Plenary Address: Technical Trends in Ferrochromium Production in Japan

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INTRODUCTION

In line with the remarkable expansion in steel production, ferro-alloy production has increased rapidly in the past few years, the growth being phenomenal in stainless-steel production in Japan. The increase in the production of stainless-steel, as well as of chromium-containing special steel, has brought about a similar increase in the production of ferrochromium.

As shown in Table 1, there were remarkable changes in the production ratios of ferrochromium varieties in the same period. Such changes resulted from the newly developed method of stainless-steel production.

Table 1

Production statistics (unit 1000 tonnes)

Fiscal year	Special Steel	Stainless Steel	Ferrochromium			Silicochromium
			HC*	MC*	LC*	
1962	1604,4	212,5	32,0	0,1	43,1	7,6
1963	2456,3	334,1	54,5	—	41,2	15,4
1964	2532,5	416,2	64,8	15,2	57,6	15,4
1965	2421,6	390,0	56,4	13,5	51,2	14,9
1966	3545,7	504,0	86,2	14,1	64,1	25,5
1967	4661,6	681,5	125,2	14,3	74,2	31,4
1968	5455,9	746,3	149,5	14,0	69,6	38,8
1969	6839,1	995,8	179,6	11,9	89,4	50,9
1970	7365,2	1216,1	282,4	6,5	119,7	37,9
1971	6833,7	1041,8	263,6	10,5	123,0	32,6
1972	7174,6	1065,5	268,5	12,5	79,0	32,1

*HC High-carbon
MC Medium-carbon
LC Low-carbon

FROM THE CONVENTIONAL METHOD TO THE OXYGEN-BLOWING PROCESS

It is well known that the carbon content of stainless steel has a vital effect on its working properties, its corrosion resistance, and its behaviour in welding.

The carbon content of the highest-quality stainless steel, excluding cutlery and other martensitic grades, should be controlled to less than 0,02 per cent, and it has now become technically possible to control carbon contents to as low as 0,008 per cent in the large-scale production of stainless steel.

High-frequency induction furnaces were used originally for the melting of stainless steel so that carbon pick-up during the melting operation was kept to a minimum. In that operation, low-carbon ferrochromium was used together with pure iron that had been refined in a separate furnace for the removal of phosphorus, sulphur, and carbon.

The carbon content of the stainless steel produced in this manner was affected largely by these cold charges, and the scrap used, which was contaminated with lubricating oil, was responsible for the addition of carbon into the stainless-steel ingot.

In the making of stainless steel in the electric-arc furnace, which was popular until the oxygen-blowing process was introduced in the U.S.A. in the early 1950s, it was difficult to control the carbon content of the final bath to lower than 0,12 per cent. This was because the content of recycled scrap was limited to about 10 per cent so that the loss of chromium into the slag would be kept to a minimum.

After that time, the silicon was reduced by the making of white slag or basic reducing slag, several additions of low-carbon ferrochromium were made, and the molten metal was reheated repeatedly before the final bath was obtained. Such operations were very time-consuming, and the carbon pick-up was also high.

With both the high-frequency induction furnace and the electric-arc furnace, the gas content of the ferrochromium causes trouble in the melting of stainless steel. Hydrogen can be removed if the ferrochromium is heated before it is added, but the removal of nitrogen and oxygen is almost impossible. Furthermore, such gases are apt to be absorbed from the atmosphere into the molten metal during the melting operation, which is the reason why the gas content of ferrochromium has to be kept as low as possible.

The oxygen-blowing process, together with improvements in the refractory lining material, has brought about a revolutionary change in the melting of stainless steel. The most significant change is that chromium of relatively high carbon content can be used in the initial charge since the oxygen-blowing and refining are applied to the high-temperature molten metal.

