Methods of Increasing the Rate of Tin Evaporation from Iron-based Melts

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The low evaporation rate is a main obstacle to the large scale application of vacuum refining of steel scrap melts with respect to tin. In this paper several possibilities of increasing the evaporation rate of tin have been investigated. Iron-based melts containing 0.3 to 0.6 mass% Sn were treated in a laboratory-scale vacuum induction melting furnace at a pressure of 10 Pa.

(1) It was confirmed that detinning is enhanced by increasing the sulphur content of liquid iron. This effect is explained by the evaporation of volatile SnS. The kinetics of SnS evaporation is discussed.

(2) Evaporation of volatile SnO from steel melts containing less than 0.024 mass% oxygen was not confirmed.

(3) The highest evaporation rate of tin in elemental state is observed from high-silicon iron melts. The most favourable conditions occur at approximately 22 mass% Si in the iron melt. This fact is discussed in terms of the thermodynamics of the liquid Fe–Si–Sn system.

(4) New process schemes of tinplate scrap recycling are considered. It is suggested to use tinplate scrap as iron-bearing material for the production of ferro-silicon alloys. The recycling of tinplate scrap in the ferro-silicon production has potential benefits over its recycling in steelmaking.

(5) It is demonstrated that the condensate gathered during vacuum refining of tinplate scrap melts can be reprocessed in the non-ferrous industry to obtain pure tin.

KEY WORDS: tinplate; steel scrap; steel refining; tin; evaporation; kinetics; vacuum; SnS; SnO; ferro-silicon; condensate.

1. Introduction

Tin is a harmful residual element in steel which causes a loss of ductility associated with an increase in strength and a deterioration in the drawing properties. Moreover, the presence of tin in steel amplifies the well known detrimental effect of residual copper on steel hot shortness.11

The main source of tin in steel is the recycled tinplate scrap. Tinplate represents a very low carbon steel sheet coated with an average5 of 5 gram tin/m², and tinplate scrap contains usually 0.2 to 0.4 mass% Sn. However a maximum tin content of 0.01 mass% for flat products and 0.035 mass% for rebar steel grades is allowed.5 Tin introduced into scrap melts remains in the final steel products because it is not oxidised preferentially to the base metal Fe and therefore cannot be removed with conventional slags. At present there exists no industrial scale process for the removal of tin from steel melts. However, the development and application of a detinning process is considered necessary because if tin is not removed from the material cycle steel–scrap–steel, this residual element will continue to accumulate5 and will eventually reach critical levels. On the other hand winning of tin from steel scrap would represent a new source of secondary tin and increase the overall recycling rate of this valuable non-ferrous metal.

Several methods to reduce the Sn content in steel have been tested, including electrolytic detinning8) of scrap, removal of the tin coating in solid state by oxidizing7,8) or sulphidizing,9) refining of scrap melts using calcium-based slags10–12) and selective evaporation13) of tin at reduced pressure of the gas phase. Apart from the electrolytic detinning, these methods have not been implemented on a commercial scale, mainly due to low degrees of removal, insufficient refining rates and high operating costs. Even though electrolytic detinning is applied on an industrial scale it is used to treat process scrap only. However, obso- lete scrap represents the greatest share of occurring tinplate scrap.3) This means that actually only a small fraction of the occurring tinplate scrap is detinned before smelting. Therefore a pyrometallurgical process of tin removal will be beneficial.

A recent study13) confirmed that the elimination of tin from iron-based melts by selective evaporation at reduced pressures is feasible on a laboratory scale. The evaporation rate of tin was determined and the effect of various process parameters on the evaporation kinetics was studied. It was
found that when the solute tin evaporates in elemental state, the refining rate is insufficient to make a large scale application of vacuum detinning attractive. On the other hand, literature data indicate that the removal of tin is enhanced by evaporation of volatile tin-bearing substances, such as sulphides,14–21) oxides22) and chlorides.23) It is also known that increasing the carbon and/or the silicon content of liquid iron accelerates the evaporation of tin.15,24,25)

Therefore the aim of the present study is to investigate the possibilities of increasing the removal rate of tin from iron-based melts treated under vacuum. New processes for recycling of tinplate scrap are suggested, too.

2. Experimental Conditions

The experimental conditions will be described briefly. A detailed presentation is available in Ref. 13).

2.1. Experimental Set-up

A laboratory-scale vacuum induction melting (VIM) furnace which has a maximum power of 100 kW at a frequency of 3 kHz was used to treat iron-based melts containing tin. The experiments were performed under argon at a pressure of the gas phase of 10 Pa. Sampling and alloying were carried out through a vacuum lock without breaking the vacuum in the reaction chamber. The test runs were conducted on melts weighing approximately 20 kg. An alumina crucible with an inner diameter of 15 cm was employed. The ratio of free surface area to volume of the melt $A/V$ is approximately $6 \text{ m}^2$.

