"THE PRODUCTION OF FERROCHROME BY THE SMELTING REDUCTION WITH TOP AND BOTTOM BLOWING CONVERTER"

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ABSTRACT

In order to develop the Smelting Reduction Process for the production of ferrochrome by directly utilizing the combustion energy from coal or coke, fundamental experiments using a 100kg high frequency induction furnace and the bench scale experiments using a top/bottom blowing converter of 1t capacity, were conducted. Results summarized in the following suggest a feasibility of the new process.

(1) With slag sufficient to keep the metal bath protected from the oxygen jet, the total chromium content in the slag can consistently be lowered to less than 1%, even under the combustion of coke with oxygen blown (atmosphere, $CO_2/(CO+CO_2)$= 0.3 ∿0.7).

(2) Appropriate slag composition is a major premise toward expediting the reduction of chromium oxide.

(3) With chromium content in the metal bath exceeding 20%, the reduction rate of chromium oxide is nearly constant. Because the reduction mainly occurs at the slag/coke interface and not at the slag/metal interface.

(4) Coke in the slag plays an important role not only in reducing oxide but also in suppressing slag-foaming and in accelerating heat transfer.

(5) The resulting product characteristically contains less [Si] and [S] and more [P], than those produced by the electric furnace processing. To reduce [P], carbonaceous material of lower phosphorus content should be used.

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1. Introduction

Conventional production of high-carbon ferrochrome by the electric furnace process often involves cost problems in countries where the electricity is very expensive as is in Japan. Therefore an economical countermeasure was proposed -- the smelting reduction process by the top/bottom blowing converter where the combustion energy from coal or coke is directly utilized. Studies were conducted in search of the feasibility of this alternative process.

Problems to be encountered and settled were as follows:

(1) to increase the reduction rate of chromium oxide at lower temperature

(2) to reduce chromium oxide under the oxidizing atmosphere

(3) to suppress slag-foaming

(4) to enhance the utilization efficiency of combustion heat of the carbonaceous material

Fundamental experiments without blowing oxygen were conducted using a 100kg high frequency induction furnace to determine conditions required for improving the reduction rate of chromium oxide. Following this, the bench scale experiments with oxygen blown were conducted using a top/bottom blowing mini-converter of 1t capacity to study the feasibility of ferrochrome production.

2. Fundamental Experiments

2.1 Procedures

Fig.1 illustrates the apparatus used in the experiment -- a 100kg capacity high frequency induction furnace. A graphite cylinder was inserted to prevent molten slag contact with magnesia lining. Chrome ore pellet, coke and flux were added onto the carbon-saturated molten Fe-Cr alloy stirred by Ar gas blown from through a porous plug set at the furnace bottom. The behaviour of chromium oxide in the slag was investigated. Experimental conditions and the composition of chrome ore pellet is respectively given in Table I and II.

Slags taken out by an iron-bar sampler were coarsely crushed to remove metal and coke particles prior to the analysis. Some slag samples were examined by microscopy and the Energy Dispersive X-ray Spectrometer (EDX).

2.2 Results

The change of total chromium content in the slag (T.Cr) after the addition of chrome ore pellet differed by region, separated in two by the 3%-boundary as shown in Fig.2.

Table I Experimental conditions

		Standard	Variation
Metal bath	Amount	70kg	—
	(Cr)	40%	0~55%
	Temperature	1600°C	1540~1650°C
Ore	Type	Partially reduced pellet	—
	Amount	6kg	—
Coke	Amount	500g	100~1200g
	Size	5~10mm	—
Slag composition	Al_2O_3 %	17%	15~30%
	MgO	17%	15~30%
	CaO/SiO_2	1.0	0.2~1.7
Slag/Metal ratio		0.08	0.02~0.15
Ar flow rate		6Nl/min	2~10Nl/min

Table II Composition of partially reduced pellet (%)

T·Cr	T·Fe	CaO	SiO_2	Al_2O_3	MgO	P	S	T·C	$\frac{M\cdot Cr}{T\cdot Cr}\times 100$	$\frac{M\cdot Fe}{T\cdot Fe}\times 100$
30.3	16.0	1.2	10.3	13.5	11.8	0.015	0.270	8.0	55.2	88.6

