Development of a practical method of Sn removal in the steelmaking process is necessary from the viewpoints of promoting use of scrap procured in the market and reducing energy consumption. It is well known that Sn promotes surface cracks of billets in hot rolling by coexisting with Cu. Although various methods of Sn removal have been investigated in laboratory experiments, enough Sn removal efficiency for commercially use has not been obtained. In the present study, Sn removal from high-S hot metal by NH₃ gas blowing was investigated in laboratory experiments as a new method of Sn removal. The laboratory experiment on Sn removal from hot metal was carried out using up to a 10 kg-scale vacuum induction melting furnace. Sn removal was accelerated while blowing NH₃ gas, and the evolution of gas bubbles were observed at the hot metal surface. Within the ranges of these experiments, higher temperature and higher concentrations of S and N were advantageous for Sn removal. The mechanism of the acceleration of Sn removal by NH₃ gas blowing could be estimated that oversaturated N or H in hot metal made small bubbles to increase the hot metal surface for SnS evaporation. In the estimation of Sn removal ratio in plant-scale operation, it could reach 40%. For further rapid Sn removal, it was necessary to maximize \[\frac{[N]}{[N]}\] of hot metal by optimizing the lance height or flow rate of NH₃ gas.

KEY WORDS: detinning; NH₃ gas; hot metal pretreatment; vacuum processing.

1. Introduction

Although blast furnace operators in Japan have achieved the highest level of energy efficiency in the world steel industry, greater use of scrap has been required in recent years in order to achieve further energy savings. Energy saving is possible because the steelmaking process using steel scrap requires only 30% of the energy necessary for reduction of iron ore in the blast furnace. Moreover, it is also important to promote utilization of low quality scrap procured in the market from the viewpoint of recycling of iron resources.

The largest obstacle to the utilization of low quality scrap is contamination of the scrap by residual (tramp) elements. Among those elements, Sn is one of the most serious problems due to the high probability of Sn contamination when recycling low quality scrap. The harmful influence of Sn on steel quality is widely known. It is also well known that Sn cannot be removed from molten iron by an oxidation process because its oxygen affinity is lower than that of Fe. To date, several studies have investigated methods of Sn removal.

The amount of steel scrap has increased since the 1980s, and many studies have examined Sn removal methods. Methods of removing Sn can be broadly classified into two types, that is, Sn removal from solid scrap and Sn removal from molten scrap. Sn removal from solid scrap was carried out in a rotary kiln or packed bed type reactor, and Sn was removed as SnO₂, SnS, or SnCl₂. However, with solid scrap, only the Sn at the surface of the scrap can be removed; in other words, it is not possible to remove the Sn contaminating the bulk of the scrap.

In contrast, Sn removal from molten scrap is applicable to all the Sn contaminant in scrap. It is also practical because the commercial steelmaking process can be applied. On the other hand, it is difficult to remove Sn from molten metal by oxidation, which is the basic technique in the steelmaking process because of its lower affinity with oxygen than that of Fe. Several laboratory studies on Sn removal have investigated the methods other than oxidation, e.g., an evaporation method under high vacuum or plasma and use of several types of fluxes including sulfur or calcium compounds such as FeS or CaC₂, but none of these methods has been realized commercially.

In addition to these methods, NH₃ gas has been seemed to have the potential to remove Sn from molten iron. Pioneering work by Ono et al. demonstrated that evaporation of molten Cu could be accelerated by NH₃ gas blowing. After the groundbreaking work, the report by Hidani et al. presented excellent research on the elimination of Cu from molten steel by NH₃ gas blowing, and also reported that evaporation of molten Sn could be accelerated by NH₃ gas.
blowing. The boiling temperatures and equilibrium vapor pressures of several Sn compounds are shown in Table 1. SnH₄ has a low boiling temperature. Although the chemical compound of the vaporized material has been still unclear and the thermodynamic characteristics of many Sn compounds have been also unclear, NH₃ gas has had the potential for Sn removal from solid scrap or molten iron.