2.2. Experimental Procedure

Blocks of cast iron or ultra low carbon (ULC) steel were smelted under argon. The melt temperature was measured by immersing a Pt–Pt/18%Rh thermocouple contained in a protective alumina sheath. Power to the furnace was adjusted manually on the basis of the temperature measurement. The iron melt was alloyed with electrolytic grade tin, lump FeS, iron ore fines and Fe–75mass%Si alloy, respectively. After homogenisation, the first sample was taken by immersing a steel cup which was screwed onto a steel rod. Then the vacuum pumps were switched on and chamber pressure was reduced to 10 Pa. 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 gas-tight furnace chamber at a controlled rate. The sampling procedure was repeated at time intervals of 5, 10 or 30 min. During the treatment the melt 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 $\pm 15$ K.

The contents of Sn, Cu and Si were analysed by inductively coupled plasma mass spectrometry (ICP-MS) using an ARL 35 000 ICP spectrometer. The contents of C and S were determined by the combustion method using a Stroehlein CSmat-600. The oxygen content was analysed using a Stroehlein ONmat-8500.

3. Results and Discussion

3.1. Removal of Sn through Evaporation of SnS

The evaporation of solute tin from Fe–4mass%C–0.7mass%Si melts was investigated at a temperature of 1 683 K and a pressure of 10 Pa. A summary of the experimental conditions and results is provided in Table 1. The variation of the tin content with treatment time for three different initial sulphur contents is illustrated in Fig. 1. It is evident that the rate of detinning increases with an increase in the initial sulphur content. An extremely high removal rate is observed in the first few minutes of vacuum treatment of the iron melt with the highest initial sulphur content of 0.14 mass% S. About 60% of the initial tin were removed from that melt just in the first 15 min of vacuum treatment (Fig. 1).

It was found that not only the tin content of the iron melts but also their sulphur content is decreasing as the treatment proceeds. Moreover in test runs VS-2, VS-3, VS-4 and VS-5 tin and sulphur evaporated on the basis of an equimolar ratio, i.e., with every mole of tin removed, one mole of sulphur is removed, too. This is illustrated in Fig. 2 which shows the number of moles of sulphur removed at a given time as a function of the number of moles of removed tin. The symbols in this figure correspond to the formation of SnS according to Eq. (1).
Since the data in Fig. 2 lie close to the line, it is evident that the volatile substance which evaporates under the current experimental conditions is SnS. This confirms the results of previous studies14–21 which indicate that tin is removed from high-sulphur iron melts by evaporation of SnS. For practical application of detinning through SnS evaporation it is of interest to know the minimum content of sulphur that is necessary to induce SnS evaporation and increase significantly the rate of tin removal. In test run VS-1 the tin content was reduced from 0.48 to 0.34 mass% while the sulphur content decreased by only 0.007 mass% (Table 1). Obviously the initial sulphur content of 0.011 mass% in this test run was too low to induce SnS evaporation and tin was removed predominantly in elemental state.

It can be seen in Fig. 3 that in the first 20 min of treatment in test run VS-2 tin and sulphur evaporated on the basis of an equimolar ratio. A deviation from the stoichiometric ratio of tin and sulphur removal is evident at the later stage of the experiment when the sulphur content was below approximately 0.015 mass%. Consequently, under the current experimental conditions tin is removed mainly by SnS evaporation at sulphur contents higher than approximately 0.015 mass%.

This conclusion is supported by the experimental results of Persson and Harris16 which indicate that the removal rate of tin increases significantly when the sulphur content of the melt is raised above 0.02 mass%. Hence the minimum sulphur content necessary to enhance the removal of tin from vacuum treated scrap melts is approximately 0.02 mass%.

3.1.1. SnS and Sn Vapour Pressures and Reacton Site

Wang et al.26 presented calculations of the vapour pressures of SnS and Sn equilibrated with carbon-saturated liquid iron containing Sn and S. Thermodynamic data given in the study of Wang et al.26 as well as in Refs. 27) and 28) was employed to calculate the vapour pressures of SnS and Sn in equilibrium with Fe–4mass%C–0.7mass%Si melt containing up to 1.0 mass% Sn and 0.2 mass% S at a temperature of 1 683 K. Figure 4 shows the calculated results. It is evident that at constant tin content the vapour pressure of SnS is at least two orders of magnitude higher than that of Sn, if the sulphur content is higher than approximately 0.05 mass%. At lower sulphur contents the difference in the values of $P_{\text{SnS}}$ and $P_{\text{Sn}}$ decreases but $P_{\text{SnS}}$ is still one to two orders of magnitude higher than $P_{\text{Sn}}$. This difference becomes one order of magnitude when the sulphur content is as low as 0.0055 mass%. Hence from a thermodynamic point of view, it is reasonable to accept that under the current experimental conditions tin is removed mainly by SnS evaporation when $[S]>0.015$ mass%, as already stated in the discussion of the kinetic results.

The results in Fig. 4 also imply that the vapour pressure of SnS is not sufficiently high to induce formation of a separate SnS gas phase in the bulk of the liquid metal. Visual observations of the free surface indicated no boiling during the vacuum treatment. Consequently, under the present experimental conditions SnS is formed by a heterogeneous reaction taking place at the interface metal/vacuum. This suggests that increasing the ratio of surface area to volume of the melt raises the removal rate of tin.

