A Comprehensive Analysis of the Furnace Interior for High-carbon Ferrochromium

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SYNOPSIS

In the manufacture of high-carbon ferrochromium low in carbon and silicon, the carbon content of the product is controlled by an ore layer formed from lumpy ore in the furnace. However, almost no research has been published concerning the structure of the layers and the reaction products. So we manufactured high-carbon ferrochromium in a test furnace; then, after shutting down, the furnace was cooled by blowing nitrogen gas into the crucible, and the resin was impregnated in the cooled charge. This enabled a study of the structure of the furnace interior, the course of the melting and reduction process, and the mechanism of decarburization at the ore layer, to be investigated.

It was found that the furnace interior is composed of a charge layer, a slag layer, an ore layer, and a metal layer. The ore layer was divided into a molten and an unmolten layer. Melting and reduction of the charge layer commences at positions near the tips of the electrodes and shows the formation of metal particles. Above the slag layer, a coke bed with a large amount of coke and metal particles was perceived, although it was narrow in comparison with that present in pig-iron or ferromanganese production. In this coke bed, the primary metal has a carbon content that corresponds to the equilibrium silicon content. The metal descends and is desiliconized and decarburized by reaction between the carbon and silicon in the metal and the chromium and iron oxides in the ore. The metal of low-carbon content accumulates at the furnace bottom. The phosphorus in the metal remains almost unchanged, while the primary metal is desulphurized in the slag to an extremely low level. However, because at the ore layer the carbon and silicon contents decrease and the viscosity increases, the metal absorbs sulphur from the ore and slag in considerable amounts.

METHOD OF EXPERIMENT

An experiment was carried out in a 500 kVA two-phase Heroult-type electric furnace (carbon-lined) at the Toyama Electric Ironworks, Ferroalloy Division, Nippon Kokan K.K. Figure 1 is a vertical section of the experimental furnace, which has a smaller distance between electrodes and lining, a thicker lining, and approximately the same electric power consumption and heat loss as commercial furnaces.

Table 1

Standard of chemical analysis of high-carbon ferrochromium

Test	Cr %	Si %	C %	P %	S %
A	60 to 65	3,0 to 6,0	8,0 max.	0,034 max.	0,045 max.
B	60 to 65	2,0 to 5,0	6,0 max.	0,040 max.	0,050 max.

