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Smelting Reduction of Chromite Ore in an Oxygen Converter

T. IZAWA*, H. KATAYAMA†, and N. SANO‡

** Research Association for New Smelting Technologies, Tokyo, Japan*
†Technical Development Bureau, Nippon Steel Corp., Tokyo, Japan
‡University of Tokyo, Tokyo, Japan

As electrical energy is more expensive in Japan than in other countries, technologies for decreasing the consumption of electrical energy in the processing of chromite ore to stainless steel have been developed. This paper describes the smelting reduction of chromite ore in the production of high-carbon ferrochromium, or the production of crude stainless steel in an advanced oxygen converter without the use of electrical energy as a heat source.

Problems in the smelting reduction of chromite ore (i.e. slag foaming, reduction rate, post-combustion, lining erosion, and so on) can be solved simultaneously by a combination of the following conditions: (1) separation of the metal bath from the oxygen jet by a thick layer of slag and by an adequate blowing operation, and (2) control of the composition of slag as (MgO) + (Al_2O_3) = 45 to 46 per cent.

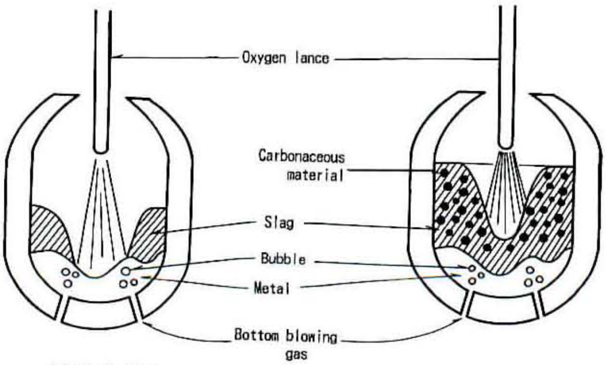
Based on these principles, a pilot-plant test for the production of high-carbon ferrochromium on a 5 t scale (30 t/d) was conducted successfully by the Research Association for New Smelting Technologies. Crude stainless steel is produced from dephosphorized pig iron and partially reduced chromite pellets by the smelting reduction process in a commercial top- and bottom-blowing converter.

Introduction

Conventionally, high-carbon ferrochromium produced in an electric furnace is used as a raw material in the production of chromium steel. In Japan, electrical energy is more expensive than in most other countries; therefore, the technology for the prereduction of chromite ore has been developed with the purpose of reducing the consumption of electrical energy[1,2]. In this decade, various research activities have been devoted to the production of high-carbon ferrochromium or crude stainless steel by the smelting reduction of chromite ore in an advanced oxygen converter. Likewise, various technologies have been developed for the reduction of chromite ore without the use of electrical energy as a heat source. This paper describes these research activities and developmental work. The symbols used are defined at the end of the paper.

Principle of the Process

Recently, the top- and bottom-blowing converter has been used for steelmaking (Figure 1). In this furnace, the stirring intensity of the molten metal and slag can be controlled by the blowing of gas through the bottom. In steelmaking with relatively little slag (50 to 150 kg/t of metal), the metal bath is decarburized by an oxygen jet, Figure 1(a); that is, oxidizing reactions occur. On the other hand, if the metal bath is separated from the oxygen jet by a thick layer of slag containing a large amount of carbonaceous materials, it is possible to proceed with reduction within the slag and to suppress the re-oxidation of the metal, Figure 1(b).



(a) Steelmaking (b) Smelting reduction

FIGURE 1. Operation of the oxygen converter for steelmaking and smelting reduction

Before smelting reduction can proceed at high productivity, it is imperative that those conditions which will stabilize a stirred bath be studied and quantified. For this purpose, the following problems have to be solved:

(1) how to suppress slag foaming
(2) how to accelerate the reduction rate of chromite ore
(3) how to increase the post-combustion ratio,

$$\left(\frac{\%CO_2}{\%CO + \%CO_2} \times 100\right),$$

to achieve the generation of sufficient heat
(4) how to suppress the erosion of the lining.

Results of Fundamental Investigations

In order to solve the problems outlined above, various types of research studies have been conducted.