3.1.2. Rate Law

A recent study13 confirmed that the evaporation of tin from iron-based melts which were essentially free of sulphur is represented by a reaction of first order, i.e., by Eq.

$$[\text{Sn}]+[\text{S}] \leftrightarrow \text{SnS} \quad (1)$$
Experimental results from test runs VS-3 and VS-4 are illustrated in Fig. 5, which shows that the experimental results of test run VS-3 by a reaction of first order. This is illustrated in Fig. 5 that the removal rate of tin from high-sulphur iron melts is not represented well by a straight line. Nevertheless, for the purpose of comparing the removal rates of tin from high-sulphur iron melts with that from sulphur-free iron melts, the initial rate of the removal reaction in the high-sulphur iron melts was expressed using the first order reaction law, too.

Thus, the rate of tin removal from various iron-based melts can be analysed by comparing the values of first-order rate constants, as shown in Fig. 6. A good linear relation is obtained for test run VS-3 and VS-4.

The rate of tin removal from high-sulphur iron melts is extremely high. This confirms that the evaporation of SnS enhances the removal of tin from iron melts treated at reduced pressure.

If the removal of tin from high-sulphur iron melts is achieved exclusively through evaporation of SnS, denoting represents a second-order reaction and the rate of tin removal is expressed by Eq. (3)

\[ Y = \frac{1}{a} \left( \ln \frac{[%Sn]}{[%Sn]_0} - \ln \frac{[%Sn]}{[%Sn]_0} \right) = k_{Sn} \frac{A}{V} \cdot t \]

where, [%Sn], [%Sn]₀, k, A, V and t denote actual Sn content of the melt (mass%), initial content of Sn (mass%), first order evaporation rate constant (m · s⁻¹), free surface of melt exposed to the vacuum (m²), volume of the melt (m³) and treatment time (s), respectively. The rate of tin evaporation from the sulphur-free iron melts is expressed by the rate constant \( k \) (m · s⁻¹) which was determined from the slope of the function ln(\(%[Sn]/%[Sn]_o\)) against \( A/V \cdot t \). This constant can be considered as an overall mass transfer coefficient, whereby greater values of \( k \) correspond to higher rates of elimination of Sn.

However, in the present study it was found that the removal of Sn from high-sulphur iron melts is not represented by a reaction of first order. This is illustrated in Fig. 5 which shows that the experimental results of test run VS-3 represented in terms of ln(\(%[Sn]/%[Sn]_o\)) against \( A/V \cdot t \) are not fitted well by a straight line. Nevertheless, for the purpose of comparing the removal rates of tin from high-sulphur iron melts with that from sulphur-free iron melts, the initial rate of the removal reaction in the high-sulphur iron melts was expressed using the first order reaction law, too. This was done by taking into account only the experimental results from the first 15 min of vacuum treatment to determine a first order evaporation rate constant \( k^* \) (m · s⁻¹) that characterises only the initial stage of treatment. This procedure is illustrated in Fig. 5, and \( k^* \) equal to 16.9 × 10⁻³ m · s⁻¹ is obtained from the slope of the function ln(\(%[Sn]/%[Sn]_o\)) against \( A/V \cdot t \). In test runs VS-2 and VS-4, \( k^* \) was obtained as 2.4 × 10⁻³ m · s⁻¹ and 15.7 × 10⁻⁵ m · s⁻¹, respectively. The rate of tin removal from various iron-based melts can be analysed by comparing the values of first-order rate constants, as shown in Fig. 6. A good linear relation is obtained for test run VS-3 and VS-4.

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\[ Y = \frac{1}{a} \left( \ln \frac{[%Sn]}{[%Sn]_0} - \ln \frac{[%Sn]}{[%Sn]_0} \right) = k_{Sn} \frac{A}{V} \cdot t \]

where, [%Sn], [%Sn]₀, [%Sn]₀, [%Sn]₀, and \( k_{Sn} \) denote the actual content of Sn in the melt (mass%), the initial content of Sn (mass%), the initial content of S (mass%) and the second-order rate constant of tin removal (m · s⁻¹), respectively, while \( a \) is defined as \( a = [%Sn]_0 - 0.27 [%Sn]_0 \). The value of 0.27 is obtained from the ratio of the atomic weight of sulphur to that of tin. It follows from Eq. (4) that, if tin is removed exclusively by evaporation of SnS, the integral \( Y \) should be a linear function of \( (A/V) \cdot t \), and \( k_{Sn} \) can be evaluated from the slope of the linear relation.

Experimental results from test runs VS-3 and VS-4 are plotted according to Eq. (4) in Fig. 7. A good linear relation
can be seen between $Y$ and $(A/V)$, indicating that under the present experimental conditions the removal of tin was achieved mainly by evaporation of SnS and that the fraction of tin eliminated by evaporation in elemental state was insignificant. From the slope of the linear relations shown in Fig. 7, the value of $k_{\text{Sn}}^{a}$ is obtained for each test run. Since $k_{\text{Sn}}^{a}$ in test run VS-4 is higher than that in VS-3, it is concluded that for melts with the same initial sulphur content an increase of the initial tin content from 0.44 to 0.58 mass% raises the rate of tin removal.

