Technology

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# Development of Resource Saving, Environmentally-Conscious, High Productivity Stainless Steel Making Process at Yawata Works<sup>\*1</sup>

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## Abstract

Yawata Works manufactures chromium-based stainless steel. The scarcity of Cr resources will increase because the reserve-production ratio is relatively small among rare metals. Therefore, full utilization of this resource is required. In addition, the international competitive environment for stainless steel has become harsh due to the increase in production capacity overseas, including China. In this report, the development of an innovative process centered on the technology for reducing and recovering Cr from SUS slag and dust using an electric furnace (YES) is described to establish environmentally-conscious, cost saving, and production of a flexible stainless steel manufacturing process.

## 1. Background and Objectives of Research and Development

Stainless steel (SUS) is divided into the chromium (Cr) type and the chromium-nickel (Cr-Ni) type. Yawata Works of Nippon Steel Corporation mainly produces ferritic SUS of the Cr composition. Various SUSs are manufactured with the requisite properties for use in automobiles, electric home appliances, kitchen utensils, containers, tanks, buildings and civil engineering structures, and many other applications.

Cr is a main constituent element of SUS and has 15 mineable years left as calculated from its confirmed mineable reserve.<sup>1)</sup> Its mineable years are relatively short among the rare metals. This means that it is an important resource. The world's crude SUS production increased to 46 million tons in 2017 or to 2.3 times more than that in 2000, thanks to economic development, mainly in China, since 2000.<sup>2)</sup> Saving the Cr resource is expected to become an increasingly important issue. According to the Soil Environment Standards of the Ministry of the Environment of Japan, SUS slag re-

<sup>\*1</sup> This report is reprinted from Reports of Achievements in Industrialization Awarded the Okochi Memorial Prize 2017. quires Cr reduction techniques and fluorspar-free processes.

Like carbon steels, SUS is oversupplied due to the expansion of the steel supply capacity by foreign manufacturers, chiefly in China. In 2016, the world's SUS plant availability dropped to 62%.<sup>3)</sup> SUS is international merchandise. The long-term continuous pursuit of further functional improvement and differentiation in SUS products and of resource saving, environmental consciousness, and production cost reduction in the manufacturing stage of both general-purpose and high-grade SUS is a source of global competitiveness in domestic and overseas markets. A more flexible production system or hither production elasticity is required to quickly respond to the increase and decrease in SUS demand under short-term economic fluctuations.

Nippon Steel developed a new resource recycling SUS making process that combines an integrated blast furnace (BF)-basic oxygen furnace (BOF) process with a strong reduction smelting electric arc furnace that can save resources by making effective use of Cr, a principal steel alloying element, can reduce the environmental impact by minimizing outside emissions, can strengthen international competitiveness, and can achieve flexible production.

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#### 2. Progress of Research and Development

The new process was developed in four steps as shown in **Table 1**. That is, basic study with a 100 kg test melting furnace (Step 1), basic technology development by the medium-scale testing of a 60 t electric arc furnace (Step 2), new installation of Yawata Environmentally-friendly Smelter (YES) and general-purpose industrial technology development by synchronous operation with an integrated BF-BOF process (Step 3), and expansion of the application rate (Step 4). This progress is described below.

(1) Step 1: Basic study with test melting furnace (2005 to 2007)

We conceived the new resource recycling system by YES in 2005. To quantitatively clarify the process concept, we experimented with a 100 kg air melting furnace. Concerning the technology for reducing Cr oxide on high-Cr hot metal, we studied the following

on a laboratory scale: (i) Cr oxide reducibility, (ii) Cr oxide reduction rate, (iii) effects of silicon (Si) and slag composition on Cr oxide reduction limit, (iv) effect of hot metal temperature, and (v) effect of hot metal bath stirring.

 Step 2: Basic technology development with 60 t electric arc furnace (2006)

At Hikari Works of Nippon Steel & Sumikin Stainless Steel Corporation, SUS was melted in AC electric arc furnaces. We conducted the reduction test of Cr oxide-containing slag with a 60 t electric arc furnace in 2006.