Firstly, it became possible to control the carbon content of the final bath to 0,03 per cent by the use of melted-

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down metal that had a carbon content of 0,3 per cent, keeping the chromium loss at the lowest possible level. After several years during which the carbon content was 1 per cent from a carbon content at the melt-down stage of 0,6 per cent, it is now possible to refine metal that has a carbon content of 2 per cent or even higher at the melt-down stage into metal with a carbon content of 0,03 per cent in the final bath.

As the carbon level increased, the ferrochromium used changed from low-carbon to medium-carbon material, and then was replaced by charge chromium. The total chromium required can now be added as charge chromium, the molten metal of 2 per cent carbon content being refined easily.

In high-temperature refining, the chromium loss is very small, and more scrap can be used. The oxygen in the chromium oxide is removed by the silicochromium or ferrosilicon during oxygen-blowing, and the molten stainless steel has the chromium content initially aimed at, any deficiency being made up by the addition of low-carbon ferrochromium.

Recent records show that the average consumption of low-carbon ferrochromium is only about 1kg per tonne of stainless-steel ingot. This means that the consumption of charge chromium is almost 200 times higher than that of low-carbon ferrochromium for the production of stainless steel.

THE AOD AND VOD PROCESSES

The AOD (argon-oxygen decarburization) and VOD (vacuum-oxygen decarburization) processes, developed by Union Carbide Corporation and Witten respectively, realized the production of extra-low-carbon stainless steel with a carbon content of 0,008 per cent (0,01 per cent max.) from charge chromium and scrap. The productivity was also improved remarkably, compared with the oxygen-blowing process in the electric-arc furnace.

The VOD Process

Molten steel with the proper chromium content and with carbon amounting to 0,3 per cent, which usually has been melted in an electric-arc furnace or in an electric-arc furnace and a Lintz-Donewitz (LD) converter, is transferred to the VOD vessel.

When molten pig iron is used, sulphur is removed by slagging off at the pig-iron ladle; when steel scrap is used, the sulphur is removed into the slag during the operation in the electric-arc furnace. After the removal of sulphur and phosphorus, the scrap and charge chromium are charged, and the carbon level of 2,0 to 2,2 per cent is reduced to 0,3 per cent by oxygen-blowing.

To minimize the loss of chromium into the slag, ferrosilicon is charged, so that the chromium oxide is reduced and the silicon content of the metal is controlled at 0,2 per cent. Then molten metal is tapped out after the slag has been removed, and it is transferred to the vacuum chamber.

Some of the sulphur can be removed during this tapping operation, but it is impossible to remove the sulphur or the phosphorus in the vacuum-chamber operation. The stainless-steel melter therefore naturally requires charge chromium of lower sulphur and phosphorus contents. The chromium loss in this vacuum-chamber operation is only about 0,3 per cent.

For adjustment of the chemical composition (i.e., Mn, Si, Cr, and C), silicomanganese, ferrosilicon, low-carbon ferromanganese, low-carbon ferrochromium, or high-carbon ferrochromium is added after the vacuum oxygen-blowing.

In this operation, because boiling occurs under vacuum, the hydrogen, nitrogen, and oxygen contents are much lower than in the melting operation under atmospheric pressure, as shown in Table 2.

Table 2
Gas content of the final metal

	Atmospheric, p.p.m.	VOD, p.p.m.
H_2	5 to 8	3
N_2	300	100
O_2	80 to 110	50 to 70

When the addition of nitrogen is necessary to increase the strength, nitrogen-bearing ferrochromium or ferromanganese is added. In other words, it is not necessary to pay attention to the hydrogen, nitrogen, and oxygen contents of the ferrochromium used in the initial charge.

As the removal of the sulphur contained in the ferrochromium is difficult during the melting of the metal to be charged to the VOD vessel, the sulphur content of the ferrochromium should be controlled at the lowest possible level. Sometimes a sulphur content no higher than 0,012 per cent is required.

The AOD Process

For the AOD process, the same raw materials are generally melted in the electric-arc furnace, and slag is taken off for the purpose of sulphur removal; but oxygen-blowing is not done. After the temperature of the molten metal has been raised to a certain level, metal is tapped out into a normal ladle and then transferred to the AOD vessel.