In the last 30 min of treatment in test run VS-4 the sulphur content was in the range of 0.008 to 0.015 mass%, hence in this period evaporation of elemental tin cannot be neglected. That is why the value of $k_{\text{Sn}}^{a}$ for VS-4 was determined from the experimental results obtained in the first 60 min of treatment.

Experimental results on detinning of iron melts published by Sehgal\textsuperscript{14} as well as Persson and Harris\textsuperscript{16} were analysed with the help of Eq. (4), too. It was found that the detinning reaction is described well by Eq. (4) when the sulphur content is higher than approximately 0.02 mass%. This confirms the present findings that tin is removed mainly by evaporation of SnS at $[S] > 0.02$ mass%. The values of $k_{\text{Sn}}^{a}$ calculated from experimental results of previous studies\textsuperscript{14,16,19,21} are plotted in Fig. 8, as a function of the pressure of the gas phase in the reaction chamber.

### 3.1.3. Effect of Pressure and Rate-determining Steps

The effect of pressure on the rate of detinning of high-sulphur iron-based melts is illustrated in Fig. 8. This figure presents experimental results which were obtained in this study as well as in previous works employing different experimental conditions which are summarised in Table 2. It was found in two of the previous studies\textsuperscript{19,21} that decreasing pressures in the range from 14666 Pa to 533 Pa increase the rate of detinning. A linear relationship between $\lg k_{\text{Sn}}^{a}$ and $\lg P$, where $P$ denotes chamber pressure (Pa), was confirmed and this was considered a proof that the overall detinning rate is limited by gas phase mass transfer of evaporating SnS.

In the present study the relationship between $\lg k_{\text{Sn}}^{a}$ and $\lg P$ obtained by Nagasaka et al.\textsuperscript{21} was extrapolated up to a pressure of 10 Pa, as indicated by the dotted line in Fig. 8. The extrapolation yields a value of $1.0 \times 10^{-3} \text{ m} \cdot \text{s}^{-1}$ for $k_{\text{Sn}}^{a}$ at a pressure of 10 Pa. It can be seen in Fig. 8 that this value is very close to the rate constants which were experimentally obtained in this study and in two previous works.\textsuperscript{14,16} Consequently, a linear relationship between $\lg k_{\text{Sn}}^{a}$ and $\lg P$ exists in the pressure range of 14666 to 10 Pa, and decreasing pressures in this range enhance the removal of tin from high-sulphur iron-based melts. It is also inferred from Fig. 8 that at pressures below 10 Pa a reduction of pressure does not further accelerate the removal of tin. Hence, in the pressure range of 1 to 10 Pa, gas phase mass transfer of SnS does not control the rate of detinning. In this pressure range the rate of tin elimination is controlled by either or both liquid phase mass transfer of tin and rate of formation and desorption of SnS at the interface metal/vacuum. The liquid phase mass transfer of sulphur probably does not limit the evaporation rate of SnS under conditions of laboratory scale induction melting, as indicated by Sehgal.\textsuperscript{14}

In the present study, it was shown that a minor increase in the initial tin content raises the rate of detinning (Fig. 7). This implies a chemical reaction control. On the other hand, it was argued in a previous work\textsuperscript{13} which employed the same experimental conditions that the evaporation of tin in elemental state is controlled primarily by liquid phase mass transfer. It was also suggested that solute elements with high atomic volumes, such as Sn or Pb, probably feature relatively small diffusion coefficients in liquid iron.\textsuperscript{13} It is believed that further studies are necessary to identify and evaluate the rate controlling steps of SnS evaporation at $P \leq 10$ Pa.

### 3.2. Removal of Sn through Evaporation of SnO

There are several possible mechanisms by which the solute element oxygen can reduce the evaporation rate of tin from liquid iron:

- Oxygen and iron may form an oxide slag layer which covers the free surface of the melt and hinders evaporation.
- Oxygen is a surface-active element which blocks reaction sites at the free surface and thus decreases the rate of metal–gas reactions.\textsuperscript{30}
- Oxygen reduces the activity of solute tin,\textsuperscript{31} hence increasing oxygen contents reduce the vapour pressure of tin dissolved in liquid iron.

However, there are two possible mechanisms by which increased oxygen contents of liquid iron may increase the

![Fig. 8](image.png)

**Fig. 8.** Effect of pressure on the rate of detinning of high-sulphur iron-based melts.

**Table 2.** Summary of the experimental conditions employed to obtain the rate constants of detinning given in Fig. 8.

| Author / Reference | Melt composition | A/V | Temp. | Pressure | $[\text{Sn}]_0$ | $[\text{S}]_0$ |
|--------------------|------------------|-----|-------|----------|----------------|----------------|
| This study         | Fe-4%C-0.7%Sn    | 0.2 | 1083  | 10       | 0.44 - 0.58    | 0.14           |
| Sehgal\textsuperscript{14} | low carbon steel | 0.4 | 1853  | 1        | 0.33 - 0.46    | 0.15 - 0.16    |
| Persson and Harris\textsuperscript{16} | low carbon steel | 5-6 | 1949 - 2018 | 30 | 0.20 - 0.29 | 0.07 - 0.11 |
| Ito et al.\textsuperscript{20} | Fe-3.8%C | 0.2 | 1723  | 523 - 14665 | -0.9 | 0.66 - 0.85 |
| Nagasaka et al.\textsuperscript{21} | Fe-C$_{\text{sat}}$ | 0.4 | 1673  | 670 - 13300 | -0.9 | 0.60 |
evaporation rate of solute tin:
• Oxygen is a surface-active element, hence local changes of oxygen content cause gradients in the surface tension of liquid metal which induce a specific metal flow that may increase the mass transfer rate.
• The solute elements oxygen and tin combine to form gaseous SnO.