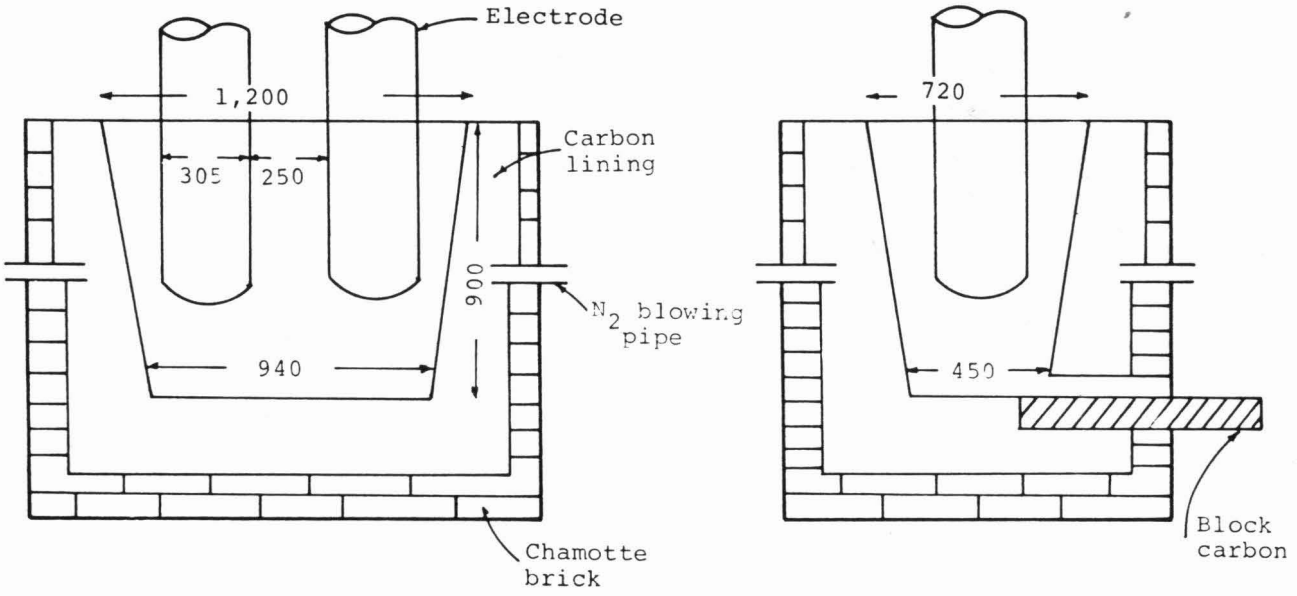

Figure 1

Experimental furnace

RESULTS OF OPERATION

The standard grades of ferrochromium were graded according to the carbon content at the user's request. To investigate the differences in operating conditions between the grades, two sets of tests were carried out, producing the two grades of alloy given in Table 1.

The running condition of the furnace was relatively stable. Five days were spent on Tests A, and seven days on Tests B. During these periods, the temperature distribution and gas analysis in the furnace were investigated. As the products showed an analysis of 6,5 per cent C and 1 per cent Si in Tests B, we considered that the furnace interior fully corresponded to the bath structure of Tests B and shut down the furnace.

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Tables 2 and 3 show the sizes of raw materials, and operating results before shut-down, respectively.

Table 2
Raw material sizes (mm)

Chromium-ore pellet	Lumpy chromium ore	Lime-stone	Quartzite	Coke	Iron-ore pellet
5 to 20	10 to 40	3 to 10	2 to 5	2 to 5	3 to 5

Table 3
Operating results before shut-down (per ton of alloy)

Chromium-ore pellet	1080 kg
Lumpy chromium ore	1080 kg
Iron-ore pellet	115 kg
Coke	475 kg
Quartzite	168 kg
Limestone	3 kg
Electrode	20 kg
Electric-power consumption	4019 kWh
Yield of chromium	85%

QUENCHING AND POURING OF RESIN

No studies on furnace quenching and pouring of resin have been reported for ferro-alloys, except for a few based on the sampling of burden from the furnace. These reports fail to define clearly the complicated structure of the crucible existing round the electrodes and the individual layers in the furnace. Since a refining period of 4 hours is required after heating, the furnace was shut down 2 hours after tapping, during which the formation of the product and desiliconization and decarburization would probably have proceeded to a considerable degree. Immediately after shutting down, an iron cover was applied to the charge surface, and the furnace was quenched rapidly by blowing nitrogen at a rate of 40 m^3/h into the furnace. When the furnace interior had been cooled to room temperature, a synthetic resin was poured into the furnace. Penetration was sufficient, and the burden could be removed successfully as a solid body. The burden, frozen with resin, was cut vertically into two pieces at the plane containing the electrodes. One piece was used for macro-observation of the cross-section, and the other was subjected to chemical analysis. The charge was separated from the resin with trichlorethylene. The product and slag were separated either manually or by use of Clerici's solution.

COMPREHENSIVE ANALYSIS OF FURNACE INTERIOR

Figure 2 is a photograph of the polished vertical section passing through the centre of the electrodes. It shows clearly the layers of charge, slag, ore, and metal, which result in the distinct structure of components round the electrodes that has been vaguely defined as the crucible. This cross-section was observed and analysed chemically. Figure 3 is the result of observations and chemical analysis of this cross-section for each of the layers.

RESULTS OF MACRO-OBSERVATION

Construction of Charge Layer

It had been thought previously that a large melting and reduction area existed round the electrodes and the lower