As is well known, a carefully controlled mixture of argon and oxygen is blown into the AOD vessel to keep the temperature in the vessel below 1700°C.

Since the loss of chromium is relatively higher in this operation than in the VOD process, the chromium is reduced by the addition of silicochromium or ferrosilicon. For the minor adjustment of chemical compositions (i.e., Mn, Si, Cr, and C), relative amounts of ferro-alloys are added as in the VOD process.

Although it is impossible to remove sulphur from the VOD vessel, it can be removed from the AOD vessel by the addition of silicochromium to form reducing slag, followed by the blowing of 100 per cent argon to cause dynamic agitation of the vessel's contents. Therefore, it is not necessary to pay attention to the sulphur content of the ferrochromium when the AOD process is used.

THE BF-LD-RH PROCESS

In place of operation in the electric-arc furnace, molten pig iron direct from a blast furnace can be used. It is transferred into a normal ladle, from where the sulphur is removed, and is then transferred to an LD converter, where the phosphorus and carbon contents are reduced. The refined metal is tapped out after the slag has been removed, and is transferred back to the LD converter, where ferrochromium is added and there is a second oxygen-blowing for further reduction of the carbon content.

It is difficult to utilize silicochromium in an LD converter for the purpose of chromium reduction, and the sulphur content in ferrochromium should be controlled at the lowest possible level.

This process is not acceptable for the production of 18/8 grade of steel, because cold charges of ferronickel, ferrochromium, and scrap amount to 25 per cent of the total charge, but it is suitable for the large-scale production of straight ferritic stainless steel.

A certain company uses the Ruhrstahl-Heraeus Chamber (R.H. Chamber) after this LD-converter operation to reduce the carbon content to 0,010 per cent, but the removal of sulphur from this chamber is impossible, and the sulphur content of ferrochromium should be kept as low as possible.

MEDIUM-CARBON FERROCHROMIUM

If medium-carbon ferrochromium is used during the process of making the bath (carbon content 0,3 per cent) to be charged to the VOD vessel, the productivity of the furnace will naturally increase. However, the merit in the use of medium-carbon ferrochromium should be calculated by comparison of the cost of carbon reduction in ferrochromium with that in stainless steel.

Sulphur should be removed by ferrochromium producers, who need not pay serious attention to the removal of such gases as oxygen, hydrogen, and nitrogen from their ferrochromium, thanks to the newly developed methods for the production of stainless steel.

The chemical specifications for impurities in the ferrochromium to be used in the production of AISI-430 (Cr 16 to 18 per cent, P 0,03 per cent max., S 0,03 per cent max. or 0,010 per cent max., C 0,06 per cent max.) by both the AOD and the VOD processes are as shown in Table 3.

Table 3

Permissible impurities in AISI-430

	AOD %	VOD %
S	0,035 max.	0,015 max.
P	0,030 max.	0,030 max.
C	8 max.	8 max.
Si	4 (3 to 6)	4 (3 to 6)
H2, N_2, O_2	No problem	No problem

Since a high silicon content in the ferrochromium used in the AOD process will bring the bath up to a very high temperature during oxygen-blowing, it becomes necessary either for more scrap to be used or for argon gas to be used as the cooling agent.

A chromium content of 55 per cent in ferrochromium is sufficient for the making of stainless steel: the chromium content of the molten metal is controlled at 17,3 per cent (in due consideration of the chromium loss of 0,3 per cent during the VOD process and to attain the ultimate chromium content of 17 per cent in the final bath), and the consumption of low-carbon ferrochromium is limited to what is required for the final adjustment of the chemical specification.

Silicochromium is used as a reducing agent in the electric-arc furnace at the stage of primary carbon removal by oxygen-blowing, but its consumption is limited since the carbon content at the melt-down stage is well controlled at about 0,3 per cent, the chromium loss during further refining being negligible and reoxidization of the chromium in the AOD process also being negligibly small.