The former mechanism, also known as Marangoni effect, and its influence on the kinetics of steelmaking reactions are discussed in Ref. 32). The latter mechanism was suggested by Hiraga et al.22) to explain their experimental results on vacuum treatment of steel melts containing initially 0.4 mass% Sn and 0.002 to 0.2 mass% oxygen in a VIM furnace (30 kW, 3 kHz). These authors found that the removal rate of tin increases with an increase of the initial oxygen content of the steel melt. However, the oxygen content of the melt was not measured during the treatment. But the oxygen content of liquid metal treated at reduced pressure for a long period of time may vary with time. Moreover, it is of interest to investigate whether the oxygen content of a steel melt changes as the solute element tin evaporates. Conclusions can be drawn on the mechanism of tin removal, if the variation of the oxygen content with treatment time is registered simultaneously with that of tin.

If the solute elements Sn and O are removed on the basis of an equimolar ratio, this would suggest evaporation of gaseous SnO. In this case detinning is achieved through the chemical reaction given by the equation

$$[\text{Sn}] + [\text{O}] \rightleftharpoons \text{SnO} (g) \quad \text{..................................(5)}$$

In two experiments of this study, the variation of oxygen content of an ULC steel melt with treatment time was registered simultaneously with the variation of tin content. The experimental conditions and results are summarised in Table 3 which gives literature data, too. The current experimental set-up is the same as that in Ref. 13). In test runs VO-1 and VO-2, samples taken from the melt at time intervals were analysed for tin and oxygen. Moreover, in experiment VO-2 the variation of oxygen activity in the melt was observed continuously using an EMF solid electrolyte sensor.

The variation of oxygen activity with treatment time is shown in Fig. 9 which also illustrates the variation of tin content. It is evident from this figure that the oxygen activity and the tin content of the melt were decreasing simultaneously with treatment time. This suggests that a tin-bearing oxide evaporates from the melt. However, a quantitative analysis shows that the evaporation of a volatile oxide is not probable since after a given time much less moles of oxygen are removed from the steel melt than moles of tin, as illustrated in Fig. 10. This means that the solute elements Sn and O are not removed from the melt on the basis of an equimolar ratio as has been observed for Sn and S (see Fig. 2).

In order to calculate the number of moles of solute oxygen which were removed (Fig. 10), the oxygen content was obtained from the measured oxygen activity. The composition of the steel melt and the interaction parameters31) of various alloying elements with oxygen were taken into account in this calculation. It was assumed that no oxygen was supplied to the melt by dissolution of the alumina crucible. It is concluded that in experiment VO-2 tin was removed primarily by evaporation in elemental state. Formation of gaseous SnO from tin and oxygen dissolved in the steel melt was not confirmed under the current experimental conditions.

This conclusion is based on EMF measurement of the oxygen activity which is usually reliable. But chemical analyses of samples taken from the melt at different stages of the vacuum treatment indicate that the oxygen content remained essentially constant. It was in the range of 0.021 to 0.024 mass%. This is in contradiction to the data obtained from the EMF measurement which suggest that the oxygen content was decreasing as the treatment proceeded.

### Table 3. Experimental conditions and results of detinning of ULC steel melts.

| Test run/Reference | Melt weight | Temp. | Pressure | [Sn]i | initial oxygen content | initial $a_{O_{2}}$ | k x $10^{3}$ |
|--------------------|------------|-------|----------|-------|------------------------|------------------|--------------|
| VO-1               | 20.5       | 6.1   | 1873     | 10    | 0.40                   | 0.012            | n.d.         | 0.8         |
| VO-2               | 20.2       | 6.1   | 1848     | 10    | 0.55                   | 0.024            | 0.0065       | 2.4         |
| 13)                | 19.8       | 6.3   | 1873     | 10    | 0.28                   | 0.004            | n.d.         | 2.5         |
| 22)                | 10         | 8.0   | 1923     | 13    | 0.40                   | 0.002            | n.d.         | 1.7         |
| 22)                | 10         | 8.0   | 1923     | 13    | 0.40                   | 0.020            | n.d.         | 2.4         |
| 22)                | 10         | 8.0   | 1923     | 13    | 0.40                   | 0.040            | n.d.         | 2.8         |
| 22)                | 10         | 8.0   | 1923     | 13    | 0.40                   | 0.066            | n.d.         | 2.8         |
| 22)                | 10         | 8.0   | 1923     | 13    | 0.40                   | 0.090            | n.d.         | 5.2         |
| 22)                | 10         | 8.0   | 1923     | 13    | 0.40                   | 0.160            | n.d.         | 5.3         |

$\delta_{O_{2}}$: activity of dissolved oxygen determined by EMF measurement (standard state- infinitely dilute solution, mass%).

n.d.: not determined.

