furnace power was reduced and temperature was measured by immersing a Pt–Pt/18%Rh thermocouple contained in a protective alumina sheath. Power to the furnace was manually adjusted on the basis of the temperature measurement to maintain the desired melt temperature. The melt was alloyed with electrolytic grade copper and tin, respectively. After homogenisation at constant input power, the first sample was taken by immersing a steel cup which was screwed onto a steel rod. The vacuum pumps were switched on and chamber pressure was reduced to a predetermined level. This moment was assumed as starting time for the vacuum treatment (t=0). The pressure was measured using a Pirani gauge and was adjusted by introducing argon into the chamber at a controlled rate. The sampling procedure was repeated at time intervals of 5, 10 or 30 min. Chamber pressure and melt temperature did not change essentially during the sampling procedure because this was carried out using the vacuum lock. After taking the last sample, normal pressure was restored by flushing argon into the chamber and the melt was cast into a mould. The ingot was used as a charge in subsequent test runs.

Power to the furnace, frequency, melt temperature and chamber pressure were monitored on a PC. The temperature was monitored continuously with an optical pyrometer and occasional measurements were made by immersing a Pt–Pt/18%Rh thermocouple into the melt, too. It is assumed that the temperature was controlled within ±15 K. The contents of Cu, Sn and Mn were analysed by inductively coupled plasma mass spectrometry (ICP-MS) using an ARL 35 000 ICP spectrometer. The contents of C, S and O were determined by the combustion method.

3. Results

3.1. Evaluation of Experimental Data and Order of Reaction

Figure 2 shows a typical example of the variation of Cu and Sn contents with treatment time. Assuming that the evaporation of solute element i represents a reaction of first order with respect to i, the evaporation rate is expressed by Eq. (1)

\[
\ln \frac{\%[i]}{\%[i]_0} = -k_i \cdot \frac{A}{V} \cdot t \quad \text{..........(1)}
\]

where, [%][i], [%][i]₀, kᵢ, A, V and t denote content of i in the melt (mass%), initial content of i (mass%), apparent evaporation rate constant (m⁻²·s⁻¹), free surface of melt exposed to vacuum (m²), volume of melt (m³) and treatment time (s), respectively. The results shown in Fig. 2 are plotted according to Eq. (1) in Fig. 3. It is evident from Fig. 3 that a plot of \( \ln (\%[i]/\%[i]₀) \) against \( A/V \cdot t \) yields a straight line. This
confirms that under the present experimental conditions the evaporation of Cu and Sn is represented by a reaction of first order. In consistency with literature data\textsuperscript{20,21} the same result was obtained for every test run of this study. Therefore, the evaporation rate of Cu and Sn was expressed by the first order evaporation rate constant $k_i$ ($\text{m} \cdot \text{s}^{-2}$) which was determined from the slope of the function $\ln(\%\left[i\right]_t/\%\left[i\right]_0)$ against $A/V \cdot t$. The rate constant $k_i$ can be considered as an overall mass transfer coefficient, whereby greater values of $k_i$ correspond to higher rates of elimination of the solute element $i$. A summary of the experimental results, together with the experimental conditions involved, is provided in Table 1.

It should be mentioned, however, that the evaporation of Sn from high-carbon iron melts containing more than 0.015 mass\% sulphur represents a second order reaction overall.\textsuperscript{22} The observed second order reaction kinetics is attributed to the removal of Sn through evaporation of volatile SnS.\textsuperscript{15,17,22} In this study the evaporation of Sn is represented by a reaction of first order because the sulphur content of the melt was kept below 0.015 mass\% sulphur in all experiments.

### 3.2. Effect of the Pressure of the Gas Phase

Figure 4 illustrates the effect of the pressure of the gas phase in the reaction chamber on the evaporation rate of Cu. It is evident that in the pressure range of 10 to 100 Pa decreasing the chamber pressure increases $k_{\text{Cu}}$ both in ULC steel melts and in Fe–18mass\%Cr–9mass\%Ni melts. It is also clear that pressures below 10 Pa do not yield a further increase in the value of $k_{\text{Cu}}$ in ULC steel melts. This result is in agreement with literature data.\textsuperscript{20} It is also inferred from the slope of the lines in Fig. 4 that pressure variations have a slightly stronger effect on the evaporation rate of Cu in ULC steel melts than on that in Fe–Cr–Ni melts.

The following relationship between log $k_{\text{Cu}}$ (m \cdot s\textsuperscript{-2}) and the chamber pressure $P$ (Pa) was derived for ULC steel melts treated in the pressure range of 10 to 100 Pa:

$$\log k_{\text{Cu}} = -0.45 \cdot \log P - 3.79 \quad \text{(2)}$$

The influence of pressure on the evaporation rate of Sn is illustrated in Fig. 5. It can be seen that the evaporation rate of Sn at a pressure of 50 Pa is the same as that at 10 Pa and 1 Pa, respectively. This result is consistent with the study of Linchevski\textsuperscript{21} who found that variation of chamber pressure has a much greater effect on the evaporation rate of Cu than on that of Sn. However, as the pressure is raised to 100 Pa the evaporation rate of Sn falls rapidly. At constant pressure, the evaporation rate of Sn in Fe–Cr–Ni melts is lower than that in ULC steel melts. A comparison of the data shown in Fig. 5 with that in Fig. 4 implies that the evaporation rate of Cu is higher than that of Sn at constant pressure.