Suppression of Slag Foaming

In a conventional oxygen converter that is used for the making of steel, molten slag foams extensively, the apparent density of the slag layer being less than 0,2 g/cm^3. If the amount of slag increases under these conditions, stable operation of the converter is disturbed by an overflow or 'slopping' of the slag. The extent of slag foaming depends on the rate of CO generation and on the composition of the slag. However, it has been found that the presence of an adequate amount of carbonaceous materials controls the apparent density of the slag layer to a level of about 1,0 g/cm^3, independent of the slag composition, as shown in Figure 2. This increase in density is due to the fact that carbonaceous materials accelerate the release of CO gas by the coalescence of small bubbles generated by the reduction reactions.

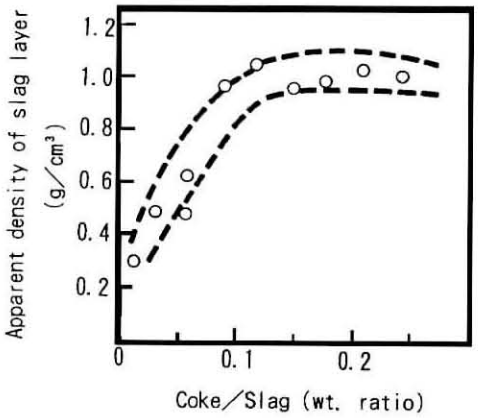


FIGURE 2. Effect of coke-to-slag ratio (by weight) on slag foaming

Acceleration of Chromite Ore Reduction

Chromite ore added to molten slag dissolves at first, and the chromium oxide in the slag is then reduced by carbon. The dissolution of chromite ore is checked by the formation of an insoluble spinel layer ($MgO.Al_2O_3$) around the ore particles. The dissolution of the chromite ore can consequently be accelerated by the addition of fluxes such as fluoride or sodium compounds[3] to the slag, by the injection of fine chromium ore into a hot spot[4,5], or by controlling the composition of the main components of the slag (MgO, SiO_2, and CaO). Figure 3 shows an example of the influence of slag composition on the reduction of chromium oxide. In this case, the addition of silica to the slag accelerates the reduction of chromium oxide by allowing it to dissolve in the slag. The rate of the reduction depends on the composition of the metal, the viscosity of the slag, the amount of carbonaceous materials, the temperature, and the stirring intensity.

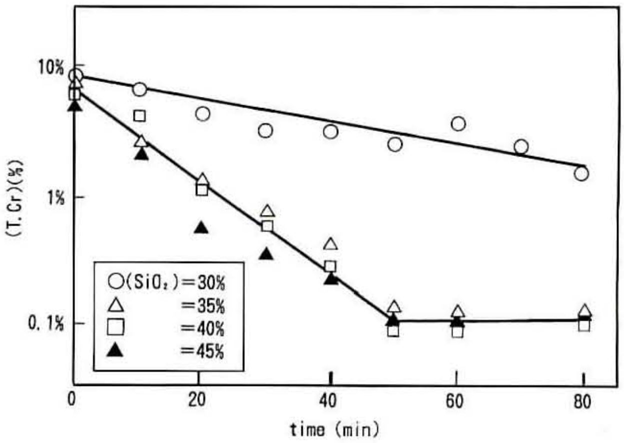


FIGURE 3. Influence of slag composition on the reduction of slag containing chromium oxide by carbon in rocking furnace

The rate formula can be expressed as follows:

for $(T.Cr) \geq$ about 3 per cent,

$$\frac{d(T.Cr)}{dt} = k_0; \qquad [1]$$

for $(T.Cr) <$ about 3 per cent,

$$\frac{d(T.Cr)}{dt} = k_1 \{(T.Cr) - (T.Cr)_f\}. \qquad [2]$$

The relationship between k_1 and the composition of the metal is shown in Figure 4. The rate constant k_1 decreases with $[\%Cr]$, but levels off at chromium contents greater than 20 per cent. This is so because, at lower chromium levels, carbon in the metal contributes to the reduction of the chromium oxide but, with chromium contents higher than 20 per cent, almost all the reduction occurs on the surface of the carbonaceous materials present in the molten slag.