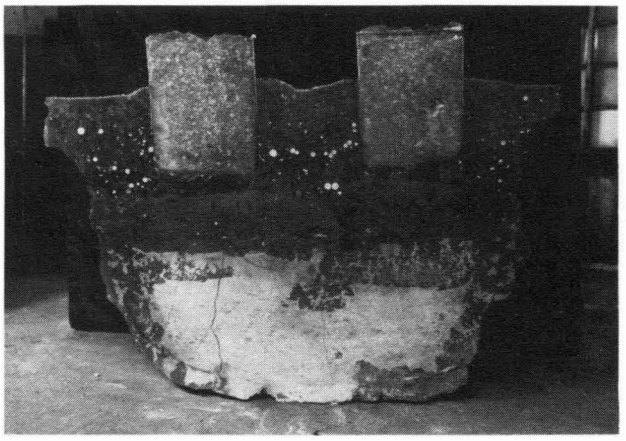
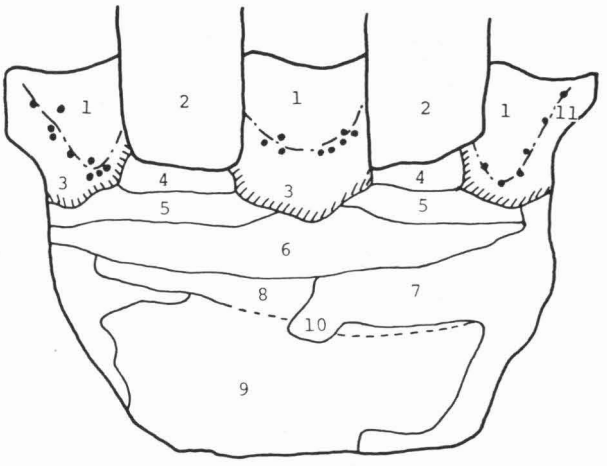


Figure 2
Interior of the furnace



1. Charge layer
2. Electrode
3. Coke bed
4. Cavity
5. Slag layer
6. Layer of unmolten ore
7. Layer of molten ore
8. Metal pool
9. Residual metal
10. Tap hole
11. Alumina ball

Figure 3
Cross-section of furnace

part of the charge layer. Contrary to expectation, this area has proved to be very narrow, as shown in Figure 2, and only slight macroscopic changes of the burden by heating in this area were noticed. There is a considerable amount of coke in the melting and reduction area, which is called 'the coke bed.' Primary metal in the furnace is found in this coke bed and underneath the electrodes. Chromium-ore pellets react with coke either in the coke bed or underneath the electrodes, and are mostly reduced through melting, while a large part of the lumpy chromium ore is found to be unreacted and remains as a residue in the furnace.

To investigate the descending pattern of burden, alumina balls as markers were twice added to the charge layer, at 30 minutes and one hour before the furnace was shut down. The results showed that the burden descended with a V-shaped distribution, at a maximum rate of 0,50 m/h between the furnace wall and the electrodes and 0,36m/h between the electrodes. The V-shaped distribution of the charge in descending can be proved by the fact that the middle part descends first because the melting and reduction of the ore occur deeper in the furnace.

A cavity is found in this vertical plane with a size of

about 5 cm. This may be explained by the fact that, during the quenching process, the charge cooled over a distance of about 5 cm, and these melts were not able to fill the cavity during the quenching process owing to the small degree of melting round the electrodes during this period.

Composition of Slag Laver

The slag layer is very dense, and, as shown in Table 4, contains more SiO_2, CaO, and S, and less MgO and Al_2O_3, than the final slag composition. It is clear that the final slag has combined with part of the ore layer that contains more MgO and Al_2O_3.

Table 4
Chemical composition of final slag and residual slag in furnace

	Cr %	FeO %	MgO %	Al_2O_3 %	SiO_2 %	CaO %	P %	S %
Final slag	3,0	1,8	30,0	26,5	35,1	3,5	0,006	0,150
Residual slag in furnace	3,1	1,1	27,6	24,8	37,4	4,3	0,007	0,170

Construction of Ore Layer

Lumpy ore remained largely unreacted in the furnace during the smelting. Half of the lumpy ore settled at the slag—metal interface and thus formed an ore layer. This layer consists of neither ore pellets nor coke but of metal particles and lumpy ore at various stages of melting. The region of the upper ore layer where lumpy ore collected is called the 'unmolten' ore layer, and the other region where softening and melting of the ore occurred with metal particles round it is called the 'molten' ore layer. This layer lies either beneath the unmolten ore layer or along the furnace wall.

Composition of Metal Layer

The metal bath layer is divided into the metal generated between taps (metal pool) and the metal not tapped out from the furnace in tapping (residual metal).