In the present study, Sn removal from hot metal by NH₃ gas blowing was investigated in laboratory experiments using a 10 kg-scale vacuum induction melting furnace in order to clarify the potential for Sn removal by evaporation and its mechanism of Sn removal.

2. Principle of Sn Removal by Evaporation

Although it is thermodynamically difficult to oxidize Sn in hot metal, Sn removal by evaporation is possible because the equilibrium vapor pressures of Sn and Sn compounds are higher than that of Fe.¹⁷ Figure 1 shows the relation between the apparent Sn removal rate constant (kₛₙ) and pressure reported in previous researches. In the majority of previous researches, the rates of Sn removal are described as shown in Eq. (1).

\[
\ln \left( \frac{[Sn]}{[Sn]_0} \right) = -k_{Sn} \frac{A}{V} t \quad \text{................. (1)}
\]

where, \([Sn]\) is the mass percent of Sn in molten iron in process, \([Sn]_0\) is the mass percent of Sn in the molten iron before Sn removal treatment, \(k_{Sn}\) is the apparent Sn removal rate constant, \(A\) is the static surface area of molten iron, \(V\) is the volume of molten iron, and \(t\) is the treatment time.

As shown in Fig. 1, \(k_{Sn}\) increases inversely with pressure.

On the other hand, previous reports indicate that S in molten iron accelerates Sn removal by reacting with Sn to form SnS as shown in Eq. (2).

\[
\text{Sn} + \text{S} = \text{SnS(g)} \quad \text{............... (2)}
\]

As shown in Table 1, SnS has a higher equilibrium vapor pressure than Sn. Figure 2 shows the relation between \(k_{Sn}\) and the mass percent of S. As shown in Fig. 2, \(k_{Sn}\) increases in proportion to the mass percent of S.

As one of the other methods of Sn removal, NH₃ gas blowing also can be expected to accelerate Sn evaporation by forming SnH₄(g) or SnN₄(g). In additions, the increasing of the surface area of the molten metal might be able to contribute to evaporation of these Sn compounds, including SnS(g). A previous report by Hidani et al. showed that the Cu removal rate constant was increased by NH₃ blowing.¹⁵

3. Experimental Method

Sn removal from hot metal was carried out in a laboratory furnace. The outlines of the experiments are shown in Fig. 3. 10 kg of hot metal with high carbon content was prepared from pure metal in a high frequency induction furnace under an Ar atmosphere in a vacuum case, and \([Sn]\) and \([S]\) were added to obtain the specified composition. The crucible was made of MgO. The induction current of the furnace was controlled to keep the hot metal temperature constant. After tuning the composition of hot metal and temperature, the vacuum case was depressurized by an oil-sealed rotary pump to maintain the vacuum pressure.

After pressure tuning, NH₃ gas was blown from the top blowing lance onto the surface of the hot metal. In addition, N₂ gas was also blown as comparable examples. During the experiment, the hot metal was sampled for use in chemical analysis.

The main experimental conditions are listed in Fig. 3. The metal temperature and composition of the hot metal, top blowing gas species, etc. were changed in a series of exper-
iments. The S source was reagent grade FeS (II), which was a stoichiometric compound. The initial concentration of [S] was controlled from 0.02 mass% to 0.14 mass% to clarify the relation between \( k_{Sn} \) and [S]. The initial concentration of [C] was tuned from 3.8 mass% to 4.2 mass% because it is well known that carbon in hot metal increases the activity of Sn. The hot metal temperature was controlled around 1723 K or 1923 K to clarify the effect of the hot metal temperature. The gas flow rate was 500 mL/min/t in all cases.

4. Results and Discussion

4.1. Effect of NH\(_3\) Gas Blowing on Sn Removal

Figure 4 shows the change in ln\([Sn]/[Sn]_0\) in top blowing with various combinations of top blowing gas species and hot metal temperature. The total treatment time was about 40 min. Top gas was blown throughout each treatment experiment. [Sn] decreased in each treatment. Also in this study, the Sn removal reaction can be described as a first-order reaction, as in previous studies concerning Sn removal by evaporation. In particular, top-blown NH\(_3\) gas removed Sn from the hot metal more rapidly than N\(_2\) gas. The value of \( k_{Sn} \) of each treatment can be calculated from the gradients of the dash line in Fig. 4.