Figure 5 shows the influence of the slag composition on the overall rate constant in an experiment in which argon was introduced by bottom blowing without any top blowing of oxygen, and the slag composition was controlled by the addition of lime. The temperature of the metal bath was 1600 ±20°C and the slag was 0 to 100°C lower in temperature. The rate constant changes abruptly when the

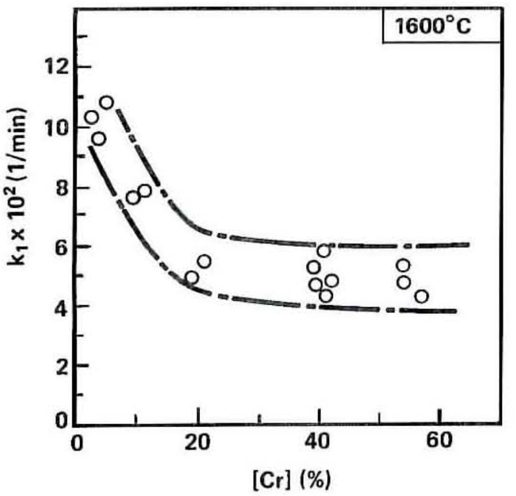


FIGURE 4. Effect of the chromium content in the metal bath on the apparent rate constant, k_1

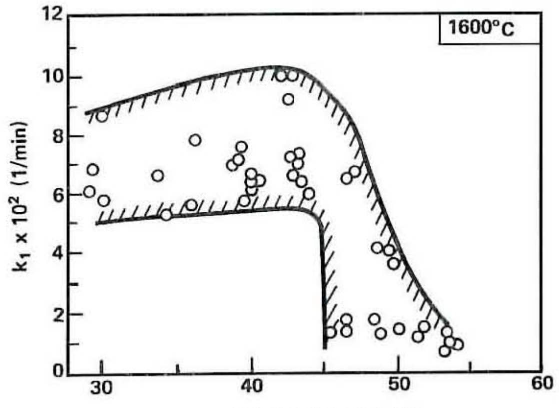


FIGURE 5. Effect of (MgO)) + (Al_2O_3) content on the apparent rate constant, k_1

(MgO) + (Al_2O_3) content reaches 45 per cent. Above that critical value, the dissolution of chromite is supposed to be suppressed.

On the other hand, in an experiment where top blowing of oxygen was used, the temperature of the slag was almost equal to that of the metal bath. Then the critical value of (MgO) + (Al_2O_3) was about 46 per cent at 1600°C. Therefore, the dissolution of chromite ore and the reduction of chromium oxide can be accelerated if (MgO) + (Al_2O_3) is less than the critical value, and this can be achieved by the addition of lime to the slag.

When oxygen is blown from the top, as well as from the bottom, into a carbon-saturated high-chromium metal bath, the total amount of chromium in the slag, $(T.Cr)$, can be decreased and kept as low as 0,3 per cent, independent of the oxygen potential of the atmosphere and the chromium content of the metal, $[T.Cr]$, (Figure 6). Therefore, the re-oxidation of chromium in the metal bath is suppressed under these conditions.

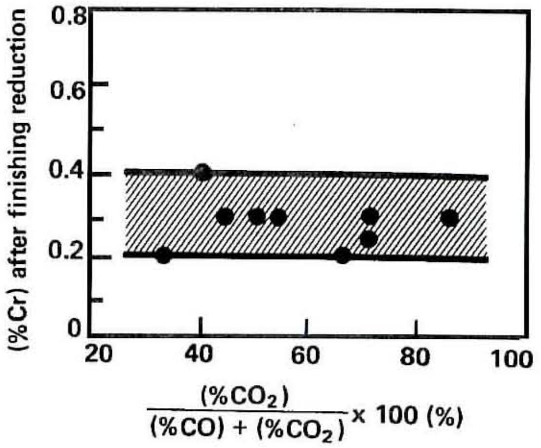


FIGURE 6. Effect of post-combustion on the chromium content of the slag in an oxygen converter with a thick layer of slag

Increase in Post-combustion Ratio

To decrease the phosphorus input, the consumption of carbonaceous material should be decreased by an increase in the post-combustion ratio in the converter. The post-combustion ratio in a conventional oxygen converter for steelmaking is lower than 15 per cent. Nevertheless, separation of the metal bath from the oxygen jet by a thick layer of slag is effective in increasing the post-combustion ratio while at the same time decreasing the formation of dust. This is shown in Figure 7.

