Development and Prospects of Refining Techniques in Steelmaking Process

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The development of refining techniques in the steelmaking process over the last 60 years and the prospects for the future were reviewed. In Japan, hot metal pretreatment started in the 1960s with the aim of reducing refining costs and improving quality, and its purposes have now transitioned to meeting new requirements for reduced treatment time, reuse of steelmaking slag and use of diverse iron sources. In converter refining, in addition to high speed decarburization, visualization of phenomena and sensing modeling techniques are becoming more important for combined use with data science techniques. In ladle metallurgy (secondary refining), techniques to realize high speed treatment and heating of the molten steel are key issues. The necessity of process revolution to contribute to a sustainable social environment is also discussed briefly.

KEY WORDS: hot metal pretreatment; converter; steelmaking slag; secondary refining; ladle metallurgy; inclusions.

1. Introduction

In 2014, the Iron and Steel Institute of Japan published a review entitled “Steelmaking Technology for the Last 100 Years: Toward Highly Efficient Mass-Production Systems for High-Quality Steels1)”, which presented an overview of the history of the development of iron and steelmaking technologies. This year, ISIJ International (formerly Transactions of ISIJ), which celebrates its 60th anniversary. During this period, ISIJ International provided information on the development of iron and steel production processes in Japan to interested parties in other countries and has also presented proposals related to technology. As part of this Special Issue commemorating its 60th anniversary, ISIJ International is publishing this review of the development of the refining process during the last 60 years, especially in Japanese integrated steel works. Table 1 shows an outline of the history of improvement and development of refining techniques since 1960. The individual techniques in each area are reviewed from Chapter 2.

2. Hot Metal Pretreatment

2.1. Development and Evolution of Hot Metal Pretreatment

2.1.1. Hot Metal Desulfurization

Hot metal desulfurization began with out-pile refining, in which sodium hydroxide or soda was added to the hot metal in a ladle outside the furnace. Subsequently, a method of stirring by nitrogen bottom blowing after top addition of calcium carbide and the shaking ladle process were adopted, but use of these techniques declined due to deviation of reaction efficiency, generation of acetylene gas and the difficulty of using the techniques in large-scale facilities. In the torpedo car injection method, a desulfurization agent was dispersed in the hot metal and reacted while floating up in the metal. Calcium carbide or sodium carbonate powder was used as the desulfurization agent, but the desulfurization slag could not be reused due to the weak stirring ability of this process. Kawasaki Steel (now JFE steel) developed a CaO powder with a surface active agent as a substitute for calcium carbide.2) In 1965, a mechanical stirring method called KR (Kanbara Reactor) was developed1,3) by Fuji Steel (now Nippon Steel). In the KR process, the desulfurization agent is entrained into the hot metal with a vortex flow generated by a rotating impeller and reacts at the interface with the hot metal. The reaction efficiency of the KR process is higher than that of the injection method, and the sulfur content in the hot metal can be reduced to less than 5 ppm by a KR process with CaO-10%CaF₂ at 1 400°C. The KR process became a popular standard technique from the 1970s. On the other hand, the issues of the KR process are reduction of desulfurization agent consumption and achieving desulfurization to below 50 ppm with CaO without CaF₂. More recent techniques will be discussed in the following. In addition, hot metal desulfurization by Mg–CaO was also
2.1.2. Hot Metal Dephosphorization and Functional Differentiation

The double slag method is one of the hot metal dephosphorization techniques which utilize the converter. However, intermediate slag discharge of the high-P slag generated by desiliconization and dephosphorization is required, and other problems include excessive slag generation, slopping, low iron yield and low productivity.

Hot metal dephosphorization was developed to reduce the load of dephosphorization in the converter in response to rising demand for lower phosphorus steels. Desiliconization before dephosphorization was adopted to reduce unit consumption of the dephosphorization agent, CaO. In addition to oxygen gas as an oxidant for Ca, mill scale, sinter dust and iron ore powder are used as oxygen sources.

In dephosphorization in the torpedo car, dephosphorization occurs as a transitory reaction while the flux floats up in the hot metal, and the desulfurization reaction occurs between the high basicity slag and the hot metal as a permanent reaction. This process was commercialized from the early 1980s. In this process, the dephosphorization slag is discharged, and the dephosphorized hot metal is then decarburized in the converter.

Dephosphorization with soda ash was also investigated. The efficiency of soda ash for the dephosphorization reaction was satisfactory, but refractory erosion by (Na₂O), treatment of slag containing (Na₂O), evaporation of Na (g) and the refining cost were problems. In view of those issues, application of soda ash was limited, and CaO-based agents were widely used.

Reducing dephosphorization with Ca–CaF₂ or CaC₂–CaF₂ fluxes was also investigated, but was not commercialized due to the need for stabilizing treatment of the reduction product, Ca₃P₂, and other issues.

### Table 1. Improvement and development of refining techniques after 1960.

<table>
<thead>
<tr>
<th>Year</th>
<th>Events</th>
<th>Hot metal pretreatment</th>
<th>Refining by converter</th>
<th>Ladle metallurgy</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>-1st. Oil shock (1973)</td>
<td></td>
<td></td>
<td>-CAS process operation (1974)</td>
</tr>
<tr>
<td></td>
<td>-Crude steel production 100 million tons</td>
<td></td>
<td></td>
<td>-Stainless steel production by LDVAC (VOD) (1979)</td>
</tr>
<tr>
<td></td>
<td>-Hot metal de-S ratio 100% (1977)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>-2nd. Oil shock (1979)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1990–1999</td>
<td>-Developing Refining technique without CaF₂</td>
<td>-SRP process (1990)</td>
<td>-Stainless steel production by</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-Melting furnace of cold iron</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>with coal (1993)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-VOD (VCR) (1991)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-Stainless steel production by</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>VODPB (1990)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>- REDA process (1995)</td>
<td></td>
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<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
</tbody>
</table>

Commercialized during this period.4)

2.2. Evolution of Mechanical Stirring (KR) Method in Hot Metal Desulfurization

2.2.1. Spread of Mechanical Stirring (KR) Method in Japan

The KR mechanical stirring method was commercialized in 1965. In comparison with the injection method, desulfurization agent consumption is higher than in the injection method because the agent is repeatedly entrained and scattered in the hot metal, but high speed desulfurization to lower sulfur contents can be realized due to its higher stirring energy, which can meet the demand for low and ultra-low sulfur content steel grades. Owing to this advantage, the injection method was largely replaced by the KR method from the 2000s, as shown in Table 2.11)

Soda ash and CaO–CaF₂ had been used as desulfurization agents in torpedo car injection, but use of those agents was banned because Na and F cause environmental problem when the desulfurization slag is reused. This was also a main reason for the changeover from injection to mechanical stirring.