Concerning the technical points of YES we developed with the 100 kg air melting furnace, or (i) reducibility with high-Cr hot metal, (ii) effect of slag composition on the reduction rate, (iii) effect of slag composition on the Cr oxide reduction limit, (iv) effect of hot

Table 1 Development review of multi-material recycling system by YES (Yawata Environmental-friendly Smelter)



\*Application ratio : YES operation ratio synchronized with LD operation for stainless. All ferrous scrap & oxide containing Cr are currently reduced.

metal temperature, and (v) effect of hot metal bath stirring, we verified with an electric arc furnace at Hikari Work by using Cr oxidecontaining slag formed in BOF at Yawata Works, confirmed that the optimum slag composition in the 100 kg air melting furnace could be applied to YES, and identified Cr oxide reduction conditions on a plant scale. We confirmed the temperature dependence of the discharge of reduced slag from an electric arc furnace by testing with a commercial-scale furnace. This was difficult to do with a 100 kg air melting furnace. Stable industrial production conditions were thus identified.

(3) Step 3: Development of general-purpose industrial technology (2005 to 2010)

As soon as the use of Cr-containing agglomerated dust was started, the detailed design of 90 t YES was conducted based on the results of Steps 1 and 2. YES was constructed in 22 months. We started up YES in April 2010 and started fully-fledged operation of the new resource recycling system by YES within the year.

When YES initially started up, it experienced time extension due to unmelting of some charge materials and abnormal wear of hot spot refractories. Measures were taken to prevent these problems as described later. Consequently, we established the technology for stably melting Cr-containing BOF slag in YES with high speed and efficiency and completed the resource recycling system technology by YES. Since manganese (Mn) in the steel scrap was concentrated by the repetition of Cr-containing steel scrap recycling operation in YES and of non-reduction operation in the BOF, the advantage of Mn recovery was enjoyed by tapping the molten steel from the BOF without the reduction of Cr oxide-containing slag for general-purpose SUS grades that need not be purified further.

(4) Step 4: Increase in application rate (2017 to date)

As originally planned, YES operation was performed at night except for special cases. In the second half of fiscal 2016, YES operation was applied to 49% of 13 SUS heats per day. The application rate of 71% is now targeted (Table 1). As former Nippon Steel Corporation and former Sumitomo Metal Industries Co., Ltd. merged in 2012 and Nisshin Steel Co., Ltd. joined the Nippon Steel group in 2017, Yawata Works increased the accepted amount of useful Cr-containing by-products from other works in the group. The YES application rate is now being increased at Yawata Works.

#### 3. Content and Characteristics of Research and Development

#### 3.1 Overview of conventional process

Typical examples of SUS manufacturing processes are the electric arc furnace-argon oxygen decarburization (AOD) method combination for Cr-Ni SUS and the BF-BOF combination or electric arc furnace-BOF-vacuum oxygen decarburization (VOD) method combination for Cr SUS.

A conventional process for making SUS by using BF hot metal is adopted at Yawata Works. This process is outlined in Fig. 1. The carbon concentration of the hot metal tapped from the BF is 4.5%. This high carbon concentration must be reduced to an appropriate level to suit the required SUS properties. Oxygen (O<sub>2</sub>) gas is blown into the hot metal in the BOF for removal of carbon as CO gas (crude decarburization). Cr materials like ferrochromium alloy (FeCr) are charged and melted. The BOF molten steel is heated by utilizing the heat of C combustion to the temperature required for secondary refining and subsequent steps. At the same time as crude decarburization, refining fluxes like lime are charged. The resultant hot metal is desiliconized by the oxidation reaction. During crude decarburization, part of Cr is oxidized into Cr oxide and melted in the slag. At the end of BOF refining, ferrosilicon alloy (FeSi) is charged to reduce the Cr oxide by Si. The Cr source is recovered from the slag into the molten steel and the molten steel is tapped from the BOF into a ladle.

Next in the secondary refining step, the ladle is vacuum pumped to lower the CO partial pressure. Under this condition, the  $O_2$  gas is blown into the molten steel for decarburization finish. The H, N, and



Fig. 1 Conventional manufacturing method for stainless steel

O gas components are removed and ferroalloys are added for composition adjustment. After secondary refining, the molten steel is cast into slabs or semifinished steel products on a continuous caster.

With this conventional process, the proportion of FeCr in the BOF blend of raw materials was high and the thermal margin was low. The recycled and reused quantity of Cr-containing by-products was thus restricted. Also, high-Cr oxides produced during decarburization refining were reduced by FeSi and recovered, resulting in the large production of slag. Furthermore, since the molten steel was tapped after the reduction and recovery of Cr oxides, the entrapment of air during the tap increased the N concentration of the molten steel and increased the denitrification load on secondary refining. **3.2 New process** 

#### 3.2.1 Overview of new process

The new process is schematically illustrated in **Fig. 2**. In the flow sheet of the new process, Cr oxide-containing slag produced in the BOF is melted together with Cr-containing steel scrap and FeCr material to reduce Cr. After that, Cr-containing YES hot metal and the pretreated BF hot metal are charged into the BOF and crudely decarburized. The crudely decarburized molten steel is tapped unde-oxidized. The formed unreduced BOF slag is recovered with a slag pan and transported to YES. The tapped molten steel is vacuum treated in the secondary refining step and cast into slabs in the continuous caster.