### 3.3. Effect of Melt Temperature

It was found that the evaporation rates of both Cu and Sn increase with an increase in temperature. The effect of temperature on the evaporation of Cu is greater than on that of Sn. These findings are illustrated in Fig. 6 which shows a plot of $\ln k_i$ versus the reciprocal melt temperature $1/T$ (K\textsuperscript{-1}). This figure also shows the temperature dependence of the rate coefficient of the vaporisation reaction $k_i^0$ (m \cdot s\textsuperscript{-2}) which was obtained by calculation as will be shown later. The straight lines which were drawn through regression analysis of experimental data confirm that the
dependence of the evaporation rate on melt temperature is given by Eq. (3) which represents an Arrhenius type equation.

$$\ln k_i = - \frac{E_i}{RT} + C_i \quad \text{..........................(3)}$$

where, $E_i$, $R$, and $C_i$ denote apparent activation energy of the evaporation of solute element $i$ (J·mol$^{-1}$), gas constant (8.314 J·K$^{-1}$·mol$^{-1}$) and a constant which is independent of temperature (m·s$^{-1}$). The apparent activation energy of the evaporation of solute $i$ was obtained from the slope of the function $\ln k_i$ against $1/T$. Under the present experimental conditions the value of $E_{Cu}$ is equal to 232 kJ·mol$^{-1}$ and that of $E_{Sn}$ is equal to 118 kJ·mol$^{-1}$.

The value of $E_{Cu}$ obtained in this study is very close to the value of 227 kJ·mol$^{-1}$ reported by Chen$^{12}$ for the evaporation of Cu in high-carbon iron melts treated at a pressure of 500 Pa in the temperature range from 1 723 to 1 883 K. The present value is also close to the one reported by Linchevski$^{21}$ who studied the evaporation of Cu in liquid iron treated in the temperature range 1 823–1 923 K at a pressure of 0.1 Pa. This author obtained a value of 290 kJ·mol$^{-1}$ for $E_{Cu}$ The charges used by Linchevski$^{21}$ and Chen$^{12}$ were 0.74 and 0.20 kg, respectively, compared to 20 kg in the present work.

The enthalpy of vapourisation of pure copper at its boiling point is equal to 307 kJ·mol$^{-1}$.$^{23}$ This value is relatively close to the experimentally obtained value of $E_{Cu}$ which indicates that the vapourisation of the soluble Cu plays a significant role in limiting the overall reaction rate under the present experimental conditions.

On the other hand, the enthalpy of vapourisation of pure tin (296 kJ·mol$^{-1}$)$^{23}$ is almost three times as large as the experimentally obtained value of $E_{Sn}$. Moreover, it is known that diffusion-limited processes usually feature relatively low apparent activation energies. Hence, vapourisation at the gas-metal interface probably does not strongly affect the evaporation rate of Sn under the present experimental conditions.

3.4. Effect of Melt Composition

Experimental results illustrated in Fig. 7 indicate that the chemical composition affects the evaporation rates of both Cu and Sn. At all investigated melt compositions, the evaporation rate of Cu is higher than that of Sn. Increasing the carbon content from 0.01 to 4 mass% raises the evaporation rate of Sn strongly and that of Cu only slightly. It has been reported that carbon in liquid iron increases the evaporation rates of Cu and Sn, respectively, and that its effect on the evaporation of Sn is stronger than that on the evaporation of Cu.$^{15,24}$ The influence of carbon on the evaporation rates of Cu and Sn is explained with the fact that carbon increases the activities of both Cu and Sn in liquid iron.$^{25}$

Figure 7 also shows that both Cu and Sn in Fe–Cr–Ni melts are eliminated at lower rates than in ULC steel melts and in high-carbon iron melts, respectively. These results are in agreement with a previous study$^{19}$ on the evaporation of Sn. They are also consistent with the study of Linchevski$^{21}$ who found that the evaporation of Cu in pure liquid iron proceeds at a higher rate than that in Fe–18mass%Cr–9mass%Ni melts. Other authors$^{14,20}$ reported that the evaporation rate of Cu in Fe–18mass%Cr–9mass%Ni melts is higher than that in high-carbon iron melts which contradicts the present findings.

It was also observed that in general melts containing both Cu and Sn feature higher refining rates than melts containing only one of the two solute elements. This interaction effect has to be studied further.

3.5. Effect of Stirring Intensity

Two test runs (V3 and V18) were carried out under different mixing conditions of the metal bath. The experiments were conducted on ULC steel melts held at a temperature of 1 873 K and a pressure of 10 Pa. The stirring intensity in test run V3 is typical for all other experiments performed at 1 873 K while that in V18 is modified to achieve a reduced stirring intensity. The modification was realised by employing a different induction coil and a crucible with larger dimensions. Also, the weight of the charge was increased from 20 kg in V3 to 43 kg in V18. The experimental conditions are summarised in detail in Table 3.