Table 2 shows a summary of conditions and result of each treatment. Each value of \( k_{Sn} \) was calculated by Eq. (1), even though the actual value of the hot metal surface was unclear because of the strong agitation by the gas evolving from the metal surface during gas blowing. In other words, \( k_{Sn} \) was calculated from the gradient of the dash line in Fig. 4 assuming \( A = 7.5^2 \times \pi \) [cm\(^2\)] (the static surface area of molten iron) and \( V = 10^3 \) [cm\(^3\)] in this study. Especially in case of NH\(_3\) gas blowing, the hot metal surface was strongly agitated by the gas evolving as reported in previous work.\(^{15}\) Therefore, \( k_{Sn} \) includes the change of the hot metal surface area by gas generation.

Figure 5 shows a comparison between previous studies and this work. N\(_2\) gas blowing showed higher \( k_{Sn} \) than pre-
previous studies. This result showed that mass transfer of SnS in gas phase was accelerated by N\textsubscript{2} gas blowing. In a previous report, Katayama et al. showed that Sn removal was accelerated by Ar blowing in atmosphere pressure condition.\textsuperscript{16} In addition, NH\textsubscript{3} gas blowing can reach higher $k_{Sn}$ than N\textsubscript{2} blowing even at a comparatively high pressure.

The mechanisms of acceleration of Sn removal by NH\textsubscript{3} gas blowing could be considered as shown in Fig. 6. Hidani et al. reported that NH\textsubscript{3} gas was thermally decomposed and formed radical N and radial H. These radical species had higher activities than N\textsubscript{2} or H\textsubscript{2} and show high concentrations of [N] and [H] in the hot metal. These high concentrations of [N] and [H] formed many bubbles of N\textsubscript{2} and H\textsubscript{2}, which increase the hot metal surface area and agitate the near-surface part of the bath, thereby accelerated Sn evaporation. In addition, SnN\textsubscript{x} or SnH\textsubscript{x} might be formed as evaporated species. In order to clarify the mechanism of acceleration of Sn removal by NH\textsubscript{3} gas blowing, the relations between $k_{Sn}$ and [N] or [S] was investigated in the following.

4.2. Effect of [N] in Hot Metal

[N] in hot metal reached a high concentration during NH\textsubscript{3} gas blowing. Figure 7 shows the analysis values and calculated values of [N] in this work. The calculated values for each experiment were calculated by Eqs. (3)-(5).

$$\log \left( \frac{a_N}{\sqrt{P_{N_2}}} \right) = -518/T - 1.063$$  

$$a_N = f_N \cdot \%N$$

$$\log f_N \approx 0.13 \cdot \%C$$

where, $a_N$ is the activity of N in hot metal, $P_{N_2}$ is the partial pressure of N\textsubscript{2}, T is the hot metal temperature, and $f_{N}$ is the Henrian activity coefficient of N. $P_{N_2}$ of each treatment was decided as follows:

$P_{N_2} = $ pressure in vacuum case (N\textsubscript{2} gas blowing)

$P_{N_2} = $ pressure in vacuum case $\times 0.25$ (NH\textsubscript{3} gas blowing)

In case of N\textsubscript{2} gas blowing, the analysis value of [N] is low and is approximately equal to the calculated value regardless of the hot metal temperature. On the other hand, in NH\textsubscript{3} gas blowing, the analysis value of [N] is notably higher than the calculated value. This high concentration of [N] may have some effects on rapid Sn removal.

It should also be noted that [N] was clearly higher at the low hot metal temperature than at the high hot metal temperature. From the viewpoint of thermodynamics, high temperatures show higher [N] than low temperatures, as described by Eq. (3). The reason for this feature can be explained as shown in Fig. 8. NH\textsubscript{3} gas could be thermally decomposed, rapidly form radical N and radical H between the blowing lance tip and hot metal surface. High activity radical N and radical H should rapidly form N\textsubscript{2} molecules and H\textsubscript{2} molecules. However, because these molecules do not have the high activity as the radicals, the partial pressure of N and H displays a peak between the blowing lance tip and hot metal surface. In case of higher temperature condition, this peak could move closer to the lance tip, as shown in Fig. 8.