The new process can recycle and melt all of the Cr-containing by-products in YES by increasing the thermal margin through the utilization of electric energy. The unreduced BOF slag is melted together with general-purpose FeCr. Cr oxides can be reduced by Si in the general-purpose FeCr and the use of the reductant FeSi can be sharply reduced. As a result, the formation of slag can be substantially reduced. Since the molten steel is not reduced before it is tapped from the BOF, the N concentration in the molten steel can be reduced and the secondary refining load can be lessened. **Figure 3** shows the change in the overall Cr mass flow in the conventional and new processes. The amount of Cr lost by outside discharge from the new process was greatly reduced as compared with the conventional process.

3.2.2 Elemental technologies comprising new process

The new process consists of the following five elemental technologies:

- (1) Technology for treating in YES with high speed and high efficiency
- (2) Technology for protecting refractories of YES
- (3) Technology for using a combination of BF hot metal and Crcontaining hot metal in YES
- (4) Technology for pretreating Cr-containing dust
- (5) Technology for producing unreduced Cr oxides in BOF
- (1) Technology for treating in YES with high speed and high efficiency

The technology for treating in YES with high speed and high efficiency is unique in the world. With electric arc furnace operation, the specific reaction area between the slag and the steel bath is small and there was insufficient time for the reaction to complete. Generally, reaching the equilibrium state is regarded as difficult.<sup>4)</sup> On the other hand, YES carried out reduction to equilibrium by optimization of fluorspar-free slag composition and of internal stirring and minimized the discharge of Cr out of the slag by reducing the amount of slag formed and by minimizing the amount of Cr oxides remaining in the slag.

First, we conducted a systematic study by experimenting with a 100 kg melting furnace and evaluated the reduction rate of Cr oxides. We confirmed that the reduction reaction of Cr oxides is generally a primary reaction under various conditions. The reaction rate is given by Equation (1):

$$\frac{d(\%Cr_2O_3)}{dt} = k(\%Cr_2O_3)$$
(1)

where *k* is the primary Cr reduction reaction capacity coefficient (1/min) and (%Cr<sub>2</sub>O<sub>3</sub>) is the Cr oxide concentration of the Cr oxides



Fig. 2 New manufacturing method for stainless steel

(mass%). Hereinafter, the magnitude of the reaction rate was evaluated by the primary Cr reduction reaction capacity coefficient k.

Figure 4 shows the reaction rate,  $Cr_2O_3$  concentration (% $Cr_2O_3$ ), viscosity, and liquid phase fraction in the reduced slag when the slag composition was changed under certain stirring conditions. After investigating correlations with various indicators, we found that the correlations were strongest when the slag basicity (%CaO)/  $\{(\%SiO_2) + (\%Al_2O_2)\}$  (basicity CSA) was used as the indicator as shown along the horizontal axis of Fig. 4. The relationship between the slag viscosity and composition in the liquid phase region was



Fig. 3 Change of mass flow of Cr





obtained by the equation of Iida.<sup>5)</sup> In the liquid phase region, the viscosity obtained by the equation of Iida was taken as the viscosity of the medium and the viscosity that accounts for the solid phase was estimated by the equation of Mori and Ototake.<sup>6)</sup> The relationship between the liquid phase fraction and the composition was calculated by the thermodynamic equilibrium calculation program SOLGASMIX.<sup>7)</sup>

In the region where the basicity CSA is less than 1.1, the higher the basicity CSA, the higher the reduction rate became and the lower the ultimate concentration ( $%Cr_2O_3$ ) after reduction got. This is considered due to the improvement of the mass transfer rate by the viscosity reduction of the molten slag. When the basicity CSA exceeded 1.1 and became excessively high, the reaction rate was seen to decline. This is probably because the slag decreased in the liquid phase fraction, entered the solid--liquid coexisting region, sharply increased in viscosity, and worsened in overall fluidity.