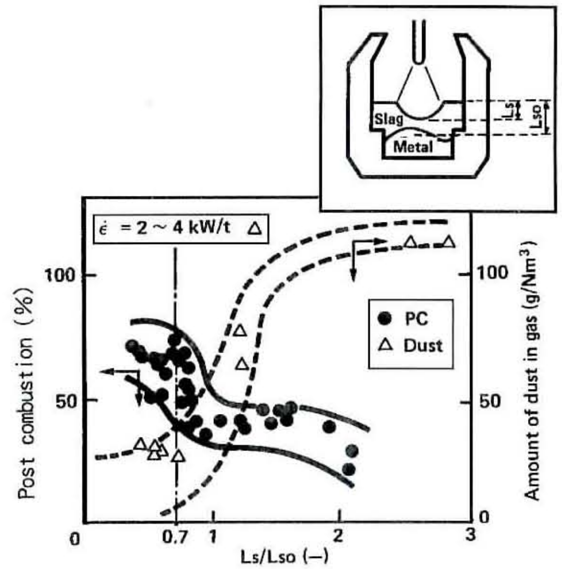


FIGURE 7. Relationship between post-combustion and L_S/L_{SO} in an oxygen converter

Suppression of Lining Erosion

Erosion of the lining depends on the slag composition and the temperature. When MgO–C was used as a lining, the conditions for decreasing the rate of lining erosion, which was about 1 mm/h or less, were as follows:

(i) bath temperature ≤ 1 610°C
(ii) post-combustion ratio ≤ 60% for coke
(iii) slag composition (MgO) + (Al_2O_3) ≧ 45%.

This is shown in Figure 8.

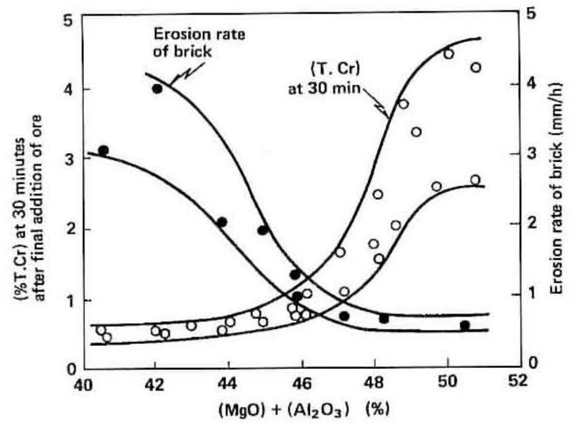


FIGURE 8. Influence of (%MgO) + (%Al_2O_3) on (*T.Cr*) in the slag and the erosion rate of brick in an oxygen converter (temperature 1590–1620 °C, brick MgO–C)

Optimum Operating Conditions

The four problems outlined can therefore be solved simultaneously through the adoption of the following operating conditions:

(a) the use of a thick layer of slag in which foaming is controlled by the presence of carbonaceous material

(b) the use of a slag composition that allows the rapid dissolution of chromite ore and suppresses lining erosion; such a slag must contain 45 to 46 per cent (MgO) + (Al_2O_3)

(c) the combination of soft blowing by top oxygen lancing and adequate stirring intensity by bottom blowing; this procedure separates the metal bath from the oxygen jet.

Production of High-carbon Ferrochromium

Based on the results of the fundamental research investigation, a smelting reduction process was developed that uses an oxygen converter for the production of high carbon ferrochromium. This developmental work was undertaken by the Research Association for New Smelting Technologies between 1981 and 1987. Members of the project team were nominated by the following 11 companies: Nippon Steel Corporation, NKK Corporation, Kawasaki Steel Corporation, Sumitomo Metal Industries Ltd, Kobe Steel Ltd, Nissin Steel Company, Japan Metals & Chemicals Company Ltd, Nippon Denko Company, Awamura Metal Industries Ltd, Daido Steel Company Ltd, and Hitachi Metals Ltd.

Experimental Converter

Table I shows some relevant details of the experimental converter. Top- and bottom-blowing converters of 1 and 5 t (30 t/d capacity) respectively were used. The pilot plant was constructed at the Kimitsu works of Nippon Steel Corporation. Tests were conducted from October 1986 to December 1987. About 1500 t of high-carbon ferrochromium were produced in these tests. Some details of the raw materials used in the experiments are shown in Table II. In the first phase of the test, partially reduced chromium pellets and coke were used and, in the second phase, fine chromium ore and carbonaceous materials low in phosphorus (anthracite or green-oil coke) were used. In addition to this, a rotary kiln was used as a prereducer of the carbon-containing pellets in the first phase of the study, and as a preheater of the fine ore and carbonaceous materials, which contained volatile matter, in the second phase of the study.