With the development of the new melting technique for stainless steel, the AOD and VOD processes will become more popular. As a result, the consumption of low-carbon ferrochromium and silicochromium will decrease, and the total chromium required for the making of stainless steel will be supplied as high-carbon ferrochromium — mostly as charge chromium.

Depending on the production method adopted, low-sulphur ferrochromium will be required.

POLLUTION

The problem of public nuisance, which has been growing more serious during the past few years, has also affected the ferro-alloy industry in Japan. Air pollution caused by furnace operation, water pollution resulting from the collection of dust by wet processes, and disturbing noise are regarded as the main public nuisances of the ferro-alloy industry.

The maximum emission of dust from ferro-alloy works was set as 900mg/Nm^3 in December 1962. Air pollution became more serious, especially by sulphur dioxide gas, and the maximum figures were revised in December 1970, as shown in Table 4.

Table 4

National emission standard of exhaust dust from electric smelting furnaces for ferro-alloys, December 1970

Silicon content of ferro-alloys %	Ordinary exhaust amount mg/Nm^3	Extraordinary exhaust amount mg/Nm^3
More than 40	600	300
Less than 40	400	200

Note: The standard value for the extraordinary exhaust amount is applicable when air pollution is feared to exceed the limit set for populous areas.

Since December 1970, Japanese ferro-alloy producers have been in a very difficult position in coping with environmental pollution.

As a means of dust collection from ferro-alloy furnaces, wet processes like those employing venturi scrubbers and Tyzen washers are used in closed furnaces, whereas the bag-filter process is generally adopted in open-top furnaces for the production of high-carbon ferromanganese. In ferrosilicon and ferrochromium production, the bag filter is used with open-top furnaces and the venturi scrubber with closed furnaces.

Several years ago, our electric furnaces for the production of ferrochromium were equipped only with cyclones for dust collection. In early 1966, we started several tests on dust-collection methods—the wet process, electrostatic precipitation, and the bag-filter process—which took us nearly three years. We found that it was impossible to reduce the density of the dust to below 500 mg/Nm^3 by the wet process, and the purification of the waste water to the regulation standard constituted another difficulty. A further test on silicochromium proved that it was impossible to reduce the density of the dust to less than 200mg/Nm^3, even by a wet electrostatic precipitator.

Finally, we came to the conclusion that the bag-filtering process, together with the cyclone as preduster, was the ideal process for our plant, but, because of the high temperature of the generated gas, glass-fibre cloth had to be used for the bag filter. In 1970, the first dust collector of the bag-filter type was installed for the 7 MVA and 15 MVA furnaces.

In the second stage, we did several tests to ascertain the best dust-collection methods for the 25 MVA furnace that was to be installed. Originally, the furnace was designed to be completely closed and to be equipped with a venturi scrubber, but two difficulties were envisaged: that of keeping the dust density below 100mg/Nm^3, and that of purifying the waste water to the regulation standard.

Finally, we changed the furnace to the open-top type and adopted the bag-filter process, which had already proved satisfactory for other furnaces.

FILTERS FOR THE 25 MVA FURNACE

The bag filter is designed to treat a total air volume of 1800 Nm^3/min on the basis that 650 Nm^3 of gas, mainly carbon monoxide, is generated for 1 tonne of charge chromium and that the dilution is 31 times.

To avoid any leakage of gas, the canopy hood is placed at the same level as the furnace shell top, and the working deck is placed 300 mm lower than this level so that the speed of the suction air into the canopy hood can be controlled at 2,0 m/s.

The gas and dust generated during tapping are blown into the canopy hood by a separate blower. The temperature inside the canopy hood is about 350 to 800°C, the average being 550°C. The gas and dust generated are guided into four ducts that are attached to the top of the hood and join to form two main vertical ducts. The exhaust gas is cooled in the vertical duct and is fed into the bag-house through the blower. The density of the dust at the inlet side of the bag-house is about 500 to 2000 mg/Nm^3, and the temperature is normally kept at between 200 and 250°C.