The results of the 100 kg melting furnace experiment clarified the following: In the region where the basicity CSA is 1.0 to 1.2, the liquid phase fraction of the slag is 100% and the viscosity of the slag is low. The formation of the steel-slag emulsion is promoted and the reduction rate becomes highest. At the same time, the  $Cr_2O_3$ concentration (% $Cr_2O_3$ ) in the reduced slag is decreased. This study is based on the assumption that fluorspar (CaF<sub>2</sub>) is not used from an environmental impact perspective. Based on the results of the 100 kg melting furnace experiment, a reduction test with a 60 t electric arc furnace was conducted under the conditions of basicity CSA of 1.0 to 1.2, stirring intensity of 0.04 kW/t, temperature of 1650°C, and Si content of 0.2%. It was confirmed that the same reduction results as those with the 100 kg melting furnace can be obtained.

The next initiative was to improve the internal stirring conditions under which the improvement of heat transfer and melting can be expected throughout the melting period. The electric arc furnace is generally a facility to produce crude hot metal by melting steel scrap. The hot metal is not stirred or is stirred by a small amount of nitrogen (N<sub>2</sub>) gas blown through the bottom or with an electromagnetic stirrer installed in the bottom. YES initially had a stirring function with the N<sub>2</sub> gas blown through three tuyeres in the bottom to ensure stirrability. In YES with high blend proportions of low-thermal conductivity charge materials, a sufficiently high stirring effect to improve the heat transfer was not obtained.

To promote the heat transfer and melting of low-thermal conductivity charge materials, we then took the initiative to increase the melting of such materials by improving internal stirring. The stirring improvement initiative was implemented in four steps as shown in **Table 2**. In Step ①, the gas type was changed from the  $N_2$  gas to argon (Ar) gas, an inert gas that is not absorbed into the hot metal. In Steps ② and ③, the gas flow rate per tuyere was increased to increase the stirring intensity. In Step ④, the number of tuyeres was doubled from 3 to 6 to further intensify the stirring effect. **Figure 5** shows the arrangement of bottom blowing tuyeres in the respective steps.

A commercial-scale electric arc furnace is shaped to distribute the slag relatively shallowly and widely as compared with the laboratory melting furnace. The uneven distribution of the slag may retard the Cr reduction reaction rate.

The bottom gas blowing positions were optimized by numerical fluid analysis (with the general-purpose thermo-fluid analysis software FLUENT) while taking into account stirring by electric heating. An example of the analysis results is shown in Fig. 6. With the AC electric arc furnace, arc discharge from the three electrodes creates electromagnetic forces in the furnace wall direction. The electromagnetic forces produce surface flow from just below the electrodes toward the furnace wall closest to the electrodes, called hot spots, but stagnant regions form between the electrodes. The bottom blowing tuyeres were arranged between the electrodes to spatially uniformize the slag velocity distribution and achieve efficient stirring. Concerning the arrangement of the tuyeres between the electrodes, the total bottom blowing gas flow rate was the same in Step ③ with one tuyere between the electrodes and Step ④ with two tuyeres between the electrodes, but the arrangement of two tuyeres between the electrodes reduced the occurrence of unmelted charge materials from 35% to 1%. As the numerical fluid analysis results show, the increase in the number of tuyeres from three to six spatially spreads and equalizes the between-electrode stirring flow on the

Table 2	History	of improvement	of bottom	blowing
			01 000000	~~~~

Ston	Data	Itom	Gas	Flow rate	Number
Step	Date	Itelli	Gas	(Nℓ/min)	of tuyere
Initial	2010.04	YES start-up	rt-up N <sub>2</sub>		3
1	2010.10	Bottom blowing	Δ.,	600	3
		Gas: $N_2 \rightarrow Ar$	AI	000	
2	2010.11	Bottom blowing	Δ.,	000	3
		Gas flow rate: #1	AI	990	
3	2011.02	Bottom blowing	Δ.,	1 200	3
		Gas flow rate: #2	AI	1200	
(4)	2011.04	Bottom blowing	Δ.,	1 200	6
		tuyere arrangement	Aſ	1200	



Fig. 5 Arrangement of bottom blowing tuyeres

hot metal surface. The stagnant regions are substantially reduced to achieve efficient stirring.