2.2.2. Development of Higher Efficiency Hot Metal Desulfurization

Desulfurization in Mechanical Stirring (KR) Method Y. Nakai et al.13) and N. Kikuchi et al.14) developed propane gas injection and top-blowing techniques to reduce the oxygen potential at the spot where the desulfurization flux is entrained into the hot metal, which resulted in improved desulfurization efficiency and reduced desulfurization flux consumption.

In the KR, fine CaO powder with a size smaller than 1 mm is added from the top. The added CaO powder agglomerates and forms larger particles with a spherical shape and size of several mm to several 10 mm, since CaO is mainly in the solid state under the conditions in hot metal desulfurization. This is a disadvantage, because a large part of the agglomerated flux does not react with sulfur.15)

To solve this problem, Y. Nakai et al.16) developed a
desulfurization flux blasting technique. Figure 1 shows the result of the technique (300 t/heat, \( N_2 = 6 \) to 20 Nm\(^3\)/min, \( CaO = 100 \) to 400 kg/min, distance between lance and hot metal surface = 0.3 to 1.4 m, hot metal temperature = 1 523 to 1 663 K). Agglomerating and enlargement of the CaO powder is suppressed, and the powder is entrained into the hot metal as fine particles under the condition that the velocity of the CaO powder is higher than the critical velocity for entrainment in terms of the wetting condition between the CaO and hot metal, as shown in Fig. 2. The efficiency of CaO for desulfurization increased by 1.3 times, and the amount of desulfurization slag was reduced by 20%. The Nakai group also quantitatively analyzed the effect of CaO blasting by modeling the solid CaO agglomeration behavior in hot metal. The CaO blasting technique has been installed in all facilities at JFE Steel. After desulfurization, the slag is recycled while still hot to utilize the de-S capacity of the unreacted CaO.

### 2.3. Hot Metal Dephosphorization

#### 2.3.1. Recent Research on Thermodynamics and Kinetics of Hot Metal Dephosphorization

Fluorspar (CaF\(_2\)) had been widely used to increase the efficiency of dephosphorization when producing lower phosphorus hot metal. The effect of CaF\(_2\) on dephosphorization has been reported.\(^{18}\) Although CaF\(_2\) promotes CaO melting and increases the oxygen potential and activity of Ca\(^{2+}\), the environmental standards for (F) elution in soil were revised, and dephosphorization techniques without CaF\(_2\) became important from the late 1990s. In analysis of the reaction rate in hot metal pretreatment, S. Ohguchi et al.\(^{19}\) developed a coupled reaction model that considers the multicomponent reaction which proceeds simultaneously in hot metal pretreatment. S. Kitamura et al.\(^{20}\) studied the effect of stirring energy, the hot metal temperature and the flux composition on hot metal dephosphorization by an analysis using the coupled reaction model. The coupled reaction model is an important tool for analyzing the hot metal dephosphorization rate. S. Kitamura et al.\(^{21}\) expanded the model to consider crystallization of the solid phase accompanying changes in the slag composition during hot metal dephosphorization. The expanded model treats the mass transfer between three phases, \(i.e.,\) solid slag (2CaO·SiO\(_2\)), liquid slag and hot metal.

X. Guo et al.\(^{22}\) reported the results of observation of the melting behavior of CaO particles into slag. K. Gu et al.\(^{23}\) discovered that metal droplets in slag swell due to CO gas and thereby increase the residence time in slag (this is called the “bloated droplet model”). As these results suggest, direct observation and measurement to understand the actual phenomena accurately are expected to become increasingly

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**Table 2.** Hot metal desulfurization process of each company.\(^{20}\)

<table>
<thead>
<tr>
<th>Company</th>
<th>Works</th>
<th>Method</th>
<th>Vessel</th>
<th>Investment Year</th>
</tr>
</thead>
<tbody>
<tr>
<td>NSC</td>
<td>Yawata No. 1</td>
<td>Injection</td>
<td>TPC</td>
<td>2003</td>
</tr>
<tr>
<td></td>
<td>Yawata No. 3</td>
<td>KR</td>
<td>Ladle</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Muroran</td>
<td>Injection</td>
<td>TPC</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Nagoya</td>
<td>Injection</td>
<td>Converter</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Kimitsu No. 1</td>
<td>KR</td>
<td>Ladle</td>
<td>2000</td>
</tr>
<tr>
<td></td>
<td>Kimitsu No. 2</td>
<td>KR</td>
<td>Ladle</td>
<td>2000</td>
</tr>
<tr>
<td></td>
<td>Oita</td>
<td>Injection</td>
<td>Ladle</td>
<td></td>
</tr>
<tr>
<td>JFE</td>
<td>Chiba</td>
<td>KR</td>
<td>Ladle</td>
<td>2001</td>
</tr>
<tr>
<td></td>
<td>Keihinn</td>
<td>KR</td>
<td>Ladle</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fukuyama No. 2</td>
<td>KR</td>
<td>Ladle</td>
<td>2000 (2004 Shut down)</td>
</tr>
<tr>
<td></td>
<td>Fukuyama No. 3</td>
<td>KR</td>
<td>Landle</td>
<td>2005</td>
</tr>
<tr>
<td></td>
<td>Kurashiki</td>
<td>KR</td>
<td>Landle</td>
<td>2001</td>
</tr>
<tr>
<td>SMI</td>
<td>Wakayama</td>
<td>KR</td>
<td>Landle</td>
<td>1999</td>
</tr>
<tr>
<td></td>
<td>Kashima No. 1</td>
<td>KR</td>
<td>Landle</td>
<td>1999</td>
</tr>
<tr>
<td></td>
<td>Kashima No. 2</td>
<td>KR</td>
<td>Landle</td>
<td>2004</td>
</tr>
<tr>
<td></td>
<td>Kokura</td>
<td>KR</td>
<td>Landle</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Kobe</td>
<td>Injection</td>
<td>Converter</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Kakogawa</td>
<td>Injection</td>
<td>TPC</td>
<td></td>
</tr>
</tbody>
</table>

0000: changed from injection to KR

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important in the future.