Fig. 9. Removal of tin from an ULC steel melt whose oxygen activity was measured with an EMF sensor during the vacuum treatment (temperature 1 848 K; pressure 10 Pa).

Fig. 10. Simultaneous removal of tin and oxygen from an ULC steel melt treated at a temperature of 1 848 K and a pressure of 10 Pa (test run VO-2).
However the disagreement between the EMF measurement and the chemical analysis does not automatically mean that the oxygen contents obtained from the EMF measurement are not correct. One should bear in mind that the chemical analysis of a metal sample gives the total oxygen content, while the EMF sensor measures the activity of dissolved oxygen. The total oxygen content includes oxygen bonded in non-metallic inclusions, and this fraction of oxygen has no effect on the elimination of tin by evaporation of Sn and SnO, respectively. Therefore, EMF measurement of the oxygen activity during vacuum treatment of liquid iron is considered a reasonable method to identify the evaporation of volatile oxides of solute elements.

In order to test whether the EMF sensor employed in test run VO-2 correctly measured the oxygen activity, iron ore fines were added to the steel melt at the end of the vacuum treatment. The aim of this addition was to test the response of the sensor to an abrupt increase in the oxygen content. The reaction of the sensor can be seen in Fig. 9. The trend of decreasing activity with treatment time was turned around shortly after the iron ore addition. The observed reaction is considered a proof that the sensor measured at least the trend of variation of oxygen content correctly.

It is difficult to perform experiments at high oxygen contents of the melt because an oxide layer may form at the free surface. This layer may be so thin that it is hardly visible. In test run VO-1, the rate of detinning was very low. Only 15% of the initial tin content were removed within 60 min. It is supposed that the reason for the low evaporation rate of tin was the presence of a surface oxide layer during the treatment. Samples taken from the melt showed that its initial oxygen content was 0.012 mass%. The oxygen content did not change with proceeding treatment and remained in the range of 0.009 to 0.015 mass% according to chemical analyses of samples taken at different stages of the treatment. The relatively low oxygen contents do not suggest the existence of an oxide layer. However, visual observations showed that the iron ore fines which were added at the beginning of the vacuum treatment did not dissolve completely in the melt. They probably formed a thin slag layer on top of the melt, hence a low detinning rate was observed. It is difficult to set a high oxygen content by addition of iron ore fines without avoiding oxide formation at the free surface. The method of increasing the initial oxygen content used in the present study has to be improved.

It is concluded that under the current experimental conditions and at initial oxygen contents of 0.004 to 0.024 mass% the removal of Sn is not enhanced by evaporation of volatile SnO. The first-order rate constant $k$ remains in the range of $0.8 \times 10^{-7}$ to $2.5 \times 10^{-6} \text{ m}^2 \text{s}^{-1}$ (Table 3). It is thought that evaporation of SnO is possible but at oxygen contents which are higher than the ones in the present study.

3.3. Evaporation of Sn from Fe–Si Melt

It was reported that increasing the silicon content of liquid iron raises the evaporation rate of dissolved tin.\textsuperscript{15,24} This is illustrated in Fig. 11 where the experimentally obtained volumetric evaporation rate constant $k'$ (s$^{-1}$) of solute tin is plotted as a function of the silicon content of liquid iron. The constant $k'$ is easily obtained when the first-order evaporation rate constant $k$ is multiplied by the ratio $A/V$. The observed effect of silicon on the kinetics of tin evaporation is explained by the fact that silicon increases the activity\textsuperscript{31} of tin and hence raises the partial vapour pressure of this residual element. It has not been reported that volatile tin-bearing compounds evaporate from high-silicon iron melts.

Morales and Sano\textsuperscript{35} used the levitation melting technique to investigate the effect of silicon on the evaporation of tin from liquid iron. It was found that in the range of silicon contents from near zero to 23 mass% the evaporation rate constant of tin increases linearly with increasing silicon content. Levitation melting experiments carried out by Esimai\textsuperscript{24} confirmed that silicon enhances the evaporation of tin from liquid iron but showed that the effect of silicon is stronger at higher silicon contents as can be seen in Fig. 11. Recently Kleinschmidt\textsuperscript{33} studied the evaporation of tin from 6 kg iron melts treated at a temperature of 1923 K under argon in an induction furnace. It was found that at 5, 10 and 15 mass% Si, respectively, almost no tin evaporated within ten minutes of treatment, while at 20 mass% Si approximately 60% of the initial tin was removed (Fig. 11).

