Development of High-Efficiency Stainless Steelmaking by Cr Ore Smelting Reduction Method

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1 Introduction

A new stainless steelmaking shop (No. 4 steelmaking shop), which was constructed as part of the Chiba Works modernization plan, was started up in July 1994, and is continuing to operate smoothly.17

The study of the production process at the new steelmaking shop was carried out from various viewpoints, including productivity, quality, the environment, and others, but in deciding the refining process, first consideration was given to securing a high degree of freedom in the selection of Cr, Ni, and other main raw materials, which account for the larger part of the cost of producing stainless steel. As a result, a decision was made to minimize the use of ferrochrome, which consumes a large amount of electric power, and adopt the smelting reduction furnace, which is a direct reduction process for Cr ore using oxygen and coke, taking advantage of the location of the new plant in an integrated steel works. Efforts were also made to enable the plant to use stainless steel scrap in large quantity. This paper describes the circumstances of the development of the stainless steel refining technology, centering on smelting reduction for the direct use of Cr ore and also including decarburization refining, the decision of the equipment specifications, and an outline of operation since startup.

2 Trend in Stainless Steelmaking Processes at Kawasaki Steel

In the 42 years since Kawasaki Steel began to produce stainless steel by the electric arc furnace at Nishinomiya Works in 1954, numerous improvements have been made in the equipment and process to improve productivity and quality and reduce costs. Figure 1 shows the trend in stainless steelmaking processes during this period, categorized by Ni type and Cr type stainless steels.

The most important changes are represented by the following:

(1) Start of the 1970s: Introduction of VOD for ferritic stainless steel and start of production of martensitic stainless steel at Chiba Works by the two-blow process in the LD converter and continuous caster

(2) 1981: Consolidation of the company's stainless steelmaking shop at Chiba Works and introduction of K-BOP (combined blowing converter)

(3) 1986: Introduction of smelting reduction process for pre-reduced Cr pellet using two K-BOP converters

(4) 1994: Introduction of smelting reduction process for Cr ore and vertical-bending continuous casting machine at the startup of No. 4 steelmaking shop

The above-mentioned process and equipment improvements were measures to improve productivity to meet increased demand for stainless steel or respond to

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high purity and other quality requirements, and at the same time, were also techniques for using low-cost raw materials to reduce costs and techniques for energy saving by shifting from electric power to coal energy. Moreover, the Chiba Works modernization plan also included the development of technologies for reducing industrial waste, etc. to realize a true urban steel works.

3 Concept of New Stainless Steelmaking Shop

Figure 2 shows an outline of the refining process at the new stainless steelmaking shop. In particular, considering the site conditions of Chiba Works as an urban steel works, the process gives high priority to recycling in order to eliminate industrial waste, based on an awareness of environmental problems. Concretely, a new refining furnace (STAR furnace) was constructed to treat stainless steel dust, and a process in which Cr-bearing dust generated by the steelmaking shop is melted, reduced, and reused as a raw material for stainless steel was completed. Stainless steel slag is recycled as roadbed material or as a submaterial for the STAR and other processes, and the gas generated by the new stainless steelmaking plant is recovered and used effectively as an energy source for the works.

Figure 3 shows a schematic outline of the STAR process. The dust discharged from the converters at No. 4 steelmaking shop is condensed from the dust collector water into slurry by the thickener. The slurry is again condensed in the tank and dried in the spray dryer and processed into raw material for the STAR furnace. The STAR furnace is a coke-packed shaft-type smelting reduction furnace with two-stage tuyeres, in which coke is supplied from the furnace top and the raw material (stainless steel dust) is blown into the furnace as powder from the upper stage of the two-stage tuyeres, and melted and reduced. As raw material, it is also possible to use pickling sludge and other materials generated in the works in the same manner, as well as the dust generated.
in the steelmaking shop. Dry dust is blown without further processing, while water-bearing dust is blown as a slurry-type material after drying in the drier. Slag produced by the stainless steel decarburizing furnace is recycled as raw material for the STAR furnace and other processes, contributing to the minimization of industrial waste.

4 Development of Smelting Reduction Process Using Cr Ore

4.1 Design Concept of Smelting Reduction Furnace

At Chiba Works, a smelting reduction process using two K-BOP converters had already been adopted at No. 1 steelmaking shop in 1985. Table 1 shows a comparison of the main differences between the smelting reduction process at No. 1 steelmaking shop and the smelting reduction process adopted at the new stainless shop.