Figure 9 shows the relation between [N] and $k_{Sn}$. With NH\textsubscript{3} gas blowing, the value of $k_{Sn}$ increases depending on Eqs. (6) and (7) at 1 723 K and 1 923 K, respectively.

$$\log k_{Sn} = 49.0 \times [\text{mass}\%N] - 3.3$$  

![Fig. 6. Schematic image of Sn removal by NH\textsubscript{3} gas blowing.](image)

![Fig. 7. Analysis values and calculated values of [N] in present work.](image)
As shown in Eqs. (6) and (7), $k_{Sn}$ shows similar dependence on $[N]$ at the two levels of hot metal temperature. This result suggests that NH$_3$ gas blowing can accelerate Sn removal by increasing the hot metal surface area for evaporation of Sn compounds, by increasing the agitation power near the hot metal surface, or by promoting evaporation of Sn as Sn-nitride or Sn-hydride.

### 4.4. Estimation of Sn Removal Mechanism by NH$_3$ Gas

From the relations between $k_{Sn}$ and $[N]$ and $[S]$, the mechanism of Sn removal by NH$_3$ gas blowing can be estimated as shown in Fig. 11. First, NH$_3$ blown from the top lance is thermally decomposed to radical N and radical H between the lance tip and the hot metal surface. It can be considered that some of the radical species react to form N$_2$ molecules and H$_2$ molecules, and other radicals are soluble in the accessible hot metal because of the high activity of the radical species. Although these radical species show high activity, and $[N]$ (and probably also $[H]$) of the hot metal reaches a high concentration, Sn compounds such as Sn-nitride or Sn-hydride do not contribute greatly to Sn removal. The excessive dissolved $[N]$ (and probably also $[H]$) are degassed from the hot metal surface. At this time, the existence of many small bubbles of N$_2$ or H$_2$ and the splashing caused by those small bubbles increase the hot metal surface area for SnS evaporation.

In the present work, the concentration of $[H]$ in the hot metal during NH$_3$ gas blowing was caused by equipment-related problems. Therefore, some ingenuity in the equipment setup will be necessary in order to investigate the effect of $[H]$ on Sn removal by NH$_3$ gas blowing in the future.
of metal is 100 tons, the pressure in the vessel is 15 Torr, and the inner diameter of the ladle is 4 meters, the weight of the hot metal can be kept to 0.014 mass%, NH₃ blowing increases the value between [S] and [N]. In case of several [S], the Sn removal ratio can reach 40% in treatment for 20 min. In order to reduce the [S] level in the hot metal remaining after high speed Sn removal, a lower vessel pressure or higher [N] is necessary. Higher [N] can be obtained by optimizing the lance height to maintain the highest activity of the radical species.

5. Conclusions

As a new method of Sn removal from hot metal, NH₃ gas blowing in a vacuum vessel was investigated at hot metal temperatures of 1 723 K and 1 923 K. The results are summarized as follows.

— The Sn removal rate constant (kSn) with NH₃ gas blowing was larger than that with N₂ gas blowing.
— The concentration of [N] during NH₃ gas blowing was notably higher than that during N₂ gas blowing.
— The concentration of [N] during NH₃ gas blowing was higher at 1 723 K than at 1 923 K.
— The value of kSn increased depending on the increase of [N] in the hot metal.
— The value of kSn was approximately proportional to [S] at 1 723 K and 1 923 K, which is consistent with previous reports on Sn removal by SnS evaporation.

— As the Sn removal mechanism by NH₃ gas blowing, it could be estimated that the evaporation area of SnS and the agitation power near the hot metal surface were increased by the large amount of gas that evolved from the hot metal surface.

— In the estimation of Sn removal ratio in plant-scale operation, it could reach 40%. For further rapid Sn removal, it is necessary to optimize the lance height to maintain the highest activity of the radical species of N and H.

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