The fact that the stirring intensity in experiment V18 was lower than that in V3 was confirmed by visual observations and photographic studies of the movement of alumina particles which were dropped on the surface of the melt. It was assumed that the velocity of the particles floating at the surface is equal to that of the metal. In test run V3 velocities in the range of 0.20 to 0.25 m·s$^{-1}$ were obtained, while the velocities in test run V18 were in the range of 0.15 to 0.20 m·s$^{-1}$. The surface velocity of induction-stirred metal is a function of the radial position.$^{26}$ In the present study,
Table 3. Experimental conditions and results at two different stirring intensities of the metal bath.

| Test run | V3 (normal stirring intensity) | V18 (reduced stirring intensity) |
|----------|-------------------------------|----------------------------------|
| Melt weight (kg) | 19.8 | 42.6 |
| Crucible diameter (m) | 0.15 | 0.205 |
| Height of molten metal (m) | 0.16 | 0.19 |
| Surface to volume ratio A/V (m⁻¹) | 6.3 | 5.4 |
| Inner diameter of induction coil (m) | 0.23 | 0.28 |
| Height of induction coil (m) | 0.29 | 0.36 |
| Power to the furnace (kW) | 12 | 31.5 |
| Coil current (A) | 41 | 65 |
| Frequency (kHz) | 2.5 | 2.9 |
| Rate constant $k_{Cu}$ (m⁻¹s⁻¹) | $5.7 \times 10^{-5}$ | $2.5 \times 10^{-5}$ |
| Rate constant $k_{Sn}$ (m⁻¹s⁻¹) | $2.5 \times 10^{-5}$ | $1.2 \times 10^{-5}$ |

![Fig. 8](image-url). Effect of the stirring intensity of the metal bath on the evaporation rates of Cu and Sn.

However, the number of velocity measurements at different radial positions is considered insufficient to determine the average radial surface velocity. The velocity measurements merely confirmed that at approximately the same radial position the surface velocities at the two stirring modes differ from one another. This is considered a proof for the fact that the aforementioned measures to alter the stirring intensity were successful.

The experimental results obtained at the two different stirring modes are illustrated in Fig. 8. It can be seen in this figure that the stirring intensity affects the evaporation rates of both Cu and Sn. At reduced stirring intensity the value of $k_{Cu}$ and $k_{Sn}$, respectively, is one half of that at normal stirring, as can be concluded from data in Table 3. This implies under the conditions of experiment V18 liquid phase mass transfer participates in the rate control of evaporation. Mass transfer is probably involved in limiting the evaporation rates at normal stirring intensity, too. Hence, refining with respect to Cu and Sn can be enhanced by increasing the stirring intensity of the metal bath.

4. Discussion

4.1. Rate Determining Steps

The evaporation of solute element $i$ from liquid metal treated at reduced pressures of the gas phase involves the following steps:

(i) convective transport of $i$ through the bulk of liquid metal to the diffusion boundary layer at the free surface

(ii) diffusion of $i$ through the liquid phase boundary layer

(iii) vaporisation of $i$ at the gas-metal interface (interfacial reaction)

(iv) diffusion of $i$ vapour through the gas phase boundary layer

(v) mass transfer of $i$ vapour through the bulk of the gas to the site of condensation

(vi) condensation

It is generally accepted that in laboratory-scale vacuum induction melting only process steps (ii), (iii) and (iv) control the kinetics of refining. Consequently, the overall reaction rate is related to three resistive steps assumed for transfer through the liquid, across the interface and into the gas phase, as shown in Eq. (4), which gives the apparent evaporation rate constant $k_i$.

$$k_i = \frac{1}{1/\delta + 1/k_{iL} + 1/k_{iV} + 1/k_{iG}}$$

where $k_{iL}$, $k_{iV}$ and $k_{iG}$ denote liquid phase mass transfer coefficient (m·s⁻¹), rate coefficient of the vaporisation reaction (m·s⁻¹) and gas phase mass transfer coefficient (m·s⁻¹).

4.1.1. Gas Phase Mass Transfer

The gas phase mass transfer coefficient $k_{iG}$ of solute element $i$ evaporating in the argon atmosphere is given by Eq. (5).

$$k_{iG} = \frac{D_{i,Ar}}{\delta} \frac{\gamma_i \cdot P_0}{\rho} \frac{M_{Fe}}{RT}$$

where $D_{i,Ar}$, $\delta$, $\gamma_i$, $P_0$, $\rho$, $M_{Fe}$ and $R$ represent interdiffusivity of $i$ vapour and Ar gas (m²·s⁻¹), thickness of gas phase diffusion boundary layer (m), Raoul's activity coefficient at infinite dilution, vapour pressure of pure liquid iron (Pa), density of iron (g·cm⁻³), atomic mass of Fe (55.85 g·mol⁻¹) and gas constant (8314510 Pa·cm³·mol⁻¹·K⁻¹), respectively. At constant gas temperature, the interdiffusion coefficient $D_{i,Ar}$ is linearly dependent on the reciprocal of the pressure in the reaction chamber $1/P$.

$$D_{i,Ar} = \frac{C_2}{P}$$

where, $C_2$ is a constant which is independent of chamber pressure, (Pa·m²·s⁻¹). On the other hand, the thickness of the gas phase boundary layer $\delta$ is pressure-dependent. However, when the chamber pressure $P$ is below 1000 Pa, it can be assumed that $\delta$ remains constant within certain limits of pressure variation. Consequently, $k_{iG}$ depends on chamber pressure only through $D_{i,Ar}$ and Eq. (5) is transformed to Eq.(7).

$$\log k_{iG} = -\log P + C_3$$

where, $C_3$ is a pressure-independent constant (m·s⁻¹). In the present study, it was found that in the pressure range of 10 to 100 Pa log $k_{iG}$ is linearly dependent on log $P$, as indicated by Eq. (2). Hence, in the pressure range of 10 to 100 Pa the evaporation rate of Cu in ULC steel melts treated at a temperature of 1 873 K is limited by the gas phase mass transfer rate. The present experimental results also show that for both Cu and Sn the evaporation rates at 1 Pa
are almost the same as those at 10 Pa. This is an indication that at pressures below 10 Pa the gas phase does not affect the evaporation.