In hot metal dephosphorization, oxidation reactions such as FeO generation and decarburization proceed simultaneously in non-equilibrium conditions. Therefore, this is a very complex but important phenomenon, since it affects CaO melting, stirring at the reaction site and iron yield. Reaction sensing techniques and further investigation to understand the mechanism are needed.

2.3.2. Evolution of Hot Metal Dephosphorization in Converter

In 1983, Kawasaki Steel (now JFE Steel) conducted tests for commercialization of hot metal dephosphorization in the Q-BOP converter, utilizing the strong stirring capacity of the Q-BOP and bottom blowing of oxygen gas and CaO powder.\(^{7,8}\) Hot metal (1 370°C, C/4.5, Si/0.2, Mn/0.40, P/0.14, S/0.02 (mass%)) was dephosphorized to C/3.7, Si/tr, Mn/0.30, P/0.010, S/0.010 (mass%) in 3 min with 20 kg/t of CaO, 3 kg/t of CaF\(_2\) and 6 Nm\(^3\) of oxygen gas with no temperature drop. However, it was difficult to maintain (P\(_2\)O\(_5\)) and (FeO) without CaF\(_2\).

In 1979, Nippon Steel commercialized SMP (Slag minimum Refining Process),\(^{26}\) in which the hot metal is desiliconized in advance and then dephosphorized in the converter, resulting in lower slag generation.

Kobe Steel commercialized a “Hot metal pretreatment furnace” in 1983,\(^{27}\) which utilized the LD converter as a designated dephosphorization and desulfurization vessel. Sumitomo Metals (now Nippon Steel) developed SRP (Simple Refining Process, Slag Recycling Process) in 1987,\(^{28}\) in which desiliconized hot metal and desulfurized hot metal are dephosphorized and decarbonized separately in two converters, and the decarburation slag is recycled to the dephosphorization converter.

In 1989, Nippon Steel Nagoya Works commercialized a process called LD-ORP (Optimizing Refining Process),\(^{29}\) in which the hot metal is dephosphorized by bottom-blowing limestone powder, and is then desulfurized by bottom-blowing soda ash. In 2000, Nippon Steel also developed MURC (Multi-Refining Converter),\(^{29–31}\) in which desulfurized hot metal and scrap are charged into the converter, desiliconized and dephosphorized, and then decarburized after deslagging, as shown in Fig. 3.

JFE Steel commercialized DRP (Double-slag Refining Process),\(^{32}\) as shown in Fig. 4. The hot metal and scrap are charged into the converter and desiliconized, after which the (SiO\(_2\)) rich slag is discharged, and the hot metal is dephosphorized. The heat of silicon oxidation can be utilized for scrap melting, and CaO consumption can be minimized by discharging the (SiO\(_2\)) rich slag. Moreover, ultra-low phosphorus steels can also be produced by the DRP process.

In the hot metal dephosphorization process, promotion and control of (FeO) generation are important for promoting early melting of CaO as a substitute for CaF\(_2\). JFE Steel developed a dynamic control technique for (FeO) generation,\(^{33–36}\) in which (FeO) generation can be directly detected by measuring the oxygen balance, as shown in Fig. 5, and lower phosphorus hot metal can be obtained stably by using a mathematical model of hot metal dephosphorization that quantifies the effect of (FeO) generation, as shown in Fig. 6. A new converter (330 t/heat) was installed at West Japan Works (Fukuyama) No. 3 steelmaking shop in 2015 to increase the capacity of hot metal dephosphorization by DRP.

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**Fig. 3.** Outline of MURC (Multi-refining converter) process.\(^{29}\)

**Fig. 4.** DRP process for primary steelmaking at JFE Steel.\(^{32}\)

**Fig. 5.** Schematic diagram of FeO calculation by oxygen balance in a top and bottom-blowing converter.\(^{35}\)
2.3.3. Hot Metal Dephosphorization by Injection Method (Torpedo Car and Ladle)

Promotion of the transitory reaction is an advantage of the flux injection method. T. A. Engh et al. did pioneering work on the transitory reaction, and the behavior of injected particles in a bath was studied by Ozawa et al. G. A. Iron and B. H. Tu, E. Kimura and Ogawa and Matsumoto. In torpedo car dephosphorization, the flux injection speed is low due to the small free board, resulting in a long treatment time. A dead zone also exists due to the insufficient mixing and stirring condition, and the reaction between the top slag and hot metal does not proceed sufficiently. As solutions to these problems, slag discharging during injection and duplex injection lance were reported.

The hot metal dephosphorization process now centers on the converter type, which was originally developed in order to utilize the reserve capacity of the converter, as the LD converter has a large free board, enabling maximum use of the oxygen top-blowing lance. The differences with the former double slag method are as follows:

1. Bottom-blowing can promote the reaction and homogenize the hot metal temperature, which enables treatment in a shorter treatment time.
2. Use in tandem with advance de-S expands the [Si] concentration range before treatment, and an increased scrap melting capacity can be expected by using the oxidation heat of that Si.
3. A higher (FeO) content in slag can be maintained and controlled, promoting dephosphorization.
4. High temperature decarburization slag can be recycled, which can contribute to CaO melting, higher iron yield and reduced slag generation.
5. It is possible to recover the uncombusted converter flue gas during de-P blowing.

3. Refining Process in Converter

The principle of the converter steelmaking process is based on the refining method using bottom air blowing developed by H. Bessemer in 1856. In the Bessemer converter, dephosphorization was difficult due to the use of acid refractories. The Thomas method enabled dephosphorization of hot metal produced from the higher phosphorus iron ore in Europe by using basic refractories.