Size, 7 ∿ 13mmϕ

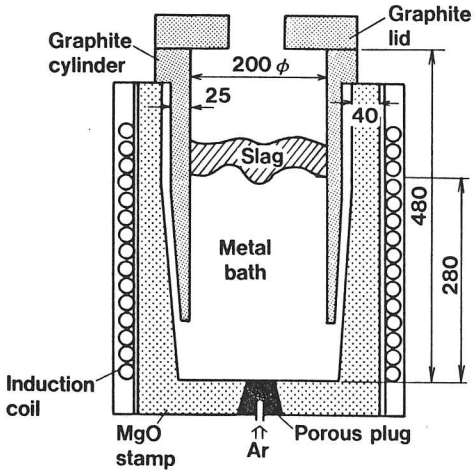


Fig. 1 Experimental furnace (100kg capacity)

In Region I where (T.Cr) exceeded 3%: In the course of time, (T.Cr) decreased linearly as expressed by the rate equation (1) of the zeroth order reaction.

$$-\frac{d(T.Cr)}{dt} = k_0 \quad \cdots\cdots\cdots\cdots\cdots\cdots \quad (1)$$

where

k_0: the rate constant (%/min.)

In Region II where (T.Cr) was less than 3%:
The reduction rate of (T.Cr) decreased in the course of time as expressed by the rate equation (2) of the first order reaction,

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

where

k_1 : the rate constant (min^{-1})

$(T.Cr)_f$: the final chromium content in slag (%)

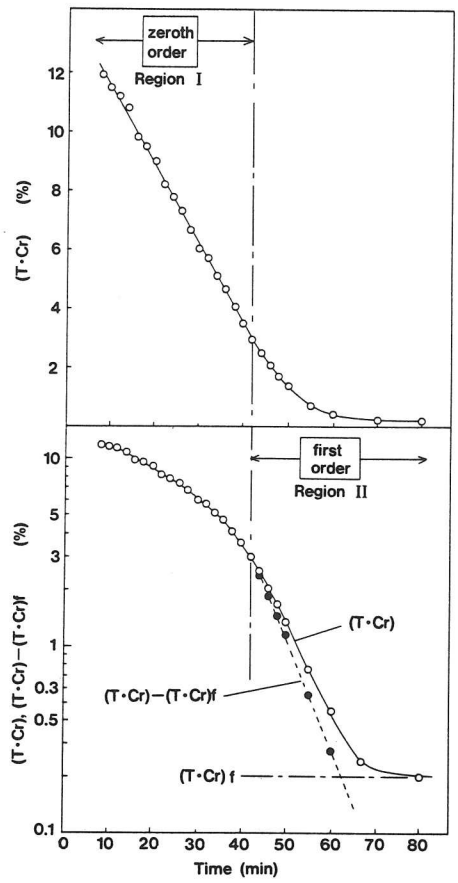


Fig. 2 Typical behaviour of chromium content in slag

(T.Cr) morphogenically consists of chromium included in suspending chrome-spinel particles, chromium dissolved in silicate slag and chromium in fine metal particles, as shown in Fig.3. In Region I, the chromium concentration dissolved in silicate slag was almost constant at about 2%, the (T.Cr) decrease corresponded to the decrease of chrome-spinel particles suspended in the slag. In Region II, spinel particles were not detectable, and the (T.Cr) decrease generally corresponded to the decrease of dissolved chromium. Chromium concentration dissolved in silicate slag in Region I was nearly consistent with the value determined by Morita et. al.[1], who studied on the slag system similar to this experiment. Based on this, changes in (T.Cr) in Region I and II may well share a common rate equation (3) of the first order reaction.

$$-\frac{d(T.Cr)}{dt} = k_1\,[(Sol.Cr)-(Sol.Cr)e] \quad \cdots \quad (3)$$

where

k_1 : rate constant (min^{-1})

(Sol.Cr) : chromium content dissolved in silicate slag (%)

(Sol.Cr)e: equilibrium value of ibid

Since values of rate constants k_0 and k_1 were found substantially the same under respective condition in the experiments, the characteristic function for the chromium reduction rate was unified and represented by k_1.