It can be seen in Fig. 5 that at a pressure of 50 Pa the evaporation rate of Sn is approximately equal to that at 10 Pa and 1 Pa, respectively. This implies that in the pressure range of 1 to 50 Pa the overall reaction rate is not limited by gas phase mass transfer. On the other hand, an increase in chamber pressure from 10 to 50 Pa usually causes resistance to the gas phase mass transfer of the evaporating species.\(^{(1,2,20,28)}\) However, the evaporation rate of Sn was not affected by the pressure increase which suggests that under the present experimental conditions the value of one or both terms \(1/k_{\text{Sn}}\) and \(1/k_{\text{Sn}}^\text{M}\) in Eq. (4) is significantly higher than that of \(1/k_{\text{Sn}}^\text{Fe}\). That is, the evaporation rate of Sn is strongly limited by the liquid phase mass transfer rate and/or the rate of the interfacial reaction. The effect of chamber pressure on the rate of the interfacial reaction is not known but it is reasonable to suppose that the rate decreases with increasing pressure. On the other hand, it is obvious that melt stirring and liquid phase mass transfer are not affected by variations in chamber pressure. Therefore the fact that \(k_{\text{Sn}}\) remained constant when the chamber pressure was raised from 10 to 50 Pa is an indication of strong resistance to liquid phase mass transfer of Sn.

**Figure 9** shows the experimentally obtained relationship between the evaporation rates of the solute elements Cu, Sn, Mn,\(^{(28)}\) Zn\(^{(29)}\) and Pb\(^{(29)}\) in laboratory-scale vacuum induction melting as a function of chamber pressure (for Mn: frequency \(=3\) kHz, \(A/V^2=7.6\) m\(^{-1}\), melt weight = 12 kg; for Zn and Pb: frequency \(=4\) kHz, \(A/V^2=12.4\) m\(^{-1}\), melt weight = 4 kg). The data\(^{(30)}\) shows that at a temperature of 1873 K, manganese and zinc feature significantly larger atomic volumes than Mn, Cu and Zn. Probably, the rate of diffusion in liquid iron of the large atoms of Sn and Pb is much slower than that of the smaller atoms of Mn, Cu and Zn. i.e., the diffusion coefficients in liquid iron of Sn and Pb are significantly smaller than those of Mn, Cu and Zn. Hence, the evaporation rates of Sn and Pb are strongly limited by liquid phase mass transfer. That is why variations in the chamber pressure have a weak effect on the evaporation kinetics of Sn and Pb.

(3) At higher pressures the convective transport of metal vapor in the gas phase gains importance with respect to diffusion. A non-linear dependence of \(\log k_i\) on \(\log P\) is observed whereby the evaporation rate decreases with increasing pressure but the decrease is not as strong as in the region of linear dependence.

On the other hand it can be seen in Fig. 9 that in a wide pressure range the evaporation rates of Sn and Pb are relatively independent of pressure and the typical S-shaped curves are not observed. The data\(^{(30)}\) in **Table 4** indicate that both Sn and Pb feature significantly larger atomic volumes than Mn, Cu and Zn. Probably, the rate of diffusion in liquid iron of the large atoms of Sn and Pb is much slower than that of the smaller atoms of Mn, Cu and Zn, i.e., the diffusion coefficients in liquid iron of Sn and Pb are significantly smaller than those of Mn, Cu and Zn. Hence, the evaporation rates of Sn and Pb are strongly limited by liquid phase mass transfer. That is why variations in the chamber pressure have a weak effect on the evaporation kinetics of Sn and Pb.

**Table 4.** Atomic volumes* of pure liquid metals at melting point.\(^{(20)}\)

| Element | Atomic volume \(V_i\) \((10^{-6}\) m\(^3\)·mol\(^{-1}\)) |
|---------|------------------|
| Mn      | 9.54             |
| Cu      | 7.94             |
| Zn      | 9.94             |
| Sn      | 17.0             |
| Pb      | 19.42            |

* - the atomic volume of a pure metal is defined as the ratio of its atomic weight \(M\) to density \(\rho\).