The first trial of the LD converter (oxygen top-blowing converter) was conducted with a 2 t-scale furnace in 1949, and a 30 t-scale converter was put into operation at VOEST in Linz, Austria in November 1952, followed by a unit of the same scale at OÉAMG in Donawitz about a half a year later. (The name “LD converter” is derived from the names of these two Austrian towns.) In Japan, the first LD converters were put into operation by NKK (now JFE Steel) and Yawata Steel (now Nippon Steel) in 1957. The rapid spread of the LD technology corresponding to the appearance of integrated steel works and increasing crude steel production in Japan during the same period. This was followed by remarkably rapid progress in LD converter technology, including the development of a pure oxygen production technology, flue-gas recovery systems and the multi-hole top blowing lance, among others. However, the LD converter was eventually replaced by the top and bottom-blowing converter at Yawata Steel in 1979, triggered by the excellent metallurgical properties obtained with the 230 t Q-BOP (oxygen bottom blowing converter) installed by Kawasaki Steel in 1976. The top and bottom-blowing converter is now the main stream in converter steelmaking, accounting for approximately 70% of world crude steel production.

3.1. Development of Refining Techniques in Converter

3.1.1. Bath Stirring and Combined Blowing Converter

It is well known that the double layer tuyere (oxygen and propane gas) for bottom gas blowing was developed by Savard and Lee and commercialized in Maxhutte, Germany. In the Q-BOP process, CaO powder is supplied with oxygen through the inner tube and propane gas is supplied through the outer tube of double layer tuyeres. In the Q-BOP, [O] (dissolved oxygen content) at blow end is lower than that in LD converter, even in the low [C] region.

At the time, the effect of oxygen bottom blowing on metallurgical properties was discussed. Nakashima and Fuji measured the mixing time of reactors such as the RH degasser, VOD and ASEA-SKF by the tracer method, and indicated that the perfect mixing time $\tau$ is a function of the stirring energy density $\varepsilon$ (W/t-steel), which is independent of the mixing method (Eq. (1)).

$$\tau = 800 \varepsilon^{-0.4}$$

Stirring energy density was researched in order to evaluate the effect of the gas blowing method (number and arrangement of tuyeres) and bath depth, and many empirical formulas were proposed. Asai analyzed the fluid motion and mass transfer, and provided the theoretical background for Eq. (1). Those researches promoted the development of the top and bottom-blowing converter in Japan. There are two types of top and bottom-blowing converters, one in which oxygen is blown from the top and bottom, and the other in which oxygen is blown from the top but bottom blowing is limited to inert gas for stirring. Steel makers developed nozzle designs and refractories for
these two methods, and all Japanese converters are now top and bottom-blowing converters, with the exception of the Q-BOP converters.

3.1.2. Development and Establishment of Top and Bottom-Blowing Converter

Nakanishi et al. proposed ISCO (Index for Selective Carbon Oxidation, Eq. (2)) as an index for explaining the reactions in the converter, based on investigations of the metallurgical properties obtained with 5 t-scale and commercial-scale converters and measurements of the mixing time with a copper tracer.

\[
ISCO = \frac{2Q_{O2}}{(2Q_{O2} + Q_d)} \cdot \left( \frac{Q_{O2}}{W / \tau} \right) \quad \ldots \quad (2)
\]

Here, \(Q_{O2}\) is oxygen gas flow rate (Nm\(^3\)/min), \(Q_d\) is dilute gas flow rate (Nm\(^3\)/min), \(W\) is molten metal weight (t) and \(\tau\) is perfect mixing time (s). The first item of the right side of Eq. (2) represents the CO partial pressure, and the second item represents the ratio of the oxygen gas flow rate and molten steel circulation flow rate, which stands for the degree of molten steel peroxidation. The relationship between ISCO and \((T.Fe)\) in slag at \(\text{[C]} = 0.05\text{ mass}\%\) is shown in Fig. 7. Kai et al. proposed BOC (Balance of Oxygen and Carbon feeding rate), which is an index of the effect of \(\text{[C]}\) on \((FeO)\) generation, as expressed in Eq. (3).

\[
BOC = Q_{O2} / (W / \tau) \cdot \left( 1 / \left[ \% \text{C} \right] \right) \quad \ldots \quad \ldots \quad (3)
\]

Kishimoto et al. suggested that the effect of the CO partial pressure of the bottom-blowing gas on selective decarburization is comparatively small, except in the ultra-low carbon region of \(\text{[C]} < 0.02\text{ mass}\%\). Many studies on the ratio of top and bottom-blowing gas were also carried out, and it was found that metallurgical properties close to those of the Q-BOP can be obtained when the ratio of the bottom gas blowing rate to the total gas blowing rate is higher than 10%.49)

3.2. High Speed Refining Techniques in Converter

3.2.1. Development of Oxygen Top-Blowing Lance

Increased iron loss by spitting and dust generation are issues of the converter decarburization process with dephosphorized hot metal due to the small amount of slag generation. Hirai et al. investigated the dust generation mechanism and indicated that the iron dust in the early stage of decarburization is mainly caused by bubble burst, while that in the later stage of decarburization is mainly caused by fume (evaporation).

When a multi-hole nozzle is used, spitting increases if the overlap of the gas jets is excessive. M. Fukagawa designed a new nozzle layout which employs nozzles with different diameters and angles side by side to decrease the overlap at the molten steel surface, as shown in Fig. 8. Wakayama Works of Sumitomo Metals (now Nippon Steel) adopted a higher free board converter and newly-designed lance, and achieved high speed decarburization (9 min) with a higher oxygen gas flow rate (5 Nm\(^3\)/t/min).

Based on cold model and 6 t-scale hot model experiments, Naito et al. designed nozzles with a condition of over-expansion that realizes a soft blowing condition, and showed that this design reduces dust generation.