Sawada and Ohashi<sup>8)</sup> analyzed the flow velocity field obtained by numerical calculation with the k-ɛ model as for the stirring velocity by the bottom blowing gas and found the following proportional relationship to hold between the average liquid flow velocity Wp and the bottom blowing gas flow rate Q in the gas-liquid mixture region:

$$Wp \propto Q^{0.52} \tag{2}$$

From Equation (2), when the gas flow rate Q is doubled, the average flow rate increases by 1.4 times. Let the average flow velocity per tuyere in Step (4) be  $Wp_{A}$ . Then, the average flow velocity in Step (3) becomes 1.4  $Wp_4$  from Equation (2). When the number of tuyeres is doubled at the same flow rate, the average flow velocity becomes  $(Wp_4 \times 2)/1.4Wp_4 = 1.4.$ 

The average heat transfer coefficient in flat plate turbulence is approximately given by Equation (3).9)

$$cm \propto \frac{u_0^{0.8}}{l^{0.2}} \tag{3}$$

where  $\alpha_{cm}$  is the average heat transfer coefficient (W/m/K),  $u_0$  is the flow velocity (m/s), and l is the flat plate length (m). Doubling the number of tuyeres from 3 to 6 is considered to have increased the average heat transfer coefficient by the 0.8 power law of the flow velocity ratio.



(a) Flow velocity distribution on the circumferential cross section at tuyere (number of tuyere: 3)



(b) Flow velocity distribution on the circumferential cross section at tuyere (number of tuyere: 6)



(c) Flow analysis results

Fig. 6 Evaluation of stirring in the furnace by flow analysis



Fig. 7 Prevention from remaining unmelted by improvement of bottom blowing

Since the heat transfer was increased by improving stirring as described above, the occurrence of unmelted charge materials was reduced below 1%. The improvement effects in the respective steps are shown in **Fig. 7**.

Based on the results of the 100 kg melting furnace experiment, the slag composition was optimized without using fluorspar (basicity CSA=1.0-1.2). Under the conditions of a hot metal temperature of  $1650^{\circ}C$  and [Si]=0.2%, the bottom blowing gas stirring force was greatly strengthened by changing the type of bottom blowing gas, increasing the bottom blowing gas flow rate, and optimizing the tuyere arrangement. As a result, it was made possible to reduce a large amount of Cr oxide-containing slag with high speed and high efficiency.

The differences between high-speed and high-efficiency reduction established with YES and reduction before BOF tapping with the conventional process are explained with the aid of an Ellingham diagram and equilibrium oxygen partial pressure.<sup>10)</sup> When decarburization in the BOF reduces the C concentration of the hot metal from 4.5 mass% to 0.5 mass%, the oxygen partial pressure increases from  $10^{-15}$  atm to near  $10^{-10}$  atm and accelerates the oxidation of Cr (**Fig. 8**).

With YES, FeCr, Cr-containing scrap, and unreduced slag are charged and melted, and Cr-containing pseudo hot metal is produced with a C content of 4 mass% close to C saturation. Melting is possible in a reducing atmosphere with a low oxygen partial pressure. Furthermore, the higher the [C] concentration, the higher the [Si] activity becomes. The [Si] activity in the reducing atmosphere of YES is five times higher than after crude decarburization in the BOF. These two effects mean that YES is predominantly advantageous in the reduction of Cr oxides (**Figs. 9** and **10**).<sup>11</sup>

With the electric arc furnace operation, the specific reaction area between the slag and the steel bath is small and there is insufficient time for the reaction to complete. Generally, it is difficult for the reduction reaction of the slag to reach the equilibrium state.<sup>4)</sup> With YES reduction, the slag composition and internal stirring are optimized as described above. As shown in **Fig. 11**, the reduction progresses approximately to the equilibrium state. The amount of Cr oxides remaining in the slag is minimized as a result.

(2) Technology for protecting refractories of YES

In the AC electric arc furnace, arc radiant heat as high as about 5000°C creates high-heat load areas or hot spots (HS) in the furnace refractory wall and near the electrodes at and after the end of the



Fig. 8 Relation between oxide standard producing free energy change and temperature

melting period. Prevention of the abnormal wear of the wall refractories is necessary for the furnace to operate stably (**Fig. 12**).

In its initial operation, YES also had the abnormal wear of the HS refractories. Measures were taken against this refractory wear. Concerning refractory wear in electric arc furnaces, Nanjo and Yasukawa<sup>12)</sup> presented the refractory wear coefficient expressed by Equation (4). Equation (4) was referred to when optimizing the energizing pattern of YES.

$$R_{\rm ef} = \frac{P_{\rm a} \times E_{\rm a}}{d^2} \tag{4}$$

where  $R_{ef}$  is the refractory wear coefficient,  $P_a$  is the arc power,  $E_a$  is the arc voltage, and *d* is the distance from the electrode to the refractory wall.