The procedure for the operation of the 5 t smelting reduction furnace was as follows. At the start of the operation, 3 t of molten metal were introduced and about 2 t of slag were formed. During the smelting–reduction period, oxygen was blown constantly and the addition of chromite ore or pellets was controlled so that the temperature of the bath was kept constant. The temperature of the metal and the slag was almost the same. After the addition of about 5 t of ore, and after the mass of metal in the furnace had reached 5 to 6 t, 10 to 30 minutes of oxygen blowing were continued in order to decrease the (*%T.Cr*) of the slag (i.e. the finishing reduction period). After the finishing reduction, about 3 t of metal and almost the same amount of slag were tapped, and the next cycle began. The cycle time was 70 to 90 minutes, and the operation was continued for five days (52 cycles) without any difficulties.

TABLE I
EXPERIMENTAL CONVERTER AND OPERATING CONDITIONS FOR THE SMELTING–REDUCTION PROCESS

1 t scale converter		5 t pilot plant	
Smelting–Reduction		**Pretreatment**	
Metal	550 kg	Rotary kiln	Inner diameter 1,7 m Length 35 m
Slag	200 kg (at the start)		
Top blowing	O_2 800 l/min at STP	**Smelting-reduction**	
Bottom blowing	O_2 180 l/min at STP Ar 70 l/min at STP	Top- and bottom-blowing converter	Top blowing of O_2: max. 2700 m^3/h at STP Inner volume 6 – 7 m^3 Metal max. 6 t Slag max. 5 t
Tuyère	1	Tuyère	2

TABLE II
CHEMICAL COMPOSITION AND SIZE OF CHROMIUM ORE AND CARBONACEOUS MATERIALS

	T.Cr	T.Fe	CaO	SiO_2	Al_2O_3	MgO	P	S	R.Cr*	R. Fe†	Fixed carbon	V.M.‡	Ash	Moisture	Size
Partially reduced pellets	26,2	13,8	0,9	9,3	11,9	9,9	0,015	0,139	55,0	90,3	9,8	–	–	0,6	5 – 15 mm
Fine chromium ore	30,7	19,6	0,4	1,9	14,6	9,8	0,003	0,011	–	–	–	–	–	0,1	< 1,0 mm (<0,5 mm, 96%)
Coke	–	1,0	0,4	6,6	3,5	0,3	0,050	0,567	–	–	84,2	2,4	11,9	1,5	5 – 25 mm
Anthracite	–	1,6	0,5	3,5	1,7	3,5	0,012	0,821	–	–	75,9	7,5	12,0	4,5	< 30 mm

* Reduction degree of chromium † Reduction degree of iron oxide ‡VM = Volatile matter

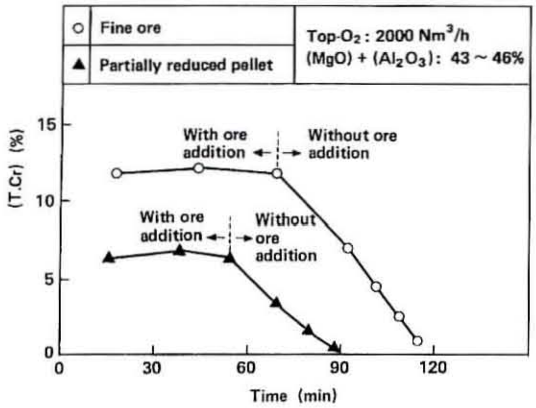


FIGURE 9. Typical behaviour of chromium in slag during smelting–reduction

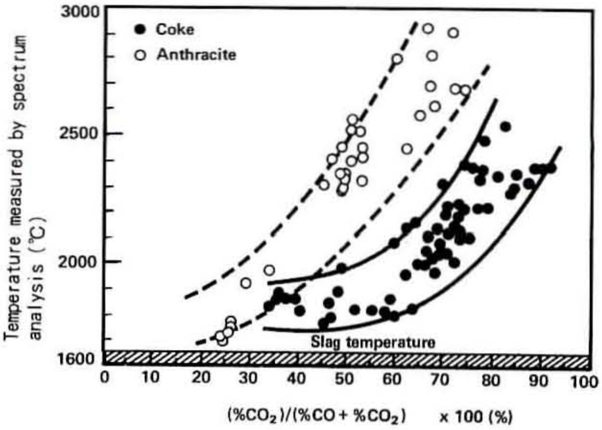


FIGURE 10. Relation between post-combustion ratio and gas temperature in the smelting–reduction furnace