3.2.2. Sensing Techniques for Converter

Various methods for detecting slopping during blowing have been reported, including detection by a surveillance camera at the furnace mouth, measuring furnace vibration with an accelerometer and detection by acoustic signals. M. Shakirov et al. reported the classification of slopping. Cicutti et al. conducted detailed research by an acoustic analysis during blowing. S. Barella et al. investigated the effect of slag viscosity on foaming behavior. M. Malathi et al. studied a spitting model based on an examination of skull. Progress in process modeling utilizing data science is expected in the near future. In this case, it will become even more important to understand the phenomena accurately by developing new sensing, direct observation and modeling techniques.

3.2.3. Stainless Steel Production by Converter Method

In 1972, Nippon Steel established a process for ferritic stainless steel production by a hot metal (blast furnace)–converter route as a substitute for the EAF (scrap melting) process. In the Nippon Steel process, positive use of the RH-OB method and a molten steel heating technique utilizing aluminum oxidation make it possible to perform treatment for the long hours required to produce ferritic stainless steel.

Kawasaki Steel Chiba Works (now JFE Steel East Japan (Fig. 7. Relation between ISCO at \(\text{[C]} = 0.05\text{ mass}\%\) and \((T.Fe)\).50)

(Fig. 8. New concept lance applied for high-speed blowing in BOF refining.)
Works (Chiba)) adopted a technology for producing stainless steel using chromium pellets by a double refining process using two top and bottom-blowing converters (K-BOP) and the RH-KTB. The K-BOP process consists of smelting reduction, slag discharge, FeCr melting and decarburization. Subsequently, a new process using chromium ore instead of chromium pellets was adopted for ferritic stainless steel production, as shown in Fig. 9. In this process, two converters (SRF: Smelting Reduction Furnace and DCF: DeCarburization Furnace) were applied, and the VOD process was adopted as the secondary refining process to meet the demands of ultra-low carbon products and higher quality stainless steel products. A vertical bending continuous caster and a heat-keeping furnace with heating/melting functions called J-First (JJE Flexible Iron Reservoir for Stainless steel) were installed. In smelting reduction of chromium ore, carbon material is used as the reducing agent. To compensate for heat loss due to the reduction reaction, a heat supply is provided by carbon and CO gas oxidation. However, when higher oxygen supply rates are used to increase productivity, dust generation and refractory erosion by post combustion of carbon were issues.

To solve these problems, Okuyama et al. and Sato et al. developed a special burner using hydrogen-based fuel in 2012. In this technique, chromium ore particles are heated in the burner flame to achieve higher heating efficiency. A comparison of the former and developed heat transfer methods is shown in Fig. 10. Because the chromium ore particles heated in the burner flame function as a heat medium, heating efficiency of 80% is achieved. The burner promotes chromium ore melting and compensates for heat loss in the reduction reaction, realizing a 20% increase in energy efficiency in a comparison assuming the same heat supply.

In addition to reducing consumption of FeCr alloy, CO₂ emissions are also reduced owing to lower consumption of carbon as a heat source, thereby contributing to lowering environmental loads.

### 3.3. Scrap Melting Using Top and Bottom-Blowing Converter

Nakayama Steel started operation of the NSR method (Nakayama Scrap melting and Refining Process) in 2002. In that process, 100% scrap melting by coal top addition in a conventional top-blowing converter was adopted. The KS converter a process for 100% scrap melting in

![Fig. 9. Stainless steel production by chromium ore smelting reduction method.](image)
the top and bottom-blowing converter. A KS converter was installed at Nippon Steel Hirohata Works after idling a blast furnace. Coal is injected from the bottom-blowing tuyeres, and waste tires are recycled as a heat source, using the carbon black contained in the tires as a substitute for coal. The rubber and steel cords in the waste tires are also collected as a by-product gas and iron source, respectively.

A “National project for recycling waste scrap, reducing dioxin gas emissions, energy saving and selective expansion of energy” was carried out in Japan from 1991 to 2000, showing that primary energy can be reduced by 25% compared with the EAF process when the energy of the recovered gas is considered.

In the near future, it will be necessary to develop a new process which minimizes CO₂ emissions while maintaining the productivity and quality of steel products. To meet this challenge, scrap sorting techniques for expanding the use of cold iron sources and carbon recycling techniques should be developed.

4. Secondary Refining (Ladle Metallurgy)

Secondary refining techniques are applied to molten steel which has been melted and undergone primary refining in a converter or an electric arc furnace in order to adjust the steel to a specific chemical composition and temperature. Secondary refining is a required process, both for maximizing the capacity of the primary refining process and for producing high purity and high cleanliness steels. The following functions are required for secondary refining:

1. Vacuum (reduced pressure) to remove hydrogen, carbon and nitrogen.
2. Stirring to deoxidize the steel and homogenize the molten steel temperature.
3. Refining with flux and slag for desulfurization, deoxidation and inclusion control (chemistries and foam).
4. Heating the molten steel by means of an arc, aluminum oxidation or gas burner.
5. Alloy addition for adjustment of the chemical composition.

Many types of vacuum refining facilities were developed from the late 1950 through the 1960s. The Bochumer method (droplet degassing process), which was the first commercial facility, was developed by Bochumer Verein in 1952 to eliminate hydrogen defects in large ingots for casting and forging.

The DH method was developed by Dortmund Horder Huttenunion in 1956, and the RH method was developed by the Ruhrstahl and Heraeus companies in 1958 as a suction-type vacuum degasser. The VAD (Vacuum Arc Degassing) and VOD (Vacuum Oxygen Decarburization) methods were developed in 1968, and the AOD (Argon Oxygen Decarburization) and LF (Ladle Furnace) methods were developed in 1967 and 1971, respectively. The types, functions and histories of development have been reported by Kajioa and Iida, and Kuwabara and Semura and Matsuura reviewed the technology development and history of development in Japan. In this chapter, these secondary refining techniques are collectively called “Ladle Metallurgy.”

4.1. Vacuum Metallurgy

Vacuum refining is broadly classified as the RH and VD types, and the RH, VD and DH methods are widely used, as shown in Fig. 11. The DH method installed at Yawata Steel (now Nippon Steel) in 1961 was the first vacuum refining facility in Japan. Although the DH method was widely used in Japan, DH has disadvantages compared with RH, such as complex equipment due to the use of an elevating type vacuum vessel and a smaller degassing capacity. In 1998, Nippon Steel developed the REDA method to compensate for the shortcomings of DH. REDA was adopted for ultra-low carbon and stainless steel production, and made it possible to produce high purity stainless steel more efficiently than that by VOD refining.