**Table 5.** Raoultian activity coefficient at infinite dilution of solute \(i\) in iron melt at 1873 K.

|          | \(\gamma^o_i\) |
|----------|----------------|
| Pure liquid iron\(^{(25)}\) | 8.6 2.8 |
| Carbon-saturated liquid iron\(^{(31,32)}\) | 23.1 10.6 |

4.1.2. Vaporisation at the Gas–Metal Interface

The vaporisation rate of the solute element \(i\) is given by Eq. (8) which is derived from the expression for the evaporation of pure liquid metals in perfect vacuum (Hertz–Knudsen–Langmuir’s equation).\(^{(20)}\)

\[
k_i^v = 10^{-3} \cdot \frac{\alpha \cdot \gamma_i^o \cdot P_0}{\rho} \cdot \frac{M_F^2}{\sqrt{2 \pi \cdot RT \cdot M_i}} \quad \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots (8)
\]

where \(\alpha\), \(R\) and \(M_i\) represent surface evaporation coefficient \((\alpha=1\) for liquid metals), gas constant \((8\) 314 Pa·l·mol\(^{-1}\)·K\(^{-1}\)) and atomic weight of \(i\) (g·mol\(^{-1}\)), respectively. It can be inferred from Eq. (8) that increasing the activity coefficient \(\gamma_i^o\) results in higher vapourisation rates. Hence, if the rate of the vaporisation reaction of \(i\) controls the overall reaction rate, alloying the melt with an element modifying the activity of \(i\) will affect the evaporation rate.

Data summarised in **Table 5** show that at a temperature of 1873 K the activity of Cu in carbon-saturated liquid iron is 2.7 times larger than that in pure liquid iron. It follows from Eqs. (4) and (8) that if the evaporation of Cu is con-
controlled solely by the interfacial reaction, the evaporation rate in carbon-saturated liquid iron should be 2.7 times larger than that in carbon-free iron melts. However, it can be seen in Fig. 7 that the evaporation rate of Cu changes only slightly with a variation in the C content. Hence, evaporation is not only controlled by the interfacial reaction. In analogy, it is concluded for the evaporation of Sn that vaporisation is not the only rate determining step because the activity of Sn in carbon-saturated liquid iron is 3.8 times larger than that in pure liquid iron, while the experimentally obtained value of \( k_{\text{Sn}} \) in the high carbon iron melt is only 1.4 times larger than that in the ULC steel melt (Fig. 7).

Values of \( k_{\text{Cu}} \) and \( k_{\text{Sn}} \) in high-carbon iron melts were calculated with Eq. (8) using literature data on the temperature dependence of \( P_{\text{Cu}}^{0} \), \( P_{\text{Sn}}^{0} \), \( P_{\text{Cu}}^{0} \) and \( P_{\text{Sn}}^{0} \). The density of the melt at 1873 K was assumed to be 6.77 g cm\(^{-3}\) according to data in Ref. 33). The values of \( \ln k_{\text{Sn}} \) are plotted as a function of the reciprocal temperature in Fig. 6. As a first approximation the dependence of \( \ln k_{\text{Sn}} \) on \( 1/T \) is linear, hence the apparent activation energy of the interfacial reaction \( E_{\text{Sn}} \) (J mol\(^{-1}\)) can be determined from the slope of the function \( \ln k_{\text{Sn}} \) vs. \( 1/T \). A value of 256 kJ mol\(^{-1}\) for \( E_{\text{Cu}} \) and 281 kJ mol\(^{-1}\) for \( E_{\text{Sn}} \), respectively, is obtained.

It can be seen in Fig. 6 that the slope of the function \( \ln k_{\text{Cu}} \) is almost the same as that of \( \ln k_{\text{Sn}} \). Correspondingly, the value of \( E_{\text{Cu}} \) is approximately equal to that of the experimentally obtained apparent activation energy of evaporation \( E_{\text{Cu}} \). This is an indication that the evaporation rate of Cu is strongly limited by the rate of the interfacial reaction.

On the other hand the slope of the function \( \ln k_{\text{Si}} \) in liquid iron is much steeper than that of \( \ln k_{\text{Sn}} \). Correspondingly, the value of \( E_{\text{Si}} \) is 2.4 times larger than that of the experimentally obtained apparent activation energy of evaporation \( E_{\text{Si}} \). Consequently, the interfacial reaction does not play a major role in limiting the evaporation rate of Sn under the present experimental conditions.

The evaporation rates of Cu and Sn in Fe–18mass%Cr–9mass%Ni melts were lower than those in ULC steel melts (Fig. 7). If it is assumed that the liquid phase mass transfer rate of the solute element \( i \) in the Fe–18mass%Cr–9mass%Ni melt is equal to that in the ULC steel melt, it follows that the observed variation of the overall evaporation rates with melt composition is due to variation of \( k_{i}^{V} \) only. It is supposed that a significant variation of \( k_{i}^{V} \) can be caused only by the effect of alloying elements on the activity coefficient \( \gamma_{i} \). Chromium raises the activities of Cu and Sn in liquid iron. Values of the interaction parameters \( e_{\text{Cu}}^{\text{Cu}} \) and \( e_{\text{Sn}}^{\text{Cu}} \) are reported in the literature.\(^{15,25}\) No data was found on the effect of Ni on the activities of Cu and Sn in liquid iron. However, experimental results suggest that \( k_{\text{Ni}}^{V} \) in the Fe–18mass%Cr–9mass%Ni melt is lower than \( k_{\text{Ni}}^{V} \) in the ULC steel melt, hence \( \gamma_{\text{Ni}} \) (Fe–18mass%Cr–9mass%Ni) < \( \gamma_{\text{Ni}} \) (ULC Steel). Since \( e_{\text{Cu}}^{\text{Cu}} = 0.01825 \) and it is assumed that \( \gamma_{\text{Cu}} \) (Fe–18mass%Cr–9mass%Ni) < \( \gamma_{\text{Cu}} \) (ULC Steel), it follows that \( e_{\text{Cu}}^{\text{Cu}} < -0.037 \). Similarly, using \( e_{\text{Cu}}^{\text{Sn}} = 0.01525 \) it was found that \( e_{\text{Cu}}^{\text{Sn}} < -0.031 \). That is, Ni decreases the activities of Cu and Sn in liquid iron.