Table 5
Chemical composition of metal layer by level

	Cr %	C %	Si %	P %	S %	
Upper part	62,5	6,3	0,6	0,029	0,078	
Middle part	68,8	8,2	0,5	0,023	0,048	
Lower part	64,5	8,1	2,5	0,025	0,094	
Tapped metal	62,4	6,5	1,0	0,031	0,065	Test B
Tapped metal	61,7	8,4	3,8	0,022	0,023	Test A

Table 5 shows that the middle part contains more chromium and carbon and less silicon and sulphur. This is because the metal was not completely tapped and some was left in the furnace. In the phase diagram for the system Fe—70%Cr—C, if the temperature of the metal bath drops below the liquidus line, chromium carbide $(Cr,Fe)_7C_3(=K_2)$ will be precipitated. From calculations based on Stokes's equation (which relates such factors as differences in density between particle K_2 and the molten metal, the particle size of K_2, the molten-metal viscosity, and the rate of descent of particle K_2), there is a strong possibility that $(Cr,Fe)_7C_3$ high in chromium and carbon would descend and collect in the lower part of the furnace as the temperature of the metal bath decreased.

Change in Metal and Slag Composition

In the charge layer, the melting and reduction area of the burden is seen only in a narrow part of the coke-bed layer. However, to investigate further the reduction process of chromium ore and the process of metal formation in the furnace, samples were taken at the levels shown in Figure 4, and microscopic observations, electron-probe micro-analysis, and chemical analyses were conducted on these samples.

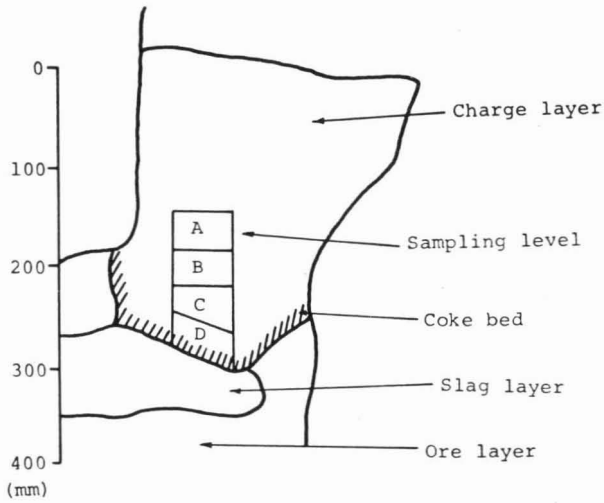


Figure 4
Sampling position

Table 6 shows that, in area B, Fe is preferentially reduced to generate metal particles low in carbon and chromium owing to the different diffusion rates of iron and chromium. In area C, these metal particles become coarser and there is an increase in the chromium content. The reason for this is that melting ore is in better contact with the coke, and the increase in temperature increases the diffusion rate of carbon with respect to chromium, resulting in a rapid chromium reduction. As melting proceeds further, increasing the chromium content in the metal, the carburization process also proceeds. In this process, the reduction of silica occurs, while, in the coke bed, primary metal saturated with carbon corresponding to the equilibrium silicon content is formed. This metal descends to the lower part of the furnace.

In the ore layer, primary metal formed in the coke bed or under the electrodes reacts with FeO and Cr_2O_3 contained in the lumpy ore and causes decarburization and desiliconization in the ore layer. The secondary metal, which is formed through this reduction, together with primary metal, forms the metal pool. The purpose of this paper is to clarify the structure of the furnace interior and also the mechanism of decarburization and desiliconization in the ore layer. Therefore, we have divided the furnace interior into the following two parts: (i) the side of the furnace wall (area A) and the middle part of the furnace interior, and (2) the part under the electrodes (area B). Figure 5 shows the relation between C and Si in the metal in the ore layer that has a chromium content of more than 60 per cent.

The Si—C (sat) line in Figure 5 shows the carbon and silicon relation for high-carbon ferrochromium alloys saturated with carbon. The arrows show changes in the

Table 6
Changes in metal and slag composition in the charge layer

Level	Metal (%)						Slag (%)							
	Cr	Fe	C	Si	P	S	Cr	FeO	SiO_2	MgO	Al_2O_3	CaO	P	S
B	3,8	89,4					15,2	1,6	0,8	28,8	50,5	0,2		
	30,6	61,4					3,8	0,4	44,5	7,7	25,5	17,4		
							1,5	1,7	40,5	55,8	0,2	0,6		
C	36,1	56,2	6,9	0,06	0,051	0,083	8,4	1,7	34,0	26,3	22,6	2,8	0,004	0,069
	54,9	35,2	8,4	0,12	0,045	0,077								
	57,0	31,8	8,7	0,39	0,048	0,058								
D	59,1	28,2	9,2	0,91	0,044	0,028	5,3	0,6	31,3	27,8	25,4	2,10	0,002	0,154
	60,6	26,4	8,6	1,53	0,043	0,012	6,1	0,4	34,3	27,3	26,3	2,50	0,003	0,168
	60,1	26,5	8,4	2,11	0,048	0,014								