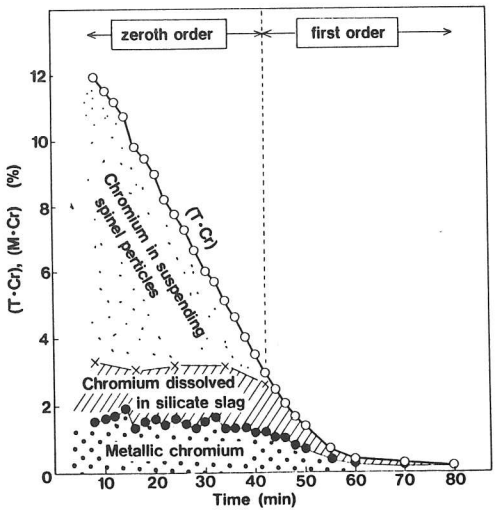


Fig. 3 Change of constituents of total chromium in slag during reduction

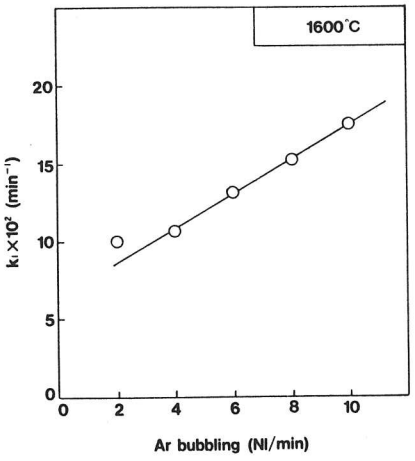


Fig. 5 Effect of stirring by Ar bubbling on the rate constant, k_l

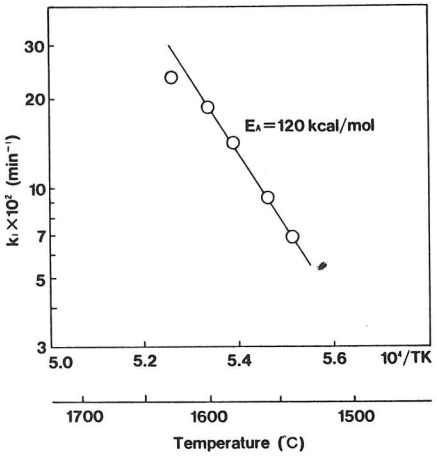


Fig. 4 Effect of temperature on the rate constant, k_l

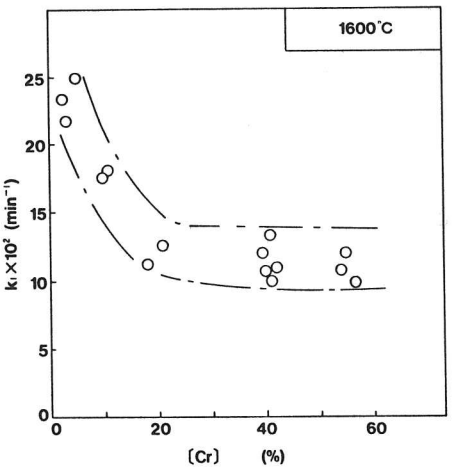


Fig. 6 Effect of chromium content in metal bath on the rate constant, k_l

Studies were conducted on various factors influencing the rate constant k_1. The results are summarized as follows:

(1) k_1 increased with temperature as shown in Fig. 4 (Activation energy: 120 kcal/mol).

(2) k_1 increased with bath-stirring intensity by increasing Ar flow as shown in Fig.5.

(3) k_1 decreased with chromium content in the metal bath increased toward 20%, while it levelled off irrespective of [Cr] over 20% as shown in Fig.6.

(4) With the amount of slag unchanged, k_1 increased with the amount of coke. However it stayed almost unchanged when the coke/slag ratio was constant, as shown in Fig.7.

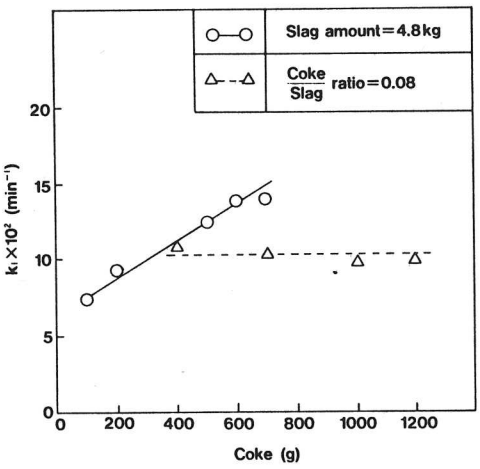


Fig.7 Effect of amount of coke and slag on the rate constant, k_l

(5) Within the following slag composition range at 1600°C metal bath temperature, the value of k_1 was large.