The conventional smelting reduction process at No. 1 steelmaking shop used semi-reduced Cr pellet to enable processing within the short time allowed by continuous casting. At No. 4 steelmaking shop, equipment was adopted which enables direct charging of Cr ore into the furnace with no need for pre-processing. First, an exclusive-use lance for Cr ore charging was adopted for direct addition of Cr ore sand into the furnace with good yield.

Second, a large inner volume was adopted for the smelting reduction furnace, making it possible to hold a large quantity of slag in the furnace, in consideration of a slag composition design that enables dilution of gangue and desulfurization, as required when raw ore is used.

Third, the oxygen flow rate was increased greatly over the conventional specification, to a maximum 950 Nm³/min, to enable smelting reduction of raw Cr ore within a specified time.

Fourth, a strongly-stirred top and bottom blowing converter with eight concentric-type bottom blowing tuyeres was adopted, based on experiments and operating experience at No. 1 steelmaking shop, to increase the Cr ore reduction rate and make it possible to melt scrap in large quantity. The bottom blowing gas flow rate was set at 0.5–1.2 Nm³/min.

4.2 Development of Lance for Cr Ore Charging

Minimizing the use of ferrochrome, which consumes a large amount of electric power, and enabling the direct use of raw Cr ore were the most important tasks for increasing the degree of freedom in blending raw materials in the smelting reduction furnace at the new steelmaking shop. The lager part of the Cr ore produced worldwide is sand, and, thus, scattering and loss into the exhaust system were feared, depending on the method of addition. Therefore, Cr ore addition experiments were carried out in advance at No. 1 steelmaking shop, and the advantages and disadvantages of the respective methods of addition were compared.

Table 2 shows an example of the particle size distribution of Cr ore. The sizes 150–600 μm are fine-grained particles which account for more than 80% of the total, and there was concern that scattering would be a problem if charging into the converter was inappropriate. Therefore, Cr ore addition experiments were conducted at No. 1 steelmaking shop with the two methods shown in Fig. 4. In method A, charging was performed by

Table 1 Main features of SR-KCB in the new stainless steelmaking shop compared with those of K-BOP in No. 1 Steelmaking shop

<table>
<thead>
<tr>
<th></th>
<th>K-BOP in No. 1 steelmaking shop</th>
<th>SR-KCB in No. 4 steelmaking shop</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr source</td>
<td>Pre-reduced Cr ore</td>
<td>Cr ore</td>
</tr>
<tr>
<td></td>
<td>Scrap</td>
<td>Scrap</td>
</tr>
<tr>
<td>Inner volume of furnace (m³)</td>
<td>173</td>
<td>372</td>
</tr>
<tr>
<td>Heat capacity (t)</td>
<td>85</td>
<td>185</td>
</tr>
<tr>
<td>Max. O2 flow rate (Nm³/min)</td>
<td>306</td>
<td>950</td>
</tr>
<tr>
<td>Bottom gas flow rate (Nm³/min)</td>
<td>0.6–0.8</td>
<td>0.5–1.2</td>
</tr>
</tbody>
</table>

Table 2 Typical example of particle size distribution of Cr ore

<table>
<thead>
<tr>
<th>Particle size (μm)</th>
<th>600</th>
<th>300</th>
<th>150</th>
<th>125</th>
<th>45</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cumulative greater than (%)</td>
<td>0.1</td>
<td>21.0</td>
<td>80.4</td>
<td>87.1</td>
<td>99.7</td>
</tr>
</tbody>
</table>

Fig. 4 Experimental method for Cr ore addition in K-BOP in No. 1 steelmaking shop
pouring the ore into the converter in one batch from a furnace-top bunker, while in method B, an exclusive-use lance was inserted through the tap hole and the Cr ore was blown directly into the converter. The exclusive-use lance in method B is a 50 A steel pipe protected by a high-alumina castable. As shown in the figure, the ore is charged with the tip of the lance aimed toward the slag surface. Blowing at 10 Nm³/min is possible using N₂ as the carrier gas.