The energizing pattern was optimized, refractory gunning repair was improved, and the operating rate was improved. During the reduction of Cr-containing BOF slag in YES, the length of arcs discharged from the electrodes was controlled to less than the thickness of the molten slag layer (**Fig. 13**). The amount of HS refractory



Fig. 9 Oxidation free energy change of C, Mn and Si in iron  $(a_M: Activity at 1 wt\%, Henry's law)$ 

wear, a problem experienced immediately after the startup of YES, was reduced to one-tenth (Fig. 14).



Fig. 11 Comparison between Cr content in slag between equilibrium value and operation results



Fig. 10 Comparison of reducing capacity of chromium oxide on various silicon activity between LD and YES



Fig. 12 Schematic diagram of AC electric furnace operation process

(3) Technology for using a combination of BF hot metal and Crcontaining hot metal in YES

To establish the new resource-recycling SUS making process by utilizing the BF hot metal, a low-cost and high-grade iron source, and by using YES with electric energy utilization and with a high degree of freedom operation, it is necessary to increase the Cr concentration of Cr-containing YES hot metal by considering the dilution of the Cr concentration by the BF hot metal. Let us assume that the amount of YES hot metal to be tapped is held constant to maximize the amount treated in the finish refining stage from the standpoint of minimizing the manufacturing cost. To change the Cr concentration of the molten steel tapped from the BOF with the Cr concentration of the finished SUS product, it is necessary to adjust the Cr concentration of YES hot metal tapped. That Cr concentration is about twice the Cr concentration of the finished SUS product. **Figure 15** shows the actual Cr distribution ratio between the slag and



Fig. 13 Appearance of electrode submerged into slag during YES operation



Fig. 14 Results of measures for preventing wear of refractory at furnace wall in YES



Fig. 15 Improvement of chromium distribution between slag and metal by YES

the hot metal tapped from YES. According to Fig. 15, YES operates in a high Cr region. As a result of operating YES with lower Cr distribution to the slag, the Cr distribution to the slag was reduced to one-fourth of that in general electric arc furnaces and the Cr oxides were successfully reduced to the theoretical equilibrium value. This was the world's first achievement of its kind for large-scale industrial furnaces.

(4) Technology for pretreating Cr-containing dust

Large amounts of pure oxygen are blown into the BOF from the top and bottom. The BOFs are capable of high-speed decarburization and have high productivity. They are widely used throughout the world as steel refining facilities. High-speed decarburization produces a large amount of CO. CO is useful as fuel gas. Nippon Steel developed the oxygen BOF gas recovery system or OG system. In 1962, the first OG equipment was implemented on the No. 1 BOF at the No. 1 steelmaking shop of Yawata Works. This BOF now produces SUS. The CO gas, previously released to the atmosphere, can now be recovered as fuel gas. To recover the CO gas formed in a large amount in the BOF, it is necessary to draw in the CO gas at a rate commensurate with its formation rate. The OG system collects dust with water and separates and recovers dust from the BOF gas.

In SUS manufacture at Yawata Works, the thermal margin was severe and the by-products were difficult to recycle. Treatment technology was developed for reducing the heat consumption to recycle the Cr-containing dust recovered by the OG process. **Figure 16** schematically illustrates the BOF dust recovery system and Cr-containing dust treatment.

The BOF gas dust is very fine in particle size. When briquetted, it still reacts with oxygen in air, accelerates the oxidation of iron, and generates heat or fire in storage tanks and the like. Given this safety risk, the BOF gas dust was oxidatively dried in its original state for a long time. When the dust is oxidatively dried, however, most of its iron is oxidized. To recycle the dust into the BOF, energy is required to reduce the iron oxides contained. For this reason, it was difficult to recycle the dust to SUS melting BOFs with a low thermal margin. A dense oxide film was formed on the surface of dust particles by a high-pressure extrusion process. This film prevented the infiltration of oxygen into the dust particles. The heating and fire risks with the dust were successfully eliminated in this way. The high-pressure extrusion process for Cr-containing dust is outlined in **Fig. 17** and is compared with the dust briquetting process in **Table 3**.

In the new resource recycling system by YES, it is essential to improve the thermal margin by using electric energy in YES. If the melting of Cr-containing steel scrap and FeCr and the reduction of Cr oxide-containing slag are performed in YES, the thermal margin in the BOF can be increased. With the combined use of the abovementioned high-pressure dust extrusion process, we succeeded in recycling all of the Cr-containing by-products, such as steel scrap, slag, dust, and scale.