(a) $(MgO)+(Al_2O_3) \leq 45\%$ Fig.8

(b) $\frac{(CaO)+(MgO)}{(SiO_2)+(Al_2O_3)} = 0.8 \sim 1.3$ Fig.9

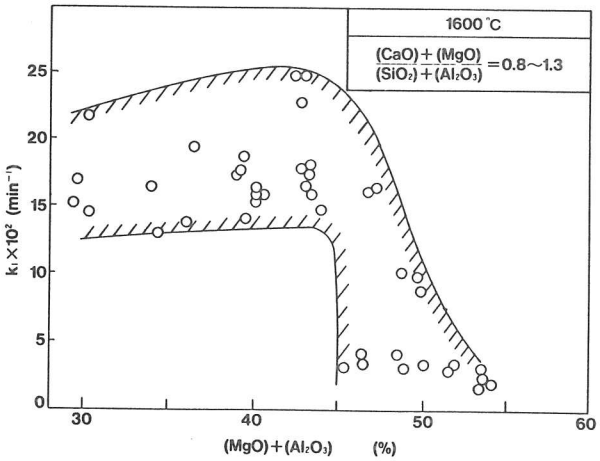


Fig. 8 Effect of $(MgO)+(Al_2O_3)$ content on the rate constant, k_1

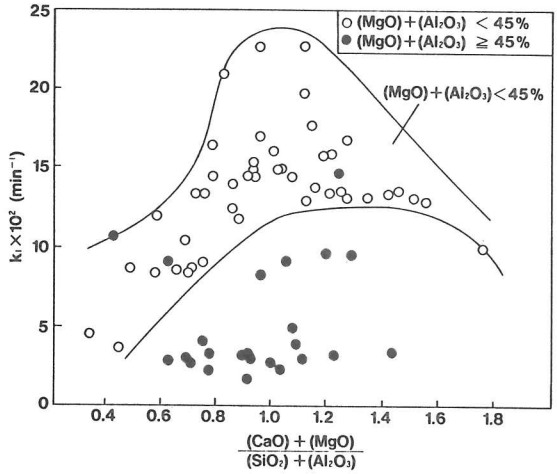


Fig. 9 Effect of slag basicity on the rate constant, k_1

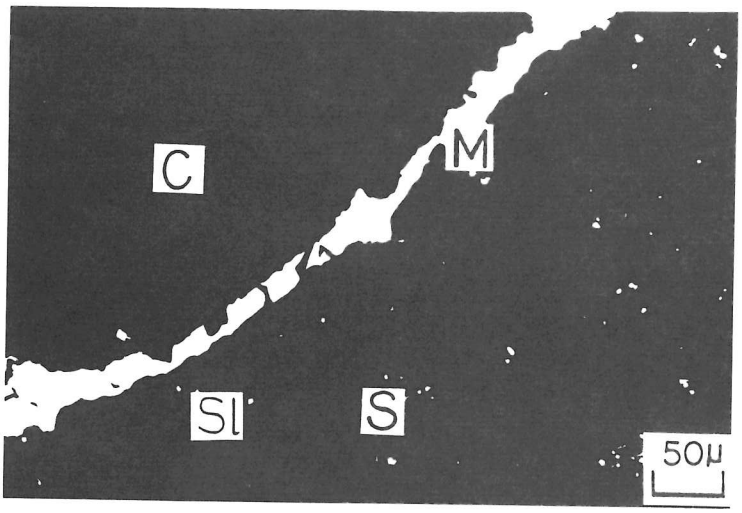
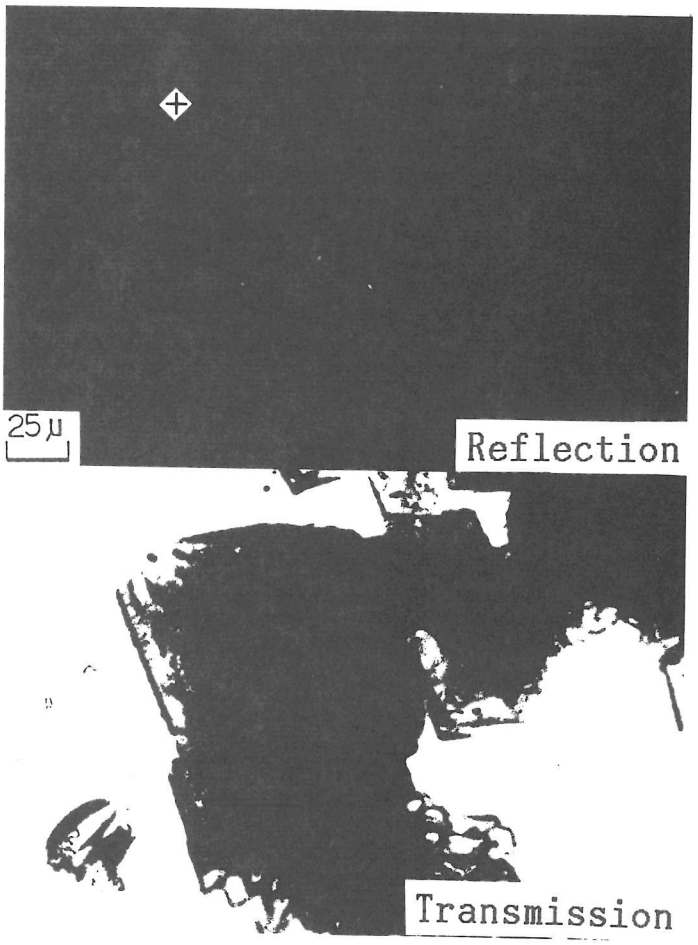


Fig. 10 Metal film observed on the boundary of coke and silicate slag.

Results (3) and (4) indicate that the dominant reduction site of chromium oxide was not at the slag/metal interface, but at the slag/coke interface. In evidence of this, metal films were frequently observed on the coke/slag boundary as shown in Fig.10.

With $(MgO)+(Al_2O_3)$ exceeding 45%, a lot of chrome-spinel particles were found remaining in the final slag. At the same time, thick $MgAl_2O_4$ films covering particles were observed as shown in Fig.11.



Composition at point + by EDX (%)

MgO	Al_2O_3	SiO_2	CaO	Cr_2O_3	FeO	TiO_2
28.9	57.5	0.7	0.3	12.2	0.1	0.3

Fig.11 Formation of $MgAl_2O_4$ phase around Chrome-spinel ($(MgO)=24\%$, $(Al_2O_3)=25\%$)

C : Coke
M : Metal
S : Chrome-spinel
Sl : Silicate slag

Although studies[2)~9)] have been conducted on the reduction mechanism of chrome ores in solid state, there are very few[10)~12)] made in liquid state.

In this study, the reduction mechanism of chromium oxide in the molten slag was inferred from the experimental results so far described as well as from structural observations on a number of slag samples by microscopy and EDX.