Experimental Results

The typical total chromium content (*%T.Cr*) during the smelting reduction period depends on the rate of chromium oxide supply, which in turn is determined by the rate of oxygen supply, the degree of post-combustion, and the extent of prereduction of the chromite ore, as well as the rate of reduction (Figure 9). The experiments were conducted in a range of (*T.Cr*) between 2 and 14 per cent while stable operations were maintained. In the final reduction period, the (*T.Cr*) was decreased from 10 per cent to less than 1 per cent within 30 minutes, and a minimum of 0,2 per cent was attained. This pattern of (*T.Cr*) change in the 1 t converter was almost identical to that in the 5 t converter.

The gas temperature in the furnace was measured by spectrum analysis and is shown in Figure 10. When the post-combustion was lower than 60 per cent with coke, the temperature was relatively low (about bath temperature plus 150°C) and the heat efficiency was high. Under these conditions, the average rate of erosion of the MgO–C lining was about 1 mm/h.

The compositions of the metal and slag produced by this process are shown in Table III. When the final reduction had been achieved, the chromium content of the metal product was 1 to 2 per cent higher than that of the product from the conventional submerged-arc electric furnace. The silicon concentration is lower, and the carbon content higher, owing to the influence of the silicon on the activity coefficient of carbon. The sulphur content is lower, because of the evaporation of sulphur (about 60 per cent) and the high partition ratio between the slag and the metal.

TABLE III
CHEMICAL COMPOSITION OF PRODUCT

Ferrochromium, %		
Constituent	This process	Conventional process
Cr	57 – 58	56 –57
C	9,0 – 9,5	8,0 – 8,2
Si	0,2 – 0,3	2 – 4
P	0,026* – 0,075†	0,03 – 0,04
S	0,004 – 0,010	0,025 – 0,040
N	0,01 – 0,02	0,020 – 0,025
Slag, %		
Constituent	This process	Conventional process
T.Cr	0,8	1,5 – 3,5
T.Fe	0,4	≈1
CaO	28,0	≈4
SiO_2	25,0	≈32
Al_2O_3	23,5	≈25
MgO	21,5	≈32

Carbonaceous materials: *Oil coke † Metallurgical coke

The nitrogen content was low, even when nitrogen gas was used as the bottom bubbling gas. The phosphorus content of the metal depended on the phosphorus content of the carbonaceous materials. When coke was used, the phosphorus content was higher than that of the conventional electric-furnace product.

To reduce the phosphorus input, the following measures should be introduced:

(1) decrease the consumption of carbonaceous material by increasing the post-combustion ratio

(2) use carbonaceous materials of low phosphorus content.

Carbonaceous materials of low phosphorus content that are available economically tend to be high in volatile matter. This volatile matter increases the gas temperature in the converter, as shown in Figure 10.

In an attempt to decrease the volatile content of the carbonaceous materials before they are introduced into the smelting–reduction furnace, these materials were pre-treated in a rotary kiln. Char obtained from anthracite or green-oil coke played almost the same role as metallurgical coke in the smelting–reduction furnace, and ferrochromium with a phosphorus content of 0,026 per cent was produced.

In this pretreatment study, both the carbonaceous material and the fine ore were pre-heated in order to exploit the heat generated by the combustion of the inflammable gas in the rotary kiln. A mixture of char and preheated fine ore can be added to the smelting–reduction furnace from the top with little carry-over. An example of the mass flow in a commercial-scale operation, calculated from the data obtained from the pilot-plant study, is shown in Figure 11.

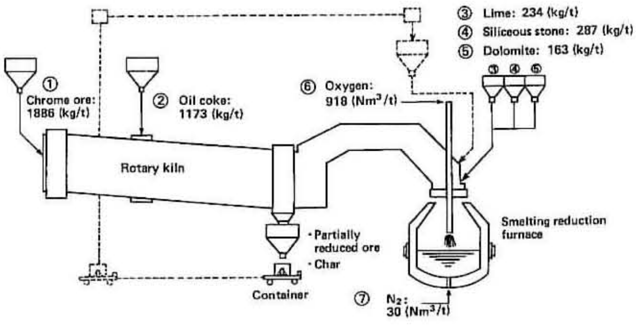


FIGURE 11. An example of the calculated mass flow in the smelting–reduction process on a commercial scale

Production of Crude Stainless Steel

If dephosphorized pig iron is used as the mother metal in the process described, crude stainless steel can be produced direct from chromite ore or from partially reduced pellets.