In these experiments, one aim was to investigate the yield of the Cr ore added to the converter. For this reason, the yield of Cr ore added to the converter was defined as the sum of the Cr ore yield in the slag and in the metal. Figure 5 shows the relationship between the converter exhaust gas flow rate and the yield of Cr ore during the experiments with the two experimental methods. Here, the conventional method means the method of charging semi-reduced pre-reduced Cr pellets from the furnace top. Semi-reduced pellets are a lump-type raw material in which the particle size 10–15 mm comprises more than 85%, and the yield of semi-reduced pellet is over 95%.

Figure 6 shows the particle size distribution of converter dust collected by the dust collector in comparison with the conventional method. When material is poured in from the furnace top (experimental method A), the dust of sizes 150–500 μm, which accounts for the larger part of the Cr ore, increases in comparison with the conventional method and experimental method B, and there is a high possibility that scattering loss will increase. An analysis of the Cr component of the dust showed that the Cr content is high in the region of 150–500 μm in experimental method A. From this result as well, it was considered that direct scattering of the Cr ore would occur with method A. In particular, when the oxygen supply rate increases, the rate of scattering becomes high. With method B, the Cr ore yield was more than 98%. Moreover, looking at the effect of the lance position, yield became somewhat higher when the Cr ore was introduced with the lance inserted deep into the converter.

The experiments described above made it clear that the method of charging loose Cr ore from the furnace top is not an appropriate method of adding Cr ore because the rate of Cr ore scattering becomes excessive as the oxygen supply rate increases. It was also found that Cr ore can be added with good yield by blowing the Cr ore into the furnace through a lance inserted in the tap hole.

Because this knowledge was also to be used in the design of the new steelmaking shop, a numerical analysis of the gas flow in the converter was carried out. The two-dimensional gas flow was analyzed using the commercial code PHOENICS. The reaction model was originally proposed by Kato et al. and was modified for the use of PHOENICS. The gas flow pattern in the furnace was calculated after adjustment to achieve agreement between the actual and calculated values of the post-combustion rate in the furnace. An example of a calculation is shown in Fig. 7. In the furnace, the oxygen supplied by the top-blowing lance generates a downward flow with the furnace center as its axis, and the upward flow increases as the distance from the wall decreases.

The gas flow velocity at the position of Cr ore addition was obtained from the calculated results. It is also conceivable that Cr ore yield is affected by the initial velocity of ore dropping at the addition position, as well as by the gas flow velocity. However, under the conditions used in these experiments, the dropping velocity was approximately 6 m/s with experimental method A and approximately 30 m/s with experimental method B.
For convenience, the difference between the gas flow velocity and the dropping velocity is defined here as the relative downward velocity of the ore. The relationship between the relative downward velocity and Cr ore yield is shown in Fig. 8. A clear relationship can be seen between the two, indicating that the Cr ore yield can be roughly estimated from the relative downward velocity.

Increasing the relative downward velocity by raising the initial velocity of the Cr ore was also considered as a method of improving the Cr ore yield, but pipe wear will become a problem if the Cr ore is transported through piping at high speed. Therefore, the initial speed during addition should be minimized. Accordingly, the most appropriate method is direct addition of the Cr ore in the vicinity of the furnace center, where the downward flow occurs.

The exclusive-use Cr ore charging lance was adopted at the new steelmaking shop based on the experimental results and the results of the numerical analysis described above. Figure 9 shows a schematic illustration of the Cr ore charging lance. The Cr ore is dried in advance to ensure good transportation properties and prevent stock hanging and to minimize the loss of heat energy, and is then transported to the furnace top and blown from the Cr lance. The Cr ore charging lance has a raising and lowering function which is independent of the top blowing lance, and is lowered to charge Cr ore only during the smelting reduction period. The lance is a water-cooled three-tube concentric design constructed to withstand the thermal load in the furnace. As a countermeasure against wear by the Cr ore, a wear-resistant ceramic was inserted.

Figure 8 shows the yield of Cr ore in the smelting reduction furnace. The yield when blowing from the exclusive-use Cr ore charging lance is 97% or more, and Cr ore sand can be used without loss, with no special pretreatment.