Chrome-spinel particles, mainly consisting of $Mg(Cr,Al)_2O_4$, disperse in the slag, fracture themselves into smaller pieces and gradually dissolve into the molten silicate slag. In the course of this dissolving process, $MgAl_2O_4$ film is formed around these particles. While $(MgO)+(Al_2O_3)$ is kept within the critical value (45% at 1600°C), the $MgAl_2O_4$ film is very thin (2∿3μm) and does not disturb the dissolution of spinel particles. However, when $(MgO)+(Al_2O_3)$ exceeds the value, the film thickens to 20∿30μm and the dissolution rate of particles extremely decreases. Chromium dissolved into silicate slag is transferred onto the coke surface and is reduced. Metal particles thus generated grow larger, sedimentate and separate from the slag.

3. Bench Scale Experiments

3.1 Procedures

Fig.12 shows the equipment for the experiments -- a top/bottom blowing mini-converter of 1t capacity. Induction heating was adopted to compensate a large loss of heat. After charging 500kg of carbon-saturated molten Fe-Cr prepared in another furnace into the converter, chrome ore pellet, coke and flux were charged intermittently into the stirred bath with oxygen blowing from top and bottom. During and after charging these materials, changes in the chromium content in the slag or melt were examined by analyzing samples taken out from the oxygen-blown bath. Experimental conditions are shown in Table III. Chrome ore pellet was similar in composition to that used in the fundamental experiments.