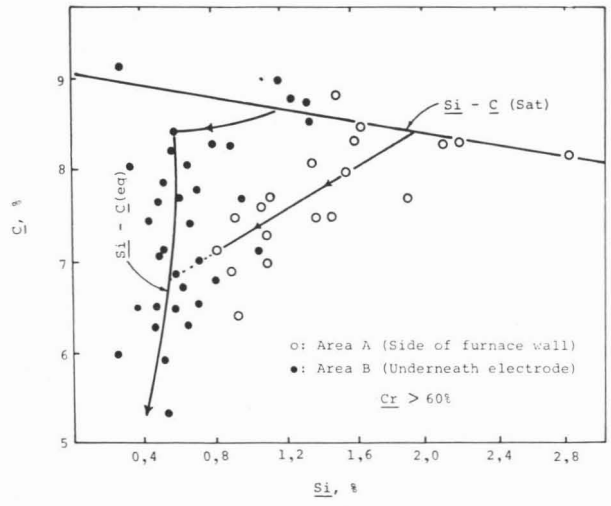


Figure 5
Change in carbon and silicon in the ore layer

carbon and silicon contents in areas A and B. What should be noted here is the difference in the way the carbon and silicon contents change between areas A and B. As area A has a higher refining temperature, the reactions

$2\,FeO + Si \rightarrow 2\,Fe + SiO_2$ .....(1)

$FeO + C \rightarrow Fe + CO$ .....(2)

proceed in parallel, followed by a decrease in the FeO content in the ore layer and a reduction of the carbon and silicon contents in the primary metal. When the FeO content decreases to below 4 per cent, the reactions

$2\,Cr_2O_3 + 3\,Si \rightarrow 4\,Cr + 3\,SiO_2$ .....(3)

$Cr_2O_3 + 3\,C \rightarrow 2\,Cr + 3CO$ .....(4)

proceed, though decarburization reaction (4) is predominant. However, because of an insufficient amount of ore for decarburization and desiliconization of the primary metal, and reaction of this metal with the carbon lining, the carbon and silicon values in the metal stay rather high.

Compared with area A, area B has a lower refining temperature and a higher content of FeO, so that the desiliconization reaction (1) takes precedence and the silicon content in the metal falls to the level at which silicon equilibrates with carbon.

Through this exothermic reaction, the temperature is raised and the decarburization reaction is accelerated. Then equation (2) precedes equation (4), which occurs when the FeO content decreases to 4 per cent. As a result, it has been proved that the carbon in the molten metal decreases slowly according to the Si—C(eq) line.

BEHAVIOUR OF SULPHUR

Of the sulphur contained in the charge during refining, 16 per cent is found in the metal and 62 per cent in the slag. The rest is vaporized towards the upper part of the furnace together with gas. The circulating phenomenon of sulphur reaches its maximum at a level of 140 mm (approximately 600°C) from the surface of the furnace, with a sulphur value half as much again as that of the initial burden. The sulphur in the primary metal initially formed in the charge layer is as high as 0,080 per cent, but with the higher carbon and silicon contents of the metal in the coke bed it falls to 0,013 per cent. With this desulphurization process, there is little possibility of desulphurization occurring by the brief contact between slag and metal, specially since the Cr_2O_3 and FeO contents in the slag are high. Therefore, in this area, it is possible that desulphurization takes place through the gas—metal reactions utilizing Mg, Ca, Na, K, etc. Primary metal considerably desulphurized in this way is rapidly resulphurized in the ore layer. Desulphurization reactions between slag and metal in the furnace are expressed by the following equations:

$MS + MgO \rightleftarrows MO + MgS$ .....(5)

$MO + R \rightleftarrows M + RO$ ..... (6)

where, M=Fe, Cr, and R=C, Si.

Judging from the above equations, at a given temperature a greater desulphurizing capacity is obtained as MgO increases and FeO and Cr_2O_3 decrease. In addition, high C and Si contents in the molten metal favour desulphurization by reducing the FeO and Cr_2O_3 contents in the slag.