Simultaneously with the improvement of Cr ore yield described up to this point, another task related to the direct use of Cr ore in the converter was countermeasures for poor reduction when charging a large quantity of hard-to-reduce Cr ore. Experiments at No. 1 steelmaking shop and experiments with a 5 t test converter confirmed that reduction is possible without problem, assuming proper slag control (dilution of gangue content) and adequate stirring of the slag and metal.
Fig. 10 Typical example of blowing pattern in SR-KCB

Fig. 11 Effect of temperature on reduction of (T.Cr) in slag

4.3 Operation of Smelting Reduction Furnace with High Degree of Freedom in Raw Material Blending

The new steelmaking shop has operated smoothly since startup in July 1994. This section describes the main operating results of the smelting reduction furnace.

Figure 10 shows an example of the operation pattern of the smelting reduction furnace. The operation pattern is divided into SR-0, when the scrap and dust metal charged into the furnace in advance are melted; SR-1, when the furnace is heated up to the specified temperature (1540-1560°C); SR-2, in which the smelting reduction of Cr ore is performed; and SR-3, which is the final reduction period. The slag composition is designed to be suitable for smelting reduction in the same manner as at No. 1 steelmaking shop, the slag basicity being set at 2.5-3.0 in consideration of the desulfurization function and re-use of slag.

Figure 11 shows the relationship between the temperature of the molten steel and (T.Cr) in the slag when using Cr ore, in comparison with semi-reduced Cr pellets. Under proper conditions, the reduction rate of Cr ore is the same level as with pre-reduced Cr pellet or higher. This appears to be because Cr ore is sandy, which is an advantage in terms of the reaction interfacial area, while pellets are lumpy in form.

Table 3 summarizes the main operating results of the smelting reduction furnace.

<table>
<thead>
<tr>
<th>Table 3 Blowing conditions and raw material balance in SR-KCB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Item</td>
</tr>
<tr>
<td>Cr ore</td>
</tr>
<tr>
<td>Scrap</td>
</tr>
<tr>
<td>Recycled metal by STAR process</td>
</tr>
<tr>
<td>Blowing time (min)</td>
</tr>
<tr>
<td>Temperature (°C)</td>
</tr>
<tr>
<td>Basicity (CaO/SiO₂)</td>
</tr>
<tr>
<td>Cr yield (%)</td>
</tr>
<tr>
<td>Tapping composition in SR KCB (Cr)</td>
</tr>
<tr>
<td>S</td>
</tr>
</tbody>
</table>

5 Development of High-Speed Decarburizing Technology by Duplex Decarburization with Strongly-Stirred Combined-Blowing Converter and VOD

5.1 High-Speed Decarburizing Technology by Strongly-Stirred Combined-Blowing Converter

When decarburizing molten iron or chrome-bearing hot metal produced by the smelting reduction furnace, high-speed decarburization is necessary in the high-carbon concentration region, and a converter which can blow at a substantially higher oxygen supply rate than the AOD becomes essential.

At the new steelmaking shop, a large amount of Cr ore is used in comparison with No. 1 steelmaking shop, and the chrome concentration of the Cr-bearing hot metal supplied to the decarburizing furnace therefore tends to increase. Based on the knowledge obtained at No. 1 steelmaking shop, a high-speed decarburizing process with little Cr oxidation was developed.

Figure 12 shows the transition of C and temperature during decarburization in the decarburizing furnace. The chrome-bearing hot metal tapped from the smelting reduction furnace has C = 5-6% and a molten steel temperature of approximately 1450°C, but the temperature drops to 1200°C or under at the start of blowing due to the effect of the previously charged scrap, etc. The fig-
Fig. 12  Schematic route of [C] and temperature in DC-KCB

![Image of Schematic route of [C] and temperature in DC-KCB]

Fig. 13  Comparison of Cr oxidation loss from blow start to 1.2% carbon in the improved method with that of conventional method

![Image of Comparison of Cr oxidation loss from blow start to 1.2% carbon in the improved method with that of conventional method]

ure shows the Cr oxidation region determined from Simkovich’s\textsuperscript{53} equilibrium equation. Here, [Cr] = 18%, [Ni] = 8%. Oxidation proceeds at lower temperatures and in the lower carbon region than the equilibrium line, which means that it is important to raise the temperature of the molten steel quickly in the initial period when C is high. For this purpose, high-speed blowing with a large oxygen supply rate in the initial period was adopted. To realize high-speed blowing, suppressing spitting is necessary, but a reduction in spitting was realized by improvement of the lance tip and optimizing the lance height. Figure 13 shows a comparison of Cr oxidation from the start of blowing to [C] = 1.2% with the conventional method and with the improved method. It was possible to reduce initial-period Cr loss substantially using the improved technique.

