Plenary Address: The Production of Medium-carbon Ferrochromium in a Bottom-blowing Converter, and its Application to Stainless Steel

by H. FRANKE* and G. DUDERSTADT* (presented by Mr Franke)

SYNOPSIS

The paper deals with the development of a new process for the refining of high-carbon ferrochromium to medium- or low-carbon ferrochromium especially suitable for the new techniques of stainless-steel making. The process involves the application of oxygen by a new bottom-blowing technique in a converter, and results in an improved recovery of chromium and a low content of impurities in the ferrochromium.

The data are based on pilot-plant, as well as on production-scale, operations. The role of this refined ferrochromium in modern stainless-steel manufacturing processes is discussed in comparison with the traditional qualities of ferrochromium.

INTRODUCTION

The consumption of chromium alloys in various forms has undergone drastic changes in the past few years. Primarily, the changes that took place in the technique of stainless-steel production considerably affected the consumption pattern of chromium alloys. Whereas, in the past, low-carbon ferrochromium was used to a large extent, there is now a pronounced tendency for the increased use of high-carbon ferrochromium. This has been made possible through changes in the processing techniques for stainless steel. The conventional process in the electric-arc furnace is being replaced more and more by processes such as oxygen blowing, vacuum decarburization, and argon—oxygen refining.

The application of high-carbon ferrochromium to these processes does not necessarily represent optimum conditions for the user, although, from the standpoint of raw material, this product is certainly very attractive. To overcome such problems as low lining life, increased furnace time, and high oxygen consumption – to name only a few examples – an alloy with a medium carbon content might offer an attractive alternative. Although in the past such an alloy did not find wide application because it was linked to the rather expensive production method typical for low-carbon ferrochromium, i.e. to silicothermic reduction, new techniques involving the application of oxygen-blowing for refining purposes may lend themselves to a more economic method of production.

The application of oxygen-blowing techniques to the refining of ferro-alloys was practised in the past, e.g., in the United States, in Japan, and in Germany. These techniques were mostly confined to the introduction of oxygen through a lance from the top. The interesting aspects of the introduction of gaseous oxygen direct to the liquid charge through the bottom of a converter has gained new momentum through the appearance of the OBM process in the field of steel production. This process has gained particular importance in the past years in the United States, where it has become known under the name of Q-BOP. Gesellschaft für Elektrometallurgie realized the advantages of employing this method for the production of ferro-alloys, and undertook an extensive study jointly with Maxhütte in Germany to assess its potential in this particular field.

In the following, we shall give a brief historical review of this development.

DESCRIPTION OF THE PROCESS AND RESULTS

Initially, a series of heatings was performed in an experimental 5-tonne OBM converter to refine high-carbon ferrochromium. The OBM technique has been described on several occasions. In principle, it involves the introduction of oxygen through one or several tuyères mounted in the bottom of the converter. The oxygen stream is surrounded by hydrocarbon gas, such as propane or natural gas, to protect the tuyères by projecting the reaction zone into the heat. The results of these initial tests were so encouraging that we decided to install a production unit at our Weisweiler works. The converter was designed for handling 10 tonnes of liquid ferrochromium. Figure 1 shows the general form of the converter, and the complete system is shown schematically in Figure 2.