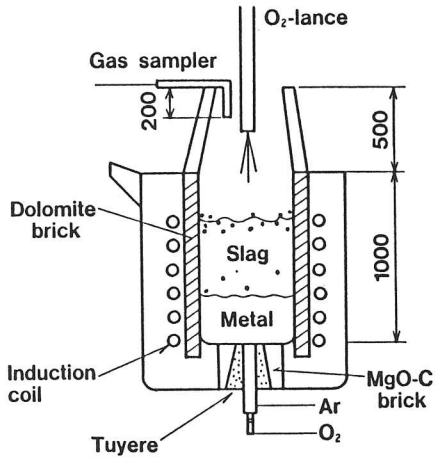


Fig.12. Experimental mini-converter (1t capacity)

Table III Experimental conditions

		Range
Metal bath	Amount	550kg
	Composition	Cr : 40%, C : 8%(Saturated)
	Temperature	~1600°C
Ore	Amount	300kg
	Type	Partially reduced pellet (M·Cr/T·Cr×100=55%)
Slag	Amount	~250kg
	Composition	Al_2O_3 : 16~20% MgO : 23~26% CaO/SiO_2 : 1.0
Coke	Amount	100~250kg/heat
	Size	10~25mm
Top blowing	Nozzle type	3holes
	Lance height	600mm
	Oxygen	1200 Nℓ/min
Bottom blowing	Combination of gases	Oxygen-Argon

Gas samples positioned at around 200mm down from the converter top collected by gas sampler were analyzed for CO, CO_2, O_2, N_2, Ar, H_2 on the gas chromatography.
In consideration of the air flown in from the converter top and mixed up with the gas, the amount of CO combusted by the air was rectified according to the equation (4) in advance of the determination of the oxidizing rate of CO of the crude gas.

Oxidizing rate of CO (%) =

$$\frac{CO_2\%-[(100-N_2\%)\times 21/79-O_2\%)\times 2]}{CO\%+CO_2\%}\times 100 \quad ...(4)$$

where: CO_2%, CO%, O_2%, N_2% are the values from the gas analysis

3.2 Results

An example of (T.Cr) behaviour is exhibited in Fig.13. While adding chrome ore pellets, (T.Cr) levelled off at around 2.5%. After the addition of pellet, (T.Cr) decreased to less than 0.5%.

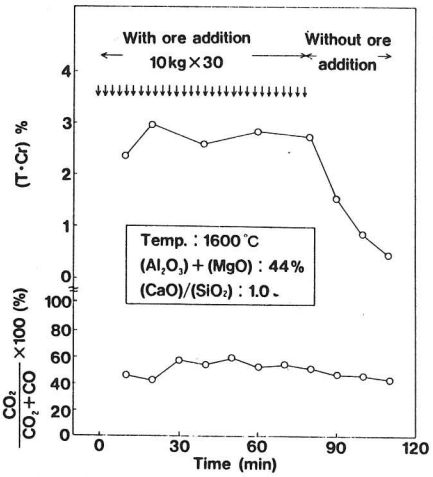


Fig. 13 Example of change of (T·Cr) during smelting reduction with 1 t top and bottom blowing converter.

Overall in our experiments, operations were very stable with excellent reproducibility. However as the coke in the slag ran short, the slag foamed and flooded out of the converter. Further in this experiment, when the amount of slag fell below 100kg or the oxygen blown from the top against the slag became intensified, the oxidizing rate of CO[CO_2%x100/(CO%+CO_2%)] decreased to less than 20% and (T.Cr) rose higher.

Judging from these, to increase the reduction, it seems necessary to maintain the appropriate amount of coke and to shield the metal bath from the oxygen jet - ie., the conditions required for the latter are a large amount of slag and the soft-blowing of oxygen from the top.

Rate of CO oxidization ranged from 30∿85% corresponding to the amount of coke in the converter, provided that the top oxygen flow was kept at a constant rate (as shown in Fig.14). However, $(T.Cr)_f$ was constant at 0.3∿0.5% independent of the CO oxidizing rate when the coke/slag ratio was 0.10 or higher (the oxidizing rate of CO≦70%) as shown in Fig.15.