In the low carbon concentration region of [C] < 1.0%, a technique for controlling the temperature within a narrow range around 1700°C is necessary in order to prevent erosion of the refractories and suppress Cr oxidation. In the past, to suppress Cr oxidation in the low carbon concentration region either increasing the dilution gas, or increasing the stirring energy has been proposed. However, the bottom-blowing stirring energy and bottom-blowing dilution gas are limited by the number of tuyeres, and thus dramatic increases are difficult. Based on numerous experiments at No. 1 steelmaking shop, Kawasaki Steel developed a technique of blowing only N\textsubscript{2} from the top lance in the final stage of refining as a technology for reducing Cr loss while holding down the increase in the temperature of the molten steel.\textsuperscript{64} At No. 4 steelmaking shop, the use of top-blowing N\textsubscript{2} in the final stage of blowing has made it possible to suppress Cr loss while maintaining an oxygen supply rate from the bottom tuyeres. Figure 14 shows the relationship of the amount of Cr oxidation in the low carbon concentration region and the stirring energy of the top-blowing N\textsubscript{2}.\textsuperscript{71} In the top-blowing N\textsubscript{2} method, Cr loss was decreased by increasing the N\textsubscript{2} flow rate (from step 1 to 2), but even with the same N\textsubscript{2} flow rate, Cr loss was reduced further by lowering the lance and using a hard blow (from step 2 to 3). Two effects of the top-blowing N\textsubscript{2} method are conceivable: (1) the dilution effect of the CO gas pressure and (2) strengthening of the metal/slag stirring energy by the top-blowing gas. However, based on the effect of the lance height described above, the influence of the increased metal/slag stirring energy is considered to be greater. As discussed above, the use of the strongly-stirred combined-blowing converter makes possible high-speed decarburization of the Cr-bearing hot metal produced by the smelting reduction furnace without causing excess oxidation of Cr.

5.2 Duplex Decarburization Process by Combined-Blowing Converter and VOD

Although Cr oxidation in the low carbon concentration region has been substantially reduced by the top-blowing nitrogen process, decarburization in the converter to the low carbon concentration region invites longer converter refining times and Cr oxidation due to decreased oxygen utilization efficiency for decarburization.
tion. Figure 15 shows an example of the relationship between converter blow-end C and Cr loss. At [C] < 0.1–0.2%, Cr loss increases sharply due to the decrease in oxygen utilization efficiency for decarburization. To solve this problem, a duplex decarburization process comprising the converter and VOD was adopted at the new steelmaking shop. Figure 16 shows the relationship between the oxygen utilization efficiency for decarburization and [C] in the DC-KCB and VOD. With the VOD, it is possible to obtain a high oxygen utilization efficiency for decarburization even in the low carbon concentration region by vacuum decarburization, and decarburization with minimal Cr loss is possible. However, because the oxygen supply rate of the VOD is small in comparison with the DC-KCB, increased treatment time becomes a problem with the VOD if [C] is raised. Accordingly, the blow end [C] at the converter is set at 0.1–0.2, and the total treatment time with the DC-KCB and VOD is minimized to match the high-speed casting time. By adopting this duplex decarburization process, it is possible to equalize the treatment time in the decarburization furnace and VOD and minimize Cr loss.

6 Conclusion

This paper has described the design concept of the smelting reduction furnace and decarburization furnace, which are the key elements in the new stainless steelmaking shop constructed as part of the Chiba Works modernization plan. The decision of the equipment specifications and the results since startup have also been discussed.

To achieve a broad increase in the freedom of main raw material selection, the smelting reduction furnace was newly designed to make it possible to use Cr ore sand directly in the converter and to melt scrap in large quantity. As the decarburizing furnace, a strongly-stirred combined-blowing converter was adopted. This converter uses dilution gas and is capable of performing high-speed decarburization of crude hot metal with Cr = 9.13% tapped from the smelting reduction furnace while suppressing Cr oxidation. A duplex decarburization process comprising the decarburization converter and VOD secondary refining equipment makes it possible to refine products including ultra-low carbon steel while minimizing Cr oxidation.

The new shop began operation in July 1994 and is performing rational stainless steelmaking in line with Kawasaki Steel’s strategy for main raw materials.

References