Accordingly, the following factors determine the resulphurization of metal in the ore layer:

(1) high FeO and Cr_2O_3 contents in the ore layer,
(2) low carbon and silicon contents in the metal achieved through reactions of decarburization and desiliconization, and
(3) high viscosity of the ore layer.

From these reactions, it can be seen that the existence of an ore layer in the furnace for decarburization makes it difficult to produce high-carbon ferrochromium low in sulphur.

CONCLUSION

The interior of an experimental furnace was investigated in detail after the production of high-carbon ferro-

chromium. The furnace burden was quenched and frozen with resin. As a result, it became possible to clarify the process of the formation of the ore layer and the mechanism of both decarburization and desiliconization reactions in the ore layer as well as the bath structure in the furnace interior.

The information obtained is given below.

Results of Macro-observation

(1) The furnace interior is composed of a charge layer and an ore layer divided into molten and unmolten sublayers.
(2) Chromium ore has a high melting-point, and rapid melting and reduction occur round the tips of the electrodes and in the coke bed, which is extremely narrow compared with the coke beds in the manufacture of pig-iron and ferromanganese.
(3) While ore pellets are metallized rapidly because they reset easily when subjected to melting and reduction, most of the lumpy ore descends before melting and forms an ore layer. This process is most often observed in the section between the electrodes.
(4) Unlike the smelting of ferrosilicon, no cavities were found round the electrodes during the manufacture of high-carbon ferrochromium.

Change in Metal Composition

(1) In the initial metal composition, FeO is preferentially reduced, but, as the ore reduction progresses, both chromium and carbon increase. Silicon increases at a late stage, and finally primary metal saturated with carbon corresponding to an equilibrium silicon content is formed in the coke bed.
(2) As no coke was observed within the ore layer, it is estimated that the FeO and Cr_2O_3 in the ore layer are successively reduced by carbon and silicon in the primary metal to produce secondary metal with a lower carbon content.
(3) The metal composition is roughly dependent on its location, the metal composition underneath or between the electrodes being quite different from that round the side of the furnace wall. This may be due to the effect of the lining or the difference in refining temperature and the FeO and Cr_2O_3 contents of the ore. Most of the product unsaturated with carbon is obtained in the centre part of the furnace.
(4) Metal found at the furnace bottom has higher sulphur contents compared with the composition of the tapped metal. This is because, when the refining temperature in that area drops, chromium carbide of composition $(Cr,Fe)_7C_3$ is precipitated and falls through the molten metal. The results correspond well with the results obtained when a commercial furnace is dug out.
(5) Phosphorus in the metal remains almost unchanged, whereas the primary metal is desulphurized in the coke bed to some extent and in the slag to an extremely low content. Substantial resulphurization in the ore layer is caused by the decreased carbon and silicon contents of the alloy and the increased oxygen potential plus an increase in viscosity, and this makes it difficult to produce an alloy low in both carbon and sulphur.

These results have proved extremely useful for facilitating the production of high-carbon ferrochromium with a relatively low carbon content in a commercial furnace. Furthermore, in consideration of these results, we studied simulated reactions of high-carbon ferrochromium in the furnace, and have obtained interesting results. Silicomanganese and silicochromium were also investigated in a similar manner. The results of these tests are of great use in commercial operation, and we expect to have an opportunity of reporting them in the near future.

DISCUSSION

*Dr K.G. Willand**:

(1) Please give us the analysis of lumpy chromium ore and chromium-ore pellets and
(2) the voltage and load used in the test furnace.
(3) Do you utilize submerged-arc operation at all times?
(4) Please describe the technique of temperature measurement.

Mr Yamagishi:

(1) The analyses of lumpy chromium ore and chromium-ore pellets were as follows in percentages:

	Cr_2O_3	FeO	SiO_2	CaO	MgO	Al_2O_3
Lumpy chromium ore	49,1	11,0	5,5	1,6	16,2	11,9
Chromium-ore pellets	54,9	14,2	6,5	0,04	11,5	10,8

(2) We operated the test furnace under the following electric conditions:

Secondary voltage	70V
Secondary ampere	4400A
Electric power load	310 kW.