Figure 12 shows the results of the smelting reduction of partially reduced pellets in a 175 t top- and bottom-blowing converter (LD–OB)[6]. In the production of crude stainless steel with a chromium content of 11 per cent, the total chromium content of the slag by the end of the pellet additions was 3 per cent and, after a stirring period of 10 minutes, 1 per cent.

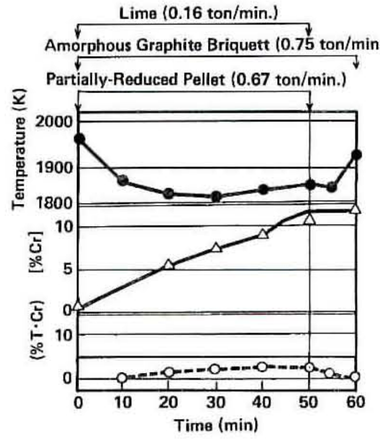


FIGURE 12. Example of the change in composition and temperature during smelting–reduction in an oxygen converter (LD–OB)[6]

Two top- and bottom-blowing converters (K–BOP) may also be used, as reported by Taoka *et al.* [7]. Their system is shown in Figure 13. In the first furnace, smelting–reduction is performed by the addition of 65 per cent prereduced pellets to dephosphorized pig iron and, in the second furnace, decarburization of the melt and scrap melting occur.

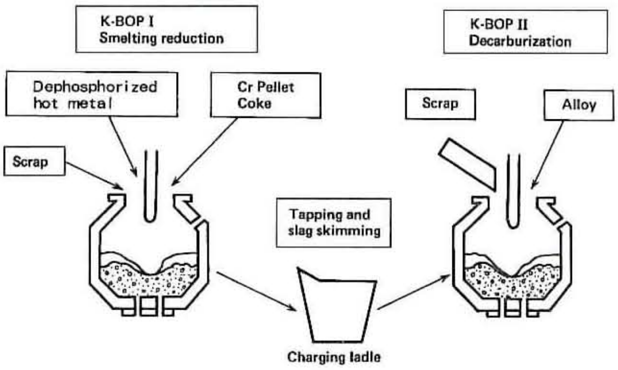


FIGURE 13. Production flow of stainless steel in the smelting–reduction process with two oxygen converters (K–BOP)

Typical changes in the chemical composition and the temperature of the molten metal are shown in Figure 14. Because of the evaporation of sulphur and a high (S)/[S] ratio in this process, the sulphur content of the crude stainless steel after the final reduction period is lower than that in the conventional process for the production of high-carbon ferrochromium.

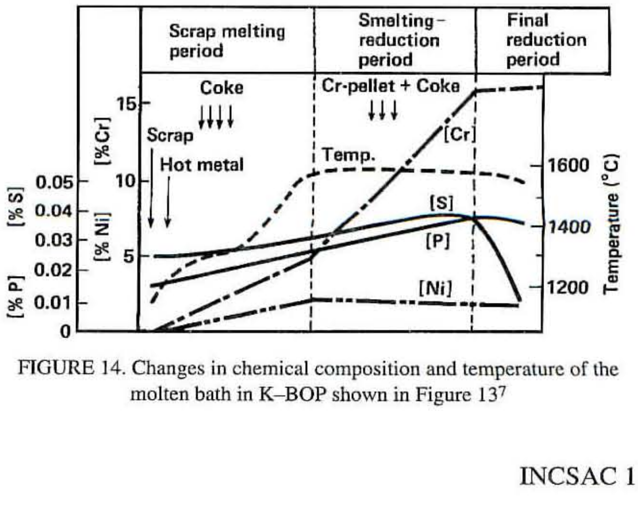


FIGURE 14. Changes in chemical composition and temperature of the molten bath in K–BOP shown in Figure 13[7]