4.1.1. RH Process

An RH was first installed in Japan at Fuji Steel Hirohata Works (now Nippon Steel Hirohata) in 1963, and was the world’s second RH facility. During the period from the late 1970s to the late 1980s, the steel production process in Japan changed rapidly, as continuous casting replaced ingot casting in the solidification process. Under these circumstances, rapid progress and development also occurred in the RH process, including the following points.

1. Increased application of ultrasonic testing to products produced by degassing and deoxidation of Al-killed steels for heavy plates.
2. Reduction of the converter load by adopting RH for general steel grades, utilizing its efficient decarburization and stirring abilities under a vacuum.
3. Application to ultra-low carbon steel to improve productivity and quality.

In the RH process, circulation of the molten steel is caused by Ar gas supplied from an immersion tube (snorkel), utilizing gas lifting effect. The circulating rate in actual plants was measured by using a ¹⁹⁵Au tracer and Cu addition. Kuwabara et al. analyzed the composition change during continuous alloy addition, compared the results with the reported data from other companies and proposed the following Eq. (4) for the circulating rate Q. Figure 12 shows the relationship between the calculated results and measured results for actual RH facilities.

\[ Q = 11.4G^{1/3}D^{-1/3}\ln\left(\frac{P_i}{P_0}\right)^{1/3} \quad (t/\text{min}) \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots (4) \]

Vacuum refining for decarburization is mainly used for the following two purposes:

1. Decarburization in the low carbon range while restraining [Cr] oxidation in stainless steel production.

VOD is the main vacuum refining process in stainless steel production. Many studied in connection with ultra-low carbon steel were carried out from the 1980s onward; in particular, establishment of mass production utilizing decarburization in the ultra-low carbon range by the RH process and decarburization of dephosphorized hot metal in the converter made important contributions to technological progress.

Sumita et al. constructed a decarburization model assuming sequential equilibrium, which approximated perfect mixing (2 tanks) between the ladle and the vacuum
vessel in the RH. The effect of operating conditions on decarburization was analyzed using this model, as shown in Fig. 13.

\[
[C] = [C]_0 \exp(-Kt) \quad \ldots \quad (5)
\]

\[
Kc = \left(\frac{Q}{V}\right) \left(\frac{ak}{Q + ak}\right) \quad \ldots \quad (6)
\]

Here, \([C]_0\) is initial carbon content, \(Q\) is circulating rate (t/min), \(V\) is inner volume of ladle (m\(^3\)), \(ak\) is capacity coefficient of decarburization (m\(^3\)/min) and \(K\) is apparent rate constant of decarburization (min\(^{-1}\)).

The following results were obtained from that analysis:

(1) 90% of decarburization proceeds in the vacuum chamber, and the remaining 10% proceeds in the upper snorkel.

(2) In the low carbon region, i.e., \([C] \leq 40\) ppm, where the decarburization rate stagnates, \(ak \leq 10\) m\(^3\)/min and \(K \leq 0.15\) min\(^{-1}\). The rate controlling step of decarburization in
the vacuum chamber is a mixed condition of mass transfer in the decarburization reaction and the circulating rate. Recent RH facilities have higher circulation rates and smaller mixing times. Kato et al.\textsuperscript{90} reported that a dead zone where the concentration distribution is non-uniform does not exist in the molten steel in the ladle. In the case of \([C] \geq 40 \text{ ppm}\), the rate controlling step comprises (i) nucleation rate of gas bubbles at the molten steel surface in the vacuum chamber and (ii) gas bubble growth and floatation separation (aggregation and unification) rate. In the case of low carbon region of \([C] \leq 40 \text{ ppm}\), (ii) is the rate controlling step. Therefore, the following points are important for accelerating the decarburization rate of ultra-low carbon steel in the RH:

(1) Increasing the degree of vacuum quickly in the early stage of decarburization by increasing the RH exhaust capacity.

(2) Increasing the circulating rate of the molten steel.

(3) Applying strong stirring to the molten steel surface in the later stage of decarburization.

RH-OB (\(O_2\) injection) was developed at Nippon Steel Muroran Works to promote decarburization of stainless steel.\textsuperscript{91} In that process, a double layered tuyere was set at the bottom of the vacuum chamber, and oxygen gas was supplied from the inner tube while oil mist was supplied from the outer tube. Control of decarburization, heating-up and the RH treatment time after completion of \(O_2\) injection are important for proper floatation and removal of the inclusions generated by oxygen blowing in this process.

The RH-KTB (RH-Kawatetsu Top lance Blowing) oxygen top blowing method was developed at Kawasaki Steel Chiba Works.\textsuperscript{92,93} The gap between the top-blowing lance and the molten steel surface is between 1.6 and 4.5 m, and oxygen gas is supplied to the molten steel surface by the lance while controlling the lance height corresponding to the target carbon content. The effects of RH-KTB are as follows:

(1) Decreased temperature drop in rimmed treatment by using carbon post combustion.

(2) Increased decarburization rate (increased capacity coefficient).

(3) Improved unit values by lowering the molten steel tapping temperature and \((%\text{T.Fe})\), because use of the RH-KTB makes it possible to increase \([C]\) at blow end in the converter.

RH-MFB (RH-Multi-Function Burner) was developed at Nippon Steel Hirotaka Works\textsuperscript{94,95} and makes it possible to supply oxygen gas and LNG from the top lance. The refractories and molten steel are heated during treatment and spare time. RH-PTB (Powder Top Blasting) was developed at Wakayama Works of Sumitomo Metals (now Nippon Steel)\textsuperscript{96,97} for production of ultra-low sulfur and carbon steels, and features blasting of iron ore powder during decarburization in the range \([C] \leq 40 \text{ ppm}\). It is thought that the iron ore powder which is entrained and scattered in the molten steel increases the reaction interface area, functions as oxygen source and also provides nuclei for CO bubbles.