(3) We always utilize submerged-arc operation by supplying the charged materials continuously.
(4) At below 1200°C, we measured the thermo-profile of the furnace by using chromel—alumel thermocouples, and we used iron pipes as protective tubes.
Above 1200°C, we measured it by W—Re thermocouples and used iron pipes as protective tubes.

*Dr R. Urquhart**:

The inclusion of a lime-bearing flux in the mix generally results in a higher chromium recovery than if lime is excluded. Can Mr Yamagishi explain this on the basis of his experiment?

Mr Yamagishi:

We have never heard of that fact. We thought that there were no such examples in experimental tests and commercial operations, and so we cannot answer this question.

Mr R. J. Botte†:

What are the chief parameters in the formation of a coke bed?

What types of control are more or less important in a coke bed?

Mr Yamagishi:

A coke bed is usually easy to create in the furnace when the melting-point of ores and fluxes in the charge is lower; a lot of coke is contained in it. Therefore, in the manufacture of high-carbon ferrochromium there is a very narrow coke bed compared with pig-iron and high-carbon ferromanganese.

We could minimize the amount of coke if we used ores that have a high melting-point and coke in amounts equal to or lower than theoretical.

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†Societe Ugine-Aciers, France.

Dr J.H. Downing:*

How do the authors explain the effect of the MgO-to-Al_2O_3 ratio on the carbon content? Does the carbon-to-silicon ratio in the saturated alloy have an influence on the carbon content of the refined alloy?

Mr Yamagishi:

We guessed that the carbon content of high-carbon ferrochromium was decreased by the following facts.

(a) As the slag with a high ratio of MgO to Al_2O_3 has a higher melting-point than normal slag, the ore layer is easily formed in the furnace.

(b) As the slag with a high ratio of MgO to Al_2O_3 has a higher value of activity of silica than normal slag, the silicon content of primary metal increases and the carbon content decreases. However, we did not reach a satisfactory conclusion, and we have been studying the problem.

We have never thought about the carbon-to-silicon ratio in the saturated alloy, but it will be a useful factor in the production of high-carbon ferrochromium.

As there is a negative interrelation between the carbon and silicon contents in high-carbon ferrochromium, if the silicon content increases, the carbon-to-silicon ratio decreases.

We think it is much better to produce high-carbon ferrochromium with a low carbon content by desiliconizing the primary metal, which aims at a low carbon—silicon ratio in the furnace. But the actions that give rise to silicon content in the operation require high-temperature operation and a lot of coke in the charge; so it is difficult to form the ore layer in the furnace.

Dr D. Slatter†:

I would be grateful if Mr Yamagishi could

(1) give more details of the nitrogen-quenching system to freeze the furnace burden, in particular the point, or points, at which the nitrogen is injected, and could

(2) comment on whether useful results could be obtained by applying this technique to a smaller electric furnace of 75 kVA capacity. In this connection, I should add that, using this furnace at the Institute of Mining Research, we have been able to produce high-carbon ferrochromium in which the carbon content has been lowered from over 8 per cent to between 6,0 and 6,5 per cent.

Mr Yamagishi:

(1) After shutting down the furnace, we closed it with an iron cover, which was separated into two parts, and sealed the gap with clay. Nitrogen gas was blown into the furnace for quenching through a pipe in the cover.

(2) If you applied our technique to your experiment, you could observe the detail of the furnace structure and gain much useful information.

Mr D. Ossin:*

(1) What is the analysis of the material that flowed away from the electrode tips and caused the cavities during cooling?

(2) How does the author explain the existence of the extensive area of so-called molten ore? Is not possible that this region is due to incomplete reaction, which in turn resulted from the cooling of the furnace?

Mr Yamagishi:

(1) The material that flowed away from the electrode was primary metal and slag. The analysis was as follows, in percentages:

	Cr	Fe	C	Si		
Primary metal	60,1	26,5	8,4	2,11		
	Cr	FeO	SiO_2	MgO	Al_2O_3	CaO
Slag	6,1	0,4	34,3	27,3	26,3	2,5

We guessed that the cavity was formed by air or carbon monoxide, which came into the space that was produced when the electrode was fixed at a constant level and the charge was lowered.

(2) In the production of high-carbon ferrochromium, the molten ore layer was placed on the hearth metal and was reduced by the metal, which came from the upper part of the furnace. The tapping metal and slag were formed in this reaction, and then the molten ore layer almost disappeared in the interval between taps.

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