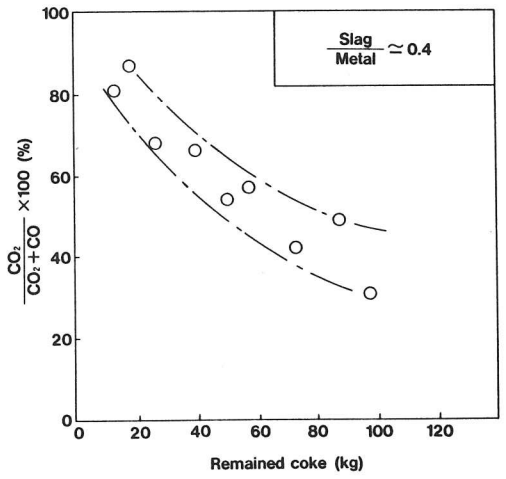


Fig. 14 Relation between the amount of remained coke and the oxidation rate of CO.

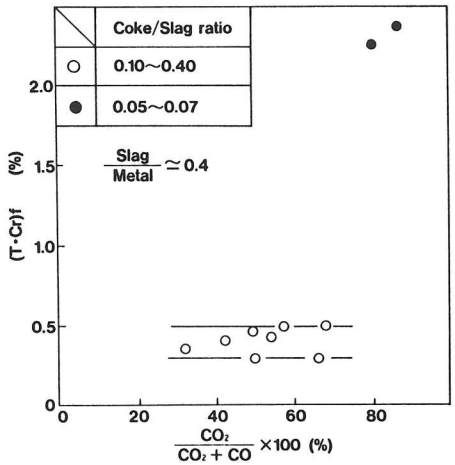


Fig. 15 Effect of oxidation of CO on the final chromium content in slag.

Typical heat balance is exhibited in Fig.16. The value of heat efficiency by coke combustion obtained from equation (5) was approximately 85%.

Heat efficiency (%) =

$$100 - \frac{\text{Heat loss}}{\text{Combustion heat of C}} \times 100 \quad \ldots\ldots (5)$$

where: Heat loss indicated as (b) in Fig.16 roughly corresponds to the superheat of the exhaust gas exceeding the temperature of the melt. The denominator is indicated as (a) in Fig.16.

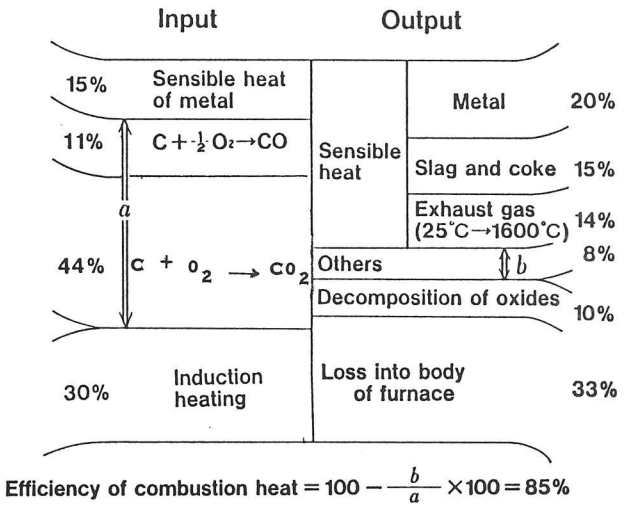


Fig. 16 Heat balance

The reason for this high heat efficiency was presumably considered that the coke superheated by the combustion (C+1/2O_2=CO, C+O_2=CO_2) made an excellent heat transfer medium.

Composition of the resulting product is exhibited in Table IV.

Table Ⅳ Metal composition (%)

	Experimental		Conventional (Reference)
	Initial	Final	
Cr	40.2	42.5	55~62
C	8.0	8.2	7.9~8.2
Si	1.1	0.2	2~5
S	0.030	0.008	0.040~0.060
P	0.027	0.038	0.020~0.035

[Cr] is determined by Cr/Fe ratio of chrome ore. In this experiment [Cr] was higher than 40% - the initial value - the reason being the pellet used was so blended to get 56% [Cr].