4.1.3. Liquid Phase Mass Transfer

A model proposed by Machlin\(^{34}\) has been widely used to describe the liquid phase mass transfer of solute elements to the free surface of induction-stirred liquid metal. Machlin’s model supposes that a layer of liquid metal adjacent to the gas phase moves as a “rigid body” and that mass transfer through this surface layer is achieved solely by diffusion. Under such circumstances, the liquid phase mass transfer coefficient \( k_{i}^{L} \) is given by Eq. (9).

\[
k_{i}^{L} = \frac{8 \cdot D_{i} \cdot u}{\pi \cdot r}
\]

where, \( D_{i} \), \( u \) and \( r \) denote diffusion coefficient of solute element \( i \) in liquid iron (m\(^{2}\) s\(^{-1}\)), average radial velocity of metal at the free surface (m s\(^{-1}\)) and radius of crucible (m).

It is evident that knowledge of the parameters \( D_{i} \), \( u \) and \( r \) is necessary to compute \( k_{i}^{L} \); however, only \( r \) is an easily measurable quantity. The measurement of diffusivities of solute elements in liquid iron is difficult and values reported in literature are widely scattered. According to Iida and Guthrie\(^{30}\) the experimentally obtained diffusion coefficients of the metallic solute elements Cr, Al, V, Ni, Mo, Co and Mn in liquid iron at a temperature of 1823 K are in the range of 2\( \times \)10\(^{-9}\) to 5\( \times \)10\(^{-9}\) m\(^{2}\) s\(^{-1}\). The same authors cite a value of 5\( \times \)10\(^{-9}\) m\(^{2}\) s\(^{-1}\) for \( D_{\text{Cu}} \) but no experimental data are available on \( D_{\text{Sn}} \). Reported data on the velocity of metal flow in laboratory-scale crucible induction furnaces are scarce and unreliable, too, since it is hardly possible to use an accurate velocity measurement technique at steelmaking temperatures. Therefore, Eq. (9) cannot be used to calculate \( k_{\text{Cu}}^{L} \) and \( k_{\text{Sn}}^{L} \) with a reasonable accuracy.

The temperature dependence of the diffusion coefficient \( D_{i} \) is represented by the Arrhenius equation

\[
D_{i} = D_{i}^{0} \cdot \exp \left( \frac{Q}{RT} \right)
\]

where, \( D_{i}^{0} \), \( Q \) and \( R \) represent diffusion constant (m\(^{2}\) s\(^{-1}\)), apparent activation energy of diffusion (J mol\(^{-1}\)) and gas constant (8.314 J K\(^{-1}\) mol\(^{-1}\)), respectively. The relationship between melt temperature and surface velocity \( u \) is not known under the current experimental conditions. However, at a constant frequency, the surface velocity of induction-stirred metal in a crucible is linearly dependent on the magnitude of coil current.\(^{26}\) In the present study, at a constant frequency of 2.5 kHz, the magnitude of the coil current at 1673 K was approximately 40 A and increased to 50 A at 1873 K, i.e., the magnitude of the current did not change significantly over the experimental temperature range. Hence, in a first approximation the surface velocity is independent of melt temperature. Then it follows from Eqs. (9) and (10) that \( k_{i}^{L} \) is largely independent on temperature only through \( D_{i} \) and Eq. (9) can be transformed to Eq. (11).

\[
\ln k_{i}^{L} = -\frac{Q}{2RT} + C_{4}
\]

where the constant \( C_{4} \) (m s\(^{-1}\)) is independent of temperature. A comparison of Eq. (11) with Eq. (3) implies that if the evaporation rate is limited solely by liquid phase mass transfer, the experimentally obtained apparent activation energy of evaporation \( E_{i} \) is equal to \( Q_{i}/2 \). Values in the range of 42 to 91 kJ mol\(^{-1}\) are reported\(^{35}\) for \( Q_{i} \) of solute elements in liquid iron but no data are available on \( Q_{\text{Sn}} \). However, if it is assumed that the value of \( Q_{\text{Sn}} \) lies in the

\[
Q_{\text{Sn}} = 256 \text{ kJ mol}^{-1}
\]

...
aforementioned range, too, it is evident that $E_{\text{Sn}}$, which equals 118 kJ · mol$^{-1}$ is an intermediate value between $E_{\text{Sn}}^1$ (281 kJ · mol$^{-1}$) and $Q_{\text{Sn}}/2$, but is much closer to $Q_{\text{Sn}}/2$ than to $E_{\text{Sn}}^0$. This suggests that the evaporation rate of Sn is limited mainly by liquid phase mass transfer under the present experimental conditions.

Ono and Ishitobi$^{35}$ measured the diffusion coefficient of Cu in carbon-saturated liquid iron in the temperature range 1623–1823 K and found that $D_{\text{Cu}}^0$ and $Q_{\text{Cu}}$ are equal to 4.15 × 10$^{-8}$ m$^2$ · s$^{-1}$ and 91 kJ · mol$^{-1}$, respectively. The experimentally obtained value of $E_{\text{Cu}}$ is five times larger than that of $Q_{\text{Cu}}/2$. Hence the liquid phase mass transfer did not affect the evaporation rate of Cu to a great extent.