In order to better explain the effect of silicon on the evaporation of tin, a thermodynamic analysis of the Fe–Si–Sn system was carried out in the present study. Literature data\textsuperscript{12} indicate that there exists a miscibility gap in the liquid Fe–Si–Sn system at a temperature of 1623 K (Fig. 12). The Fe–Si–Sn system is characterised by a wide two-phase region where a liquid ferro-silicon phase and a liquid tin
phase coexist. The tin phase contains more than 90 mass% Sn, the rest is Fe and Si. The tin content of the ferro-silicon phase changes with its silicon content as shown in Fig. 12. It is evident that the solubility of tin in the ferro-silicon phase is a non-linear function of the silicon content and that it features two minima. At a temperature of 1 623 K the lowest equilibrium solubility of tin in the ferro-silicon phase is 0.91 mass% and is observed at 22.58 mass% Si.34) This suggests that the activity of tin dissolved in iron-based melts which contain approximately 22 mass% Si is unusually high. Consequently, the partial vapour pressure of tin dissolved in iron melts of this particular composition is relatively high, even at low tin contents. Therefore it is expected that the evaporation of tin from such high-silicon iron melts is highly favoured. Experiments were conducted to confirm this hypothesis.

In Fig. 13 the evaporation of solute tin from a Fe–21.5 mass%Sn melt is compared to that from Fe–4mass%C–0.7mass%Si melt, ULC steel melt and Fe–18mass%C–9mass%Ni melt, and the experimental conditions and results are summarised in Table 4. The experimental set-up is the same for all test runs which implies that the stirring conditions are very similar. Also, the test runs were performed at a pressure of 10 Pa, and gas phase mass transfer of evaporating species does not control the overall evaporation rate at such a low pressure. It is evident from Fig. 13 that the highest evaporation rate was observed with the Fe–21.5mass%Si melt. Consequently, setting the silicon content of iron melts to approximately 22 mass% Si is most beneficial to the removal of tin by vacuum treatment. It should be noted, however, that the elimination of tin from high-sulphur iron melts was faster than that from the Fe–21.5mass%Si melt, as shown in Fig. 6.

The effect of silicon on the evaporation of tin from Fe–Si–Sn melts should be further studied. Of particular interest is the combined effect of melt temperature, carbon content and silicon content. In a recent study,35) the activity of tin in iron-based melts containing Si and C was predicted using a mathematical model. It was found that the activity coefficient of tin in liquid Fe–Si–Sn melts at a temperature of 1 873 K features a maximum at approximately 39 mass% Si.

The practical implications of the present findings will be discussed later in view of the possibility to recycle tinplate scrap in the production of ferro-silicon alloys.

### 3.4. Condensation and Efficiency of Refining

Test run VS-5 was carried out exclusively with the aim to investigate the condensation of vapours emanating during the vacuum treatment. A Fe–4mass%C–0.7mass%Si melt was treated with 0.29 mass% Sn, 0.59 mass% Cu and 0.064 mass% S and was treated at a pressure of 10 Pa and a temperature of 1 673 K for 30 min. After the treatment, the melt was cast into a mould and the furnace was cooled down. The gas-tight furnace chamber was opened at room temperature and the condensed material which had settled at the inner walls of the chamber as well as at the induction coil was gathered. The chemical composition of the condensate is given in Table 5.

The high contents of tin and sulphur in the condensate are a proof of the evaporation of a volatile compound of Sn and S. It can be inferred from the data in Table 5 that the ratio of atomic percentage of tin to that of sulphur is close to unity. Consequently the volatile substance evaporating from the melt consists of SnS. This conclusion is in agreement with the results of Ito, Kishimoto and Mori19) who confirmed by X-ray diffraction analysis the presence of SnS in the condensate which was captured during detinning of iron containing initially 1.0 mass% Sn and 0.7 mass% S.

The copper content of the condensate is much lower compared to its tin content. This indicates that no copper-bearing sulphides evaporate under the present experimental conditions. The presence of manganese in the condensate is explained with the high vapour pressure of this metal, while the presence of carbon may be due to evaporation of volatile CS and CS2, as indicated in the study of Ohno.36) Vacuum refining of steel melts is an expensive process. On one hand it was demonstrated that condensate featuring

![Fig. 13. Evaporation of tin from various iron-based melts treated at a pressure of 10 Pa.](image)

| Table 4. Experimental conditions and results for the evaporation of tin from various iron-based melts treated at a pressure of 10 Pa. |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| Melt composition | Melt weight (kg) | A/V | Temp. (°C) | [Sn] (mass%) |
| Fe-18mass%C-9mass%Ni | 19.8 | 6.4 | 1873 | 0.11 |
| ULC steel melt | 19.8 | 6.3 | 1873 | 0.28 |
| Fe-4mass%C-0.7mass%Si | 20.5 | 5.9 | 1673 | 0.10 |
| Fe-21.5mass%Si | 21.2 | 5.1 | 1673 | 0.36 |

| k x 10^5 |
|-----------------|-----------------|-----------------|-----------------|
| Fe-18mass%C-9mass%Ni | 2.8 |
| ULC steel melt | 2.8 |
| Fe-4mass%C-0.7mass%Si | 2.8 |
| Fe-21.5mass%Si | 2.8 |

![Table 5. Composition of condensate.](image)

| Element | mass% |
|-----------------|-----------------|-----------------|-----------------|
| Sn | 60 |
| S | 15 |
| Fe | 4 |
| Cu | 3 |
| Mn | 2 |
| C | 2 |

| at.%Sn | at.%S |
|-----------------|-----------------|-----------------|-----------------|
| 1.1 |

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remarkably high tin contents is gathered during the vacuum treatment of high-sulphur iron-based melts. On the other hand, it is known that tin ore concentrates contain 5 to 70 mass% Sn and that these concentrates are obtained only after a complex benefication of tin ores which usually feature tin contents as low as 0.01 to 0.5 mass%. It is also known that sulphur and iron are common accompanying elements in the production of primary tin and that technologies for their removal are widely used. Hence condensate obtained from the detinning of high-sulphur iron-based melts is a valuable secondary material which can be easily reprocessed in the non-ferrous metallurgical industry to recover tin. In this way the cost of vacuum refining of steel melts with respect to tin can be reduced by winning of pure tin from obsolete tinplate scrap.