In Chiba Works of Kawasaki Steel (now JFE Steel East Japan Works (Chiba)), the decarburization behavior of ultra-low carbon steel when a mixed gas of hydrogen gas and Ar gas was supplied from the circulating gas nozzle was examined.\textsuperscript{98} It was found that hydrogen was once dissolved into molten steel, and the phenomenon of degassing by the hydrogen provided nuclei for decarburization in the low carbon region. The effect of hydrogen injection was investigated, revealing that the decarburization rate increased in the ultra-low carbon region of \([C] \leq 15 \text{ ppm}\), and as a result, a lower final carbon content can be achieved.\textsuperscript{98}

Okuyama et al.\textsuperscript{99} and Sumi et al.\textsuperscript{100} conducted cold model experiments to investigate the oxygen jet behavior from a laval nozzle under reduced pressure, and compared the measured dynamic behavior of the jet with the results of a numerical analysis.

The nitrogen removal reaction is affected by chemical composition, and especially by surface active elements. It is known that the apparent nitrogen removal rate constant is expressed by a second order reaction of \([N]\), and is lowered by increasing \([O]\) and \([S]\). \([O]\) is more effective than \([S]\.) The rate controlling steps of nitrogen removal are the removal rate of absorbed nitrogen at the molten steel surface and desorption of \(N_2\) (g).

In the RH process, absorption and removal of nitrogen proceed at the same time due to air leakage from cracks in the snorkel. Therefore, it is important to minimize nitrogen absorption caused by air leaks. The following techniques for reducing nitrogen absorption have been reported:

(1) Tapping without deoxidation in the converter.

(2) Increasing the \((Ar)\) gas flow rate for circulation.\textsuperscript{101}

(3) Improving \(Ar\) gas sealing performance at the snorkel and flange.

(4) Use of a snorkel without a flange.\textsuperscript{102}

Other examples have also been reported. Mukawa et al.\textsuperscript{103} investigated mixing \(CO\) gas in the circulation gas \((Ar)\) to promote nitrogen removal. Yano et al.\textsuperscript{104} reported the effects of tapping without deoxidation, suppression of gas leakage from the flange part and application of a sealed tundish as countermeasures to prevent nitrogen pickup.

As a non-vacuum approach, nitrogen removal by slag was examined. The nitrogen removal ratio was increased by using CaO–Al\(_2\)O\(_3\) slag to control the chemical composition so as to increase the nitride capacity.\textsuperscript{105} Yamaguchi et al.\textsuperscript{106} conducted basic research including nitrogen removal from slag to the gas phase in addition to removal from the molten steel to the slag.

Arai et al.\textsuperscript{107} developed PERM (Pressure Elevating and Reducing Method) to promote inclusion removal by floatation. Nitrogen gas bubbles can be generated by utilizing the difference between solubility of nitrogen under atmospheric pressure and reduced pressure. This technique was applied to a 50 t-scale VOD for carbon and stainless steels and a 250 t-scale RH for bearing steel. The oxygen removal rate was more than doubled, and the total oxygen content and average inclusion size in slabs were decreased.

Desulfurization techniques for molten steel by adding desulfurization flux in a vacuum chamber were reported by Mizukami et al.\textsuperscript{108,109} Sato et al.\textsuperscript{110} and Soejima et al.\textsuperscript{111} Desulfurization techniques by flux injection were investigated at Kawasaki Steel Mizushima Works (now JFE Steel West Japan Works (Kurashiki))\textsuperscript{112} and Nippon Steel Ohita Works.\textsuperscript{113}
4.1.2. VOD (Vacuum Oxygen Decarburization)

The VOD method was developed by Witten (Germany) in 1967, and the first unit in Japan was installed at Nissin Steel for use in stainless steel refining in 1968. Examples of development include a VOD method for ultra-low carbon and nitrogen stainless steel (Katayama et al.\textsuperscript{114}) and the KTG (Kawasaki Steel Tokyo Yogyo Gas Blowing System) method (Kakiuchi et al.\textsuperscript{115,116} and Oguchi et al.\textsuperscript{117}) using a single hole nozzle for gas injection in place of a porous plug, which was the main stream in ladle refining at the time. Promotion of nitrogen removal by oxidant powder blasting was also investigated.\textsuperscript{118,119}

4.1.3. VCR (Vacuum Converter Refiner: Vacuum AOD)

In stainless steel refining, decarburization can be conducted from a higher carbon content by the AOD method. However, the decarburization rate by AOD is low in the low carbon region, and as the result, the final carbon content is higher. Although the CO gas partial pressure can be lowered by introducing a large amount of Ar gas, this causes a cost increase. Daido Special Steel developed VCR, which was a modified AOD with a vacuum refining function.\textsuperscript{120} The company began operation of a 70 t-scale AOD-VCR process for stainless steel production in 1991\textsuperscript{121} as shown in Fig. 14.

As a feature of the VCR process, decarburization is conducted by using dissolved oxygen and oxides in the slag, and by not O\textsubscript{2} blowing under the vacuum condition. Nippon Steel introduced this process for stainless steel refining as the V-AOD process in 1996. With the V-AOD process, decarburization was improved by oxygen blowing (without diluting gas) under reduced pressure ([C] \leq 0.6%), resulting in a shorter refining time and lower consumption of Si alloy for chromium reduction in the slag.\textsuperscript{122}

4.2. Secondary Refining (Ladle Metallurgy) without Vacuum Treatment

Secondary refining without vacuum treatment began with Ar gas injection through a special lance or bottom tuyeres and was used for various purposes, including adjustment of the chemical composition, deoxidation, inclusion removal, desulfurization and homogenization of the molten steel temperature.

Gas bubbling from a special lance, such as the Scan lance method, TN (Thyssen Nieder Rhein) method and CaSi wire feeding method were commercialized in the 1980s. ASEA-SKF was the first method which utilizes stirring by an electromagnetic induction coil set outside of the ladle.\textsuperscript{78}

Nippon Steel developed CAS-OB (Composition adjustment by Sealed Argon Bubbling-Oxygen Blowing),\textsuperscript{123} which is a simplified secondary refining process using Ar gas bubbling for deoxidation and adjustment of the chemical composition. Nippon Steel\textsuperscript{124} also developed KIP (Kimitsu Injection Process) for desulfurization by flux injection. Those techniques were later modified as CAS-OB under reduced pressure and V-KIP by providing a vacuum function.