The present results as well as literature data$^{20,28}$ indicate that at chamber pressures below 10 Pa the evaporation rate of solute $i$ is not affected by pressure variation. Hence, the resistance to mass transfer of evaporating species in the gas phase is negligible, i.e., the value of $k_i^G$ is much greater than that of $k_i^L$ and $k_i^V$. Consequently, Eq. (4) is transformed to Eq. (12).

\[ k = \frac{1}{k_i^L} + \frac{1}{k_i^V} \] ..............................(12)

As already shown $k_i^V$ can be calculated for a given temperature and chemical composition of the melt from known thermodynamic data. On the other hand, $k_i$ is experimentally determined from the variation in the content of $i$ with treatment time. Hence, the liquid phase mass transfer coefficient $k_i^L$ can be derived from Eq. (12).

The value of $k_i^L$ in high-carbon iron melts was derived from Eq. (12) after the experimentally obtained values of $k_{\text{Cu}}^L$ and the calculated values of $k_{\text{Cu}}^L$ were inserted in this equation. A value of 5.0 × 10$^{-5}$ m · s$^{-1}$ was obtained for $k_{\text{Cu}}^L$ at the experimental temperature of 1863 K. At 1773 and 1673 K, the computation of $k_{\text{Cu}}^L$ yields values of 2.4 × 10$^{-5}$ m · s$^{-1}$ and 0.9 × 10$^{-5}$ m · s$^{-1}$, respectively. On the other hand, when the values of $D_{\text{Cu}}$ obtained from Eq. (10) and data of Ono and Ishitobi$^{35}$ are inserted in Eq. (9) together with the computed values of $k_{\text{Cu}}^L$, the surface velocity of liquid metal $u$ is obtained. At a temperature of 1863 K a value of 0.006 m · s$^{-1}$ is computed for $u$. The surface velocity decreases with a decrease in melt temperature and is as low as 0.0005 m · s$^{-1}$ at 1673 K. However, both visual observations and photographic studies indicate that the actual surface velocity is at least one order of magnitude higher than the calculated one. Moreover, surface velocities in the range of 0.1 to 0.3 m · s$^{-1}$ have been measured or estimated in similar induction furnaces.$^{20,26,37}$ The disagreement between the calculation on one side and the observations on the other side may be due to one or several of the following reasons:

- At a chamber pressure of 10 Pa the resistance from the gas phase against the mass transfer of copper vapour is not negligible, hence the evaporation rate is not given by Eq. (12).
- Eq. (8) has been derived under the assumption of free evaporation but under the current experimental conditions such assumption is not justified.
- Use of Eq. (8) is justified but thermodynamic data on $\gamma_{\text{Cu}}^0$ and/or $P_{\text{Cu}}^0$ which are obtained under equilibrium conditions are irrelevant under the non-equilibrium conditions of the evaporation test runs.
- Machlin’s model$^{34}$ of liquid phase mass transfer is not relevant under the present experimental conditions.
- The melt surface was not clean from reaction products.
- The values of $D_{\text{Cu}}$ in carbon-saturated liquid iron obtained by Ono and Ishitobi$^{35}$ are at least one order of magnitude higher than the actual ones. Even though the gap between the observed surface velocities and the computed ones is probably due to the last item, it is thought that generally the approach to determine $k_i^L$ using Eq. (12) is erroneous due to the great sensitivity of $k_i^L$ to the experimentally obtained values of $k_i$ and the computed values of $k_i^V$.

Another approach to obtain $k_i^L$ is to compute it with Eq. (9) from measured or estimated values of $D_i$ and $u$. However, computed values of $k_i^L$ are highly sensitive to changes in the surface velocity and the apparent activation energy of diffusion, as illustrated in Fig. 10. For example, at a constant surface velocity of 0.25 m · s$^{-1}$ and at $E_i^0$ equal to 100 kJ · mol$^{-1}$, the value of $k_i^L$ is one order of magnitude lower than that at $E_i^0$ = 50 kJ · mol$^{-1}$. Comparison of the two sets of values of $k_i^L$ at constant $E_i^0$ but at different surface velocities shows a significant variation in $k_i^L$; too. Data in Fig. 10 are plotted at a constant value of $D_i^0$, but it can be inferred from Eq. (10) that variations in $D_i^0$ cause considerable changes in the computed value of $k_i^L$; too. It is obvious that the reliability of $k_i^L$ values computed with Eq. (9) becomes questionable because of uncertainties in the estimation of $D_i$ and $u$.

In this study, a value of 0.9 × 10$^{-4}$ m · s$^{-1}$ was obtained for the first-order apparent evaporation rate constant of solute Mn in high-carbon iron melts treated at a pressure of 10 Pa and at a temperature of 1873 K. It has been reported that at 10 Pa the evaporation of Mn in liquid iron represents a first-order reaction whose rate is limited almost completely by liquid phase mass transfer.$^{29}$ Therefore the liquid phase mass transfer coefficient of Mn under the present experimental conditions is estimated to be approximately 1.0 × 10$^{-4}$ m · s$^{-1}$. If it is assumed that the liquid phase mass transfer rates of solute metallic elements do not differ significantly from one another, it follows that under the present
experimental conditions \( k_{Cu}^L \) and \( k_{Sn}^L \) in high-carbon iron melts treated at a pressure of 10 Pa and a temperature of 1873 K are in the order of \( 1.0 \times 10^{-4} \) m s \(^{-1} \), too.