4. New Processes for Recycling of Tinplate Scrap

4.1. Process Based on the Evaporation of SnS

The high rate of detinning of high-sulphur iron-based melts suggests that scrap melts contaminated with tin can be alloyed with sulphur and subsequently treated at reduced pressure to remove tin by evaporation of SnS. Saturation with carbon would be beneficial, too, since this element raises the activities of Sn and S and thus increases the vapour pressure of SnS.17 The most important advantage of this process would be its high productivity due to high removal rates of Sn. After the vacuum treatment the melts should be decarburised and desulphurised which is considered a great disadvantage. However, on a commercial scale, desulphurisation is widely applied, while detinning of scrap melts is still impossible. In the present study the sulphur contents at the end of the vacuum treatment were in the range of 0.004 to 0.034 mass% (Table 1). It was also found that at initial Sn contents of 0.4 to 0.6 mass%, i.e., at contents which would be typical for a tinplate scrap melt, the elimination rate of tin is considerably high as long as the sulphur content of the melt remains higher than approximately 0.06 mass%. As the vacuum treatment proceeds, the sulphur content is reduced to below 0.06 mass% and a decrease in the rate of detinning is observed. In general the final sulphur content depends on the initial Sn and S contents and on treatment time. But in order to ensure sufficiently high productivity of a possible large scale process, vacuum refining should be terminated as soon as the sulphur content drops to approximately 0.06 mass%. It is thought that the application on a larger scale of detinning based on SnS evaporation is technically feasible, but at present it is hindered by the economics of tinplate scrap recycling and that of desulphurisation.

4.2. Process Based on the Evaporation of SnO

Even if the evaporation of tin is accelerated by increasing the oxygen content of steel melts, this effect may have no practical application because in a large-scale vacuum refining process it would be difficult to keep the content of dissolved oxygen relatively high and, at the same time, prevent the formation of a slag layer at the metal/vacuum interface. That is why a detinning process based on the evaporation of SnO is not considered practical. However, it is of interest whether tin in solid state, i.e., as metal coating on tinplate,

![Fig. 14. Flowsheets of conventional ferro-silicon production and a new recycling process for tinplate scrap.](image)

evaporation losses of iron will be much lower than in case of vacuum treatment of steel melts, since liquid Fe–Si alloys feature a strong negative deviation from Raoult’s law, i.e., the activity of iron is strongly decreased by the presence of silicon. Hence the vapour pressure of iron is reduced and its evaporation rate decreased. That is why it is expected that the Fe content of the condensate will be sufficiently low and its Sn content sufficiently high. This will make the condensate an attractive source of secondary tin for the non-ferrous metallurgy.

5. Conclusions

Several methods to enhance the evaporation of tin from iron-based melts were studied in a vacuum induction melting furnace on a laboratory scale. New process schemes of tinplate scrap recycling were considered, too. The following conclusions are drawn:

(1) It is possible to increase significantly the rate of tin elimination under vacuum by raising the sulphur content of liquid iron above 0.02 mass%. The increased removal rates of tin are due to evaporation of volatile SnS.

(2) The removal of tin from high-sulphur iron melts represents a second-order reaction. The reaction site is the interface metal/vacuum.

(3) In the pressure range of 1 to 10 Pa, gas phase mass transfer of evaporating SnS does not limit the rate of detinning.

(4) Condensate gathered during the vacuum treatment of high-sulphur, tin-containing iron melts features high tin contents and represents valuable material which can be reprocessed in the non-ferrous metallurgical industry to recover Sn and thus reduce the expected high cost of vacuum refining of tinplate scrap melts.

(5) By means of continuous EMF measurement of oxygen activity and chemical analysis of oxygen content during the vacuum treatment of an ULC steel melt it was proven that tin evaporates in elemental state from steel melts containing less than 0.024 mass% oxygen. Increasing the oxygen content above 0.024 mass% may induce evaporation of volatile SnO, but this possibility to enhance the removal of tin is considered impractical for a large scale vacuum refining process. It is more reasonable to study the chemical reactions between the solid tin coating on tinplate and the gas phase during heating and smelting in an adequate furnace.

(6) The highest evaporation rate of tin in elemental state is observed from high-silicon iron melts. The most favourable conditions occur at approximately 22 mass% Si in the iron melt. The recycling of tinplate scrap in the ferrosilicon production has potential benefits over its recycling in steelmaking.

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