(5) Technology for producing unreduced Cr oxides in BOF

YES started its operation with sharply reduced Si sources. The amount of slag consequently formed decreased substantially and there was insufficient slag available to cover the hot metal surface. As shown in the schematic diagrams of **Fig. 18**, hot metal splashing during high-speed decarburization with top and bottom blown oxygen in the BOF increased the skulling of the BOF mouth and the top blowing oxygen lance. These situations made it difficult for the BOF to continue its stable operation.



Fig. 16 Schematic diagram of LD dust recovery and recycling system



Fig. 17 Extrusion procedure of dust containing chromium

	Appearance	Oxygen distribution	Composition and property							
Briquette (Conventional)	Somm	0 Croc Area 32,81 3,4 22,84 6,3 22,84 6,3 24,66 11,7 24,66 11,7 24,67 11,7 24,7 24,7 24,7 24,7 24,7 24,7 24,7 24	<composition> (mass%)</composition>							
			T.Cr	T.Fe	M.Fe	FeO	Fe <sub>2</sub> O <sub>3</sub>	CaO	Metallization	
			5	65	4	21	63	3	6%	
			<property></property>							
			0	Open pore		Average oxygen (%)				
				(%)		Line analysis		I	Plane analysis	
				20.1		22.2			21.5	
		Ave 21.54								
Extruder (This method)	50mm	0 Ocnc. Area 2 8,000 0.4.4 22,01 1.0 39,000 2.4 22,01 1.0 39,010 2.4 22,01 1.0 39,010 2.4 22,41 5.2 22,45 7.6 24,06 0.4 24,06 0.4 24,07 0.4 24,07 0.4 24,07 0.4 24,08 0.4 24,07 0.4 24,07 0.4 24,07 0.4 24,07 0.4 24,07 0.4 24,08 0.4 24,09 0.4 24,07 0.4 24,00 0.4 2	<composition> (mass%)</composition>							
			T.Cr	T.Fe	M.Fe	FeO	Fe <sub>2</sub> O <sub>3</sub>	CaO	Metallization	
			8	60	20	47	5	10	33%	
			<property></property>							
			Open pore			Average oxygen (%)				
				(%)		Line analysis		I	Plane analysis	
				9.2		15.2			16.1	
		Aug 16 10 0.0								

 Table 3 Comparison of agglomeration method

We then attempted to skill ourselves in operating the BOF and decided to form slag by continuously charging part of FeCr from the top of the BOF. As a result, the skulling of the furnace mouth and the top blowing oxygen lance was inhibited and the technology was established for tapping the BOF without reducing the slag. With BOF tapping with the unreduced slag, the Cr oxides in the slag are



Fig. 18 Schematic diagram of metal droplet (spitting) during BOF operation

not reduced and the molten steel is not deoxidized. As a result, the molten steel is tapped into the ladle with its high O concentration and transported to the next secondary refining step. When tapped, the molten steel contacts air and absorbs N. Choh and Inoue<sup>13</sup> expressed the effect of the O concentration on the N absorption rate between the gas and the molten iron by Equation (5).

$$\frac{d[N]}{dt} = \frac{A}{V} \cdot \frac{k}{[O]^{2/3}} \left( [N]_{eq} - [N] \right)$$
(5)

where  $[N]_{eq}$  is the equilibrium mass concentration of N in the molten iron and in equilibrium with the gas phase (mass%), [N] is the mass concentration of N at time *t* (mass%), *k* is the absorption rate constant of N, *V* is the volume of molten iron (m<sup>3</sup>), and *A* is the gasmetal interface area (m<sup>2</sup>).

When the molten steel is tapped with the unreduced slag from the BOF, the O concentration of the molten steel remains high according to Equation (5). The surface chemical reaction rate constant sharply declines and the absorption reaction of nitrogen from atmosphere air is suppressed.

Figure 19 shows the actual N concentration distributions in the molten steel tapped into the ladle with and without slag reduction before tapping from the BOF. With BOF tapping without slag reduction, the concentration distribution of N in the molten steel in the ladle was clearly lower. This confirms the effect of tapping without slag reduction in inhibiting the N absorption. This helps to reduce the denitrification load on the revolutionary degassing activator (REDA) or VOD process to reduce the N content for the production of high-purity ferritic SUS and to improve the productivity of the process. This also helps to reduce the use of expensive materials, such as titanium and ferroniobium, to prevent grain boundary corrosion (corrosion resulting from the formation of Cr-depleted phases by the formation of Cr carbonitrides at the grain boundaries), a problem with high-purity ferritic SUS, and to reduce the manufacturing cost without detracting from product quality. It also contributes to the improvement of formability by increasing the purity of SUS or reducing the N content of SUS.