Extreme low [Si] as compared with products from the conventional process is probably attributable to the lowered SiO_2 activity induced by high (CaO) in the slag, as well as to the oxygen potential at the reduction site not sufficiently low to reduce SiO_2.

Reasons for low [S] originate in the desulphurization by the slag ((S)/[S] ratio = 30∿40), as well as in the gasification of sulphur as shown in Fig.17.

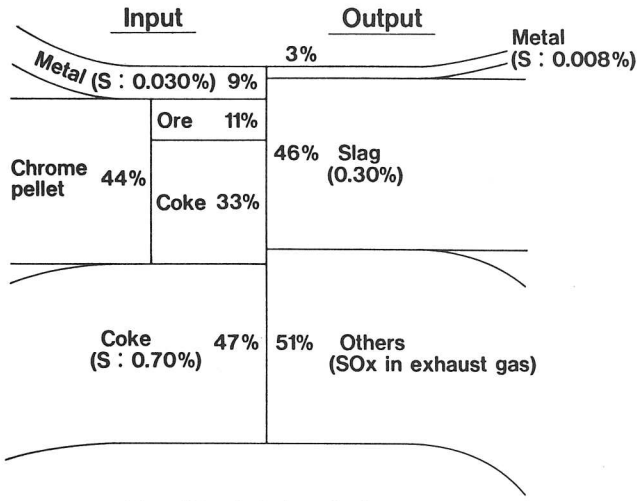


Fig. 17 Sulphur balance

Nearly all the phosphorus input, of which major source is the coke, was concentrated in the metal as shown in Fig.18. Larger consumption of coke required for this particular process yields more [P] as compared with the case of the conventional production process. Accordingly, use of carbonaceous material of lower phosphrus content is required to suppress the rise of [P].

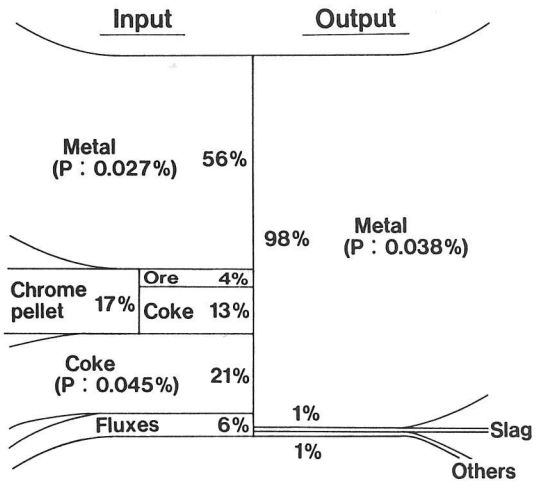


Fig. 18 Posphorus balance

4. Summary

Results from the fundamental experiments and the bench scale experiments in developing a new ferrochrome production process by smelting reduction using a top/bottom oxygen blowing converter are summarized as follows:

(1) With the slag sufficient to keep the metal bath protected from oxygen jets, final chromium content in the slag can be lowered to less than 1% even under the combustion of coke with oxygen blowing (atmosphere: $CO_2/(CO+CO_2) = 0.3 \sim 0.7$).

(2) Appropriate slag composition range for the reduction of chromium oxide is:

(a) $(MgO) + (Al_2O_3) \leq 45\%$

(b) $\dfrac{(CaO)+(MgO)}{(SiO_2)+(Al_2O_3)} = 0.8 \sim 1.3$

(3) With [Cr] exceeding 20%, the dominant reduction site is at the slag/coke interface, not at the slag/metal interface. Accodingly, the reduction rate of chromium oxide is basically independent of [Cr].

(4) Coke in the slag plays an important role not only in reducing oxide but also in suppressing slag-foaming and in accelerating heat transfer.

(5) Low [Si] and [S] as well as high [P] are the outstanding product features as compared with those produced by the conventional electric furnace process using metallurgical coke. [P] decreases by using carbonaceous materials of low phosphrous content.

Overall and principally, the results well indicate the feasibility of the new process. For further development, additional feasibility study is indispensable clarifying influences -in larger scale trials- on the reactions, wear errosion, accuracy of heat efficiency of the entire system involving utilization of sensible heat and latent heat from the exhaust gas, chances in direct utilization of raw chrome ore or coal, etc. These are undoubtedly the problems to be encountered.

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