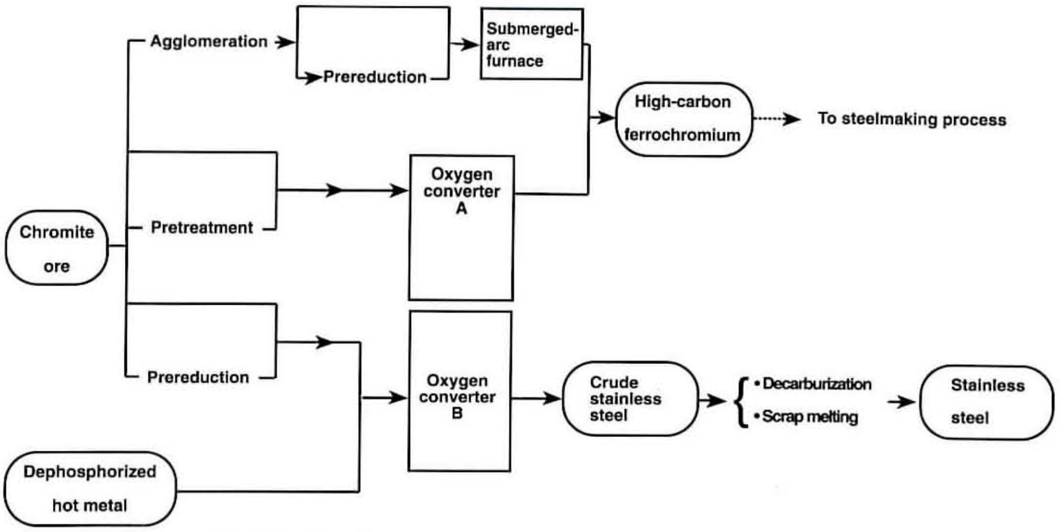


FIGURE 15. Various routes from chromite ore to molten stainless steel

The post-combustion is about 25 per cent. In this process, it is also possible to increase the amount of scrap by the addition of coke in the second furnace. The utilization of smelting–reduction technology has succeeded in improving productivity and lowering energy costs in the making of stainless steel.

Considerations

In the processes for the beneficiation and reduction of chromite ore, many technological advances have been made in Japan, and the process routes that can be considered at present are shown in Figure 15.

A comparison between the production of high-carbon ferrochromium in an oxygen converter and in a conventional electric-arc furnace is given in Table IV. The new process has decided advantages over the conventional process in many respects, but the economic advantages of the new process depend in large measure on the cost of electrical energy.

The actual location of the plant will largely determine whether the production of high-carbon ferrochromium, or that of crude stainless steel in an oxygen converter, will be more economical. If there is a steelmaking plant in the vicinity, the direct use of the molten product is effective for increasing the energy efficiency, and this advantage applies in both cases.

Regarding the pretreatment of chromite ore, the following considerations are of vital importance. In the production of high-carbon ferrochromium, the use of prereduced pellets will lighten the burden of the smelting–reduction step. However, with higher degrees of post-combustion, the necessity of using prereduced pellets decreases. Therefore, pretreatment of ore or carbonaceous material should be considered from the standpoint of utilizing the energy of the exhaust gas from the smelting–reduction furnace and decreasing the content of volatile matter in the carbonaceous materials. However, in the manufacture of crude stainless steel, the use of prereduced ore is effective in shortening the smelting reduction period.

Summary

As electrical energy is expensive in Japan, a technology for decreasing the consumption of electrical energy in the reduction of chromite ore has been sought. In this decade, the process of smelting reduction in an oxygen converter has been developed. At present, the following three processes are possible:

(1) production of high-carbon ferrochromium in a conventional electric-arc furnace

(2) production of high-carbon ferrochromium in an oxygen converter without the use of electrical energy as the heat source

TABLE IV

COMPARISON OF THE SMELTING–REDUCTION PROCESS WITH THE CONVENTIONAL SUBMERGED-ARC PROCESS

Items		Smelting–Reduction process	Conventional submerged-arc process
Materials	Cr ore	Fine ore can be used direct	Lumpy ore or agglomerated ore is necessary
	Carbonaceous	Many sorts of carbonaceous materials can be used	Size control of carbonaceous materials is necessary
Heat source		Combustion of carbonaceous materials and gas	Electric energy (1600 to 4000 kWh/t)
Product		[Si] and [S] level are lower than conventional [P] level depends on the carbonaceous materials used	[Si] level is high

(3) production of crude stainless steel from chromite ore or partially reduced pellets in an oxygen converter.

The process choice depends on the location of the plant, on economic circumstances, and on various other considerations. A practical process for efficient production should be selected after all these variables have been taken into consideration.

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List of Symbols

( ) = Component in the slag phase

[ ] = Component dissolved in the metal phase

$(T.Cr)$ = Total chromium content of the slag phase

$(T.Cr)_f$ = Final total chromium content of the slag phase