The LF (Ladle Furnace) method was developed in 1970. In the LF process, molten steel is stirred by Ar gas for deoxidation and desulfurization. Because the molten steel temperature is decreased by alloy addition, the molten steel is heated with a graphite electrode arc. In the 1980s, NK-AP (NKK Arc refining process) was commercialized for production of ultra-low sulfur and oxygen steels by using a flux injection lance and a heating device with a graphite electrode.\textsuperscript{125}

4.2.1. Inclusion Control in LF Method

Yoshio et al. investigated the composition of inclusions with sizes of 1 \textmu m and larger using a technology called ASPEx Explorer (Automated industrialized SEM with Omega Max EDX).\textsuperscript{126} The material examined was case hardened (SCM) steel (C/0.22, Si/0.26, Mn/0.68, Ni/1.62, Cr/0.56 (mass%)) produced by the EAF (150 t)-LF-RH-CC process.

At Sanyo Special Steel, the composition of oxide inclusions in RH is controlled to a MgO–Al\textsubscript{2}O\textsubscript{3} system by controlling the amount of added CaO and CaF\textsubscript{2}, which contribute to reducing the total oxygen content by floatation (Fig. 15). A high productivity process for ultra-clean bearing steel was developed by thoroughgoing control of the EAF-LF-RH-CC process.\textsuperscript{127}

4.2.2. Inclusion Control

Many studies about alumina inclusion were reported. Tozawa et al.\textsuperscript{128} analyzed agglomeration and floatation behavior of alumina cluster generation by fractal theory. Miki et al.\textsuperscript{129} investigated the effect of Ar bubble on inclusion removal behavior in RH process. Moreover, Sasai et al.\textsuperscript{130–132} reported alumina generation and removal behavior through distinguished basic researches.

Harada et al.\textsuperscript{133} proposed an inclusion generation model based on the coupled reaction model. Oxide metallurgy\textsuperscript{134–135} is an example a technology which utilizes inclusions and precipitations to control the microstructure of steel products. Utilization of finer secondary oxide inclusions, which are generated during solidification, to achieve a finer microstructure was reported.\textsuperscript{154–159} Finer inclusions or precipitates can be utilized for microstructure control. In particular, finer secondary oxide inclusions are generated under higher solidification rates, and thus can be utilized in the thin slab casting and strip casting processes. In the future, further investigation of microstructure control by inclusions and precipitations will be needed.
4.3. Issues and Prospects for Ladle Metallurgy

Further development of new techniques for producing high purity and high cleanliness steels is necessary in order to meet the demand for high quality steel products. Although decarburization in the low carbon region has been established by vacuum refining processes, in the future, process control for [C], [O], [Total O] and temperature using accurate reaction models, data science techniques and quick heating techniques will be needed. For nitrogen removal, a simplified process for the EAF, slag utilization techniques and a technique for removal of nitrogen from slag are required. Where desulfurization is concerned, ultra-low sulfur steel can already be produced, but high speed desulfurization and heating techniques are necessary to meet increasing demand for ultra-low sulfur steels. Further investigation of inclusions and precipitates is needed for ultra-clean steel and improvement of the microstructure of steel products.

5. Summary – Issues and Prospects of Refining Process

5.1. Issues in Steelmaking Process and Response to Environmental Problems

Crude steel production in Japan grew rapidly after 1960 and reached 100 million tons per year for the first time in 1973. Today, Japan’s crude steel production remains around 100 million tons per year. In 2018, Japan was the world’s third largest producer, following China and India. Japanese integrated steel works are located on the coast, and import high quality iron ore and coal. They have optimized production process aiming at mass production of high quality steels. As described in this paper, the production process has been functionally differentiated into hot metal pretreatment, combined-blowing converter and secondary refining.

On the other hand, “Contribution to the sustainability of the global environment and suppression of global warming” is an urgent issue for the steel industry. In 2008, Japan launched a national project called “Steel production process by hydrogen reduction: (COUSEE 50 project[162])” with the aim of reducing CO₂ emissions by 30% by 2030. Moreover, in 2018, the Japanese Iron and Steel Federation (JISF) adopted a vision called “Challenge for zero carbon steel (making)” as a countermeasure against global warming. The JISF announced a roadmap and set the target of reducing CO₂ emissions to zero by 2100. In the future, higher energy efficiency processes for scrap and reduced iron melting processes which can produce high quality steels with high productivity will be required.

5.2. Issues and Prospects of Refining Process

Issues of the refining process are 1) utilization of big data, AI and data science for control of the refining process and improving its efficiency, 2) Development and practical realization of sensing and modeling, 3) Utilization of robots for integrating and simplifying the production process, 4) Expansion of scrap utilization, including waste scrap and reduced iron, and removal or detoxification of tramp elements and 5) Development of flux which has a higher refining ability and promotes 3R (Reduce, Reuse and Recycle) of steelmaking slag.

In the future, iron sources will become more diverse, and as a result, higher energy efficiency melting processes and 3R of steelmaking slag will required. Therefore, new pretreatment processes for reducing tramp elements, phosphorus and sulfur will be needed. In converter refining and ladle metallurgy, refining control techniques utilizing data science based on elucidation of the mechanism of phenomena by visualization, etc., modeling and high temperature sensing technologies for accurate process control will be necessary. Moreover, in addition to process omission and multi-functionality, development of new stirring and rapid heating techniques that enable higher speed and more stable production is desired.

5.3. Necessity of Basic Research

It is necessary to develop new techniques corresponding to the abovementioned points. Therefore, basic research is becoming more important, such as visualization of high temperature phenomena, sensing technique, process modeling, physical and chemical properties of molten metal, slag flux. Moreover, basic researches for developing new process are highly required, such as reduced iron production, melting process of cold iron sources (steel scrap and reduced iron), and promoting 3R (Reduce, Reuse and Recycle) of steelmaking slag and dust. Those new process are needed to be established for minimizing environmental load.