It was demonstrated that it is difficult to determine the liquid phase mass transfer rate of Cu and Sn at a reasonable accuracy. However, on the basis of the observed temperature dependence of \( k_i \) it is concluded that in high-carbon iron melts the evaporation rate of both Cu and Sn is mixed-controlled by liquid phase mass transfer rate and rate of the interfacial reaction. The evaporation rate of Sn is controlled mainly by the liquid phase mass transfer rate while the evaporation rate of Cu is largely limited by the rate of the interfacial reaction.

Equation (8) predicts that the vapourisation rate of Cu in ULC steel melts is lower than that in high-carbon iron melts due to the effect of carbon on the activity of Cu. On the other hand the observed evaporation rates of Cu in ULC steel melts and high-carbon iron melts are approximately the same (Fig. 7). But the evaporation rate of Cu in high-carbon iron melts was found to be largely limited by the rate of the interfacial reaction. Hence, in ULC steel melts the evaporation of Cu is controlled mainly by the interfacial reaction, too. Moreover, the limiting effect of vapourisation on the overall reaction rate is probably greater in ULC steel melts than in high-carbon iron melts.

Unlike the observed evaporation rates of Cu, those of Sn in ULC steel and high-carbon iron melts are quite different from one another (Fig. 7). That is why the rate determining step in the evaporation of Sn in ULC steel melts cannot be derived from knowledge of the rate determining step in the evaporation of Sn in high-carbon iron melts. However, it is supposed that the observed limiting effect of the interfacial reaction, which was weak in case of high-carbon iron melts, becomes stronger with ULC steel melts. Correspondingly, the importance of liquid phase mass transfer probably diminishes as the carbon content is decreased. It is not clear which of the two process steps plays the more important role.

4.1.4. Industrial Equipment for the Evaporation of Cu and Sn

The lowest chamber pressure attainable in the present large scale vacuum treatment equipment is approximately 50 Pa. As already shown, however, at 50 Pa there exists a resistance to mass transfer of evaporating species in the gas phase, while at pressures below 10 Pa the gas phase does not affect the evaporation rate of Cu and Sn. Therefore, a chamber pressure of 10 Pa is optimal for the refining with respect to Cu and Sn. It is recommended that new equipment capable of treating liquid metal at a chamber pressure of 10 Pa should be designed.

In general, increasing the melt weight deteriorates the mixing conditions in the metal bath. Hence the limiting effect of the vapourisation reaction observed under the current experimental conditions probably diminishes in evaporation tests carried out on a larger scale where the importance of mass transfer increases. Consequently, enhancement of the liquid phase mass transfer of evaporating solutes is of primary importance with regard to the industrial application of vacuum refining. Moreover, since the evaporation of Cu and Sn does not proceed in the bulk of the metal but only at the gas–metal interface, it is necessary to enhance the liquid phase mass transfer particularly in the vicinity of the interface. However, gas stirring which is known to enhance mass transfer across the melt free surface is not recommended because the volume of stirring gas represents an additional load to the vacuum pumping system and prevents it from achieving sufficiently low chamber pressures. Therefore new equipment should be developed which not only allows treatment at chamber pressures as low as 10 Pa but also features increased stirring intensity of the metal in the vicinity of the reaction interface.

5. Conclusions

The evaporation of Cu and Sn in iron-based melts treated at reduced pressure of the gas phase was studied in a vacuum induction melting furnace on a laboratory scale. The following conclusions are drawn:

(1) The evaporation of Cu represents a reaction of first order. The evaporation of Sn conforms to the first order rate law, too. The evaporation rate of Cu is higher than that of Sn.

(2) The evaporation rate of Cu increases as the chamber pressure is lowered from 100 to 10 Pa. At chamber pressures below 10 Pa no further acceleration of the refining process is achieved. At pressures above 10 Pa the evaporation of Cu is controlled by gas phase mass transfer. A linear relationship exists between the logarithms of the apparent evaporation rate constant and the chamber pressure. At pressures of 10 Pa or lower the evaporation rate of Cu is limited by a combination of both vapourisation at the gas–metal interface and liquid phase mass transfer. The effect of the former is stronger under the present experimental conditions.

(3) The evaporation rate of Sn increases significantly as the chamber pressure is lowered from 100 to 50 Pa. Under the present experimental conditions the gas phase mass transfer did not control the evaporation of Sn over the pressure range from 1 to 50 Pa. In this pressure range the evaporation rate of Sn in high-carbon iron melts is mixed-controlled by vapourisation and liquid phase mass transfer. The effect of the latter is greater.

(4) The evaporation rates of both Cu and Sn are considered insufficient to achieve refining on a commercial scale. Measures enhancing the evaporation of these solute elements have to be taken in order to make vacuum refining attractive. It is suggested that vacuum treatment should be carried out at a chamber pressure of 10 Pa and at higher stirring intensity of the metal bath. Increasing melt temperature would be beneficial, too, especially for the evaporation of copper. Alloying the melt with carbon is recommended to increase the evaporation rate of tin. The alloying element chromium increases the evaporation rates of Cu and Sn while the presence of nickel reduces them.

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