There are six chambers for each series in the bag-house, which contains 220 glass-fibre bags. The gas speed in the bag-house is about 0,74 m/min, and the dust collected inside the bag is removed by reversed gas blowing every 15 to 30 minutes. The pressure inside the bag is generally kept at about 300 mm of water.

The temperature of the gas thus cleaned and emitted into the open air is about 150 to 200°C, and the density of the dust is checked regularly by the Authorities. The maximum is 10 mg/Nm^3, and the average is 0,1 to 5 mg/Nm^3; the sulphur dioxide content is below 30 p.p.m.

The dust collected in the bag-house, together with the cyclone dust and chromium concentrates, is carried into a hopper by chain conveyor and bucket elevator to a pan pelletizer for pelletization. The pellets are fed back to the furnace, together with the chromium ore.

However, such detrimental elements as Zn, Na, and K are apt to be condensed during the recycling of the dust pellets to the furnace, and this problem should be solved in future. The composition and particle-size distribution of the collected dust are shown in Table 5.

It is important to pay attention to the glass-fibre cloth of the filter, since its deterioration will directly affect smooth operation as well as costs.

The glass-fibre cloth was originally expected to last for one year, but we now expect it to last for 2½ years. According to the operation record for the 2 years 8 months ending in July 1973, no replacement of the bag was necessary in two bag-houses, and about 20 per cent of the bags in another bag-house were replaced.

The first stage of our antipollution programme has thus been completed, and, as shown in Table 6, the density of the dust in 1970 (890 mg/Nm^3) was reduced to a maximum of 10 mg/Nm^3, while the total emission of dust from the plant (2100 g/min) was reduced to 38 g/min, despite the installation of a 25 MVA furnace.

Table 5

Chemical composition and particle-size distribution of the collected dust

Chemical composition	High-carbon ferrochromium		Silicochromium
	Cyclone %	Bag filter %	Bag filter %
Cr_2O_3	30 to 45	3 to 5	0,3 to 2,0
C	4 to 7	1 to 2	0,5 to 1,0
SiO_2	5 to 10	10 to 15	70 to 85
CaO	1 to 2	1 to 5	0 to 2
MgO	15 to 25	20 to 40	2 to 15
Al_2O_3	7 to 13	5 to 10	0 to 20
K_2O+Na_2O		7 to 12	
ZnO		20 to 30	
Moisture		3 to 5	3 to 5
Particle	<60>100 mesh 7%	<72>5 μm 74%	<37>11 μm 20%
size	>200 mesh 30%	>1,4 7%	>1,7 12%
(typical)	>325 mesh 23%	<1,4 19%	<1,7 68%
	>325 mesh 40%		
Specific gravity	3,1 (Bulk 1,9)	3,5 (Bulk 0,2)	2,4 (Bulk 0,1-0,2)

Table 6

Comparison between the dust contents before and after the installation of bag filters

		Dust in exhaust gas				National emission standard (for ferro-alloys)			
Furnace no.	Capacity of transformer MVA	Before Dec. 1970		After Apr. 1972		Before Dec. 1970		After Dec. 1970	
		mg/Nm^3	g/min	mg/Nm^3	g/min	mg/Nm^3	g/min	mg/Nm^3	g/min
24*	5	280	912	10 max.	4 max.	900	360	600	240
25†	15	560	672	10 max.	12 max.	900	1 080	400	480
27†	7,5	690	276	10 max.	4 max.	900	360	400	160
15,22†	2,5 + 3	690	240	Under suspension		900	313	400	0
28†	25			10 max.	18 max.			400	720
Sum		890	2 100	10 max.	38 max.		2 113		1 600
Rate of exhaust			100,0		1,8 max.				
					1,8		100,0		
					2,4				100,0

* Silicochromium

† High-carbon ferrochromium

As a result of the incorporation of antipollution measures, we have a very good relation with the community, and we think that every industrial enterprise should endeavour to fight against public nuisance for the sake of mutual prosperity.