Fig. 19 Nitrogen in the ladle after tapping with or without reduction in the BOF before tapping

#### 4. Results of Research and Development

We developed and implemented the new resource recycling SUS making process by introducing YES. We maximized the reuse of Crcontaining by-products in SUS manufacture, minimized the outside discharge of Cr from Cr-containing by-products, reduced the use of Cr, a rare metal, reduced the slag formation, reduced the residual Cr content, reduced the environmental impact by eliminating the use of fluorspar, strengthened our international competitiveness, and achieved flexible production to quickly respond to demand fluctuations.

(1) Resource saving

We recycled Cr-containing by-products using the new resource recycling system by YES. As compared with the conventional process, the consumption of FeCr was reduced by 11%, the consumption of the reductant FeSi was reduced by 88%, the consumption of FeMn was reduced by 3%, the consumption of lime was reduced by 67%, and the production of slag was reduced by 38%. Consequently, the raw material cost was significantly slashed, the thermal ener-

gy required for melting the lime was reduced, and the loss of Cr to the slag and flux was reduced.

(2) Environmental impact reduction

The reduction of Cr oxide-containing slag in YES does not use any fluorspar, conventionally used as slag fluidizer. We developed technology for reducing a large amount of Cr oxides with high speed and high efficiency and without the use of fluorspar, and established it as an industrial production process. As a result, the formed slag contained no fluorspar. This means that we established YES operation technology that meets the Soil Environment Standards of the Ministry of the Environment of Japan. The high-efficiency reduction technology with YES reduced the volume of primary refining slag (BOF or YES slag) by 38%, halved the residual Cr concentration in the slag from 4% to 2%, and reduced the environmental impact.

(3) Productivity improvement

As the Cr oxide reduction technology with YES was established, reduction treatment before tapping from the BOF was rendered obsolete and the suppression of N absorption during tapping helped to reduce the [N] concentration after tapping. This in turn helped to reduce the use of expensive materials, such as titanium and ferroniobium, to prevent grain boundary corrosion (corrosion resulting from the formation of Cr-depleted phases by the formation of Cr carbonitrides at the grain boundaries), a problem with high-purity ferritic SUS, and to improve formability by increasing the purity of SUS products or reducing the N content of SUS products. As the denitrification load in secondary refining was reduced, productivity was improved by shortening the secondary refining time and reducing the retreatment ratio for N removal in the secondary refining step. (4) Strengthening of international competitiveness

We accomplished the total recycling of Cr-containing by-products by applying the new process. The desulfurizing function of YES, a melting and reducing electric arc furnace, enabled the switch from low-sulfur FeCr to general-purpose FeCr. At the same time, the reduction of the N content of SUS products helped to reduce the consumption of materials, such as titanium and ferroniobium, and to ensure the stable supply of high-formability SUS products. As a result, our international competitiveness was strengthened.

(5) Improvement of production elasticity

We accomplished the total recycling of Cr-containing by-products by applying the new process. The consequent recovery of iron sources as well as Cr sources created new iron sources and improved the upward flexibility of iron sources.

#### 5. Future Prospects

In the Cr-type SUS manufacturing process, Cr-containing steel scrap was difficult to recycle, the slag volume increased, and Cr escaped outside. The conventional process had problems with resource saving, environmental impact, and competitiveness.

We developed the new process for reducing a large amount of Cr oxides with high speed and high efficiency. Resource saving was achieved by totally recycling Cr-containing by-products and by sharply reducing the consumption of the reductant FeSi. The environmental impact was lessened by reducing the amount of slag produced, by minimizing the amount of residual Cr oxides in slag, and by eliminating the use of fluorspar. We have strengthened our international competitiveness and have become able to contribute to society through the stable supply of environmentally-friendly SUS products.

The new process is the culmination of five years of research and development between 2005 and 2010 and of seven years of operation know-how after its commercial application. The new process received the Japan Institute of Metals and Materials Technical Development Award in September 2017; the Award for Resource-Recycling Technologies and Systems and the METI Minister's Award from the Japan Environmental Management Association for Industry in October 2017; the Okochi Memorial Grand Production Prize from the Okochi Memorial Foundation in March 2018; and the Commendation for Science and Technology (Development Category) by the Minister of Education, Culture, Sports, Science and Technology in April 2019. We will strive to expand the application of our new SUS steel manufacturing process so that it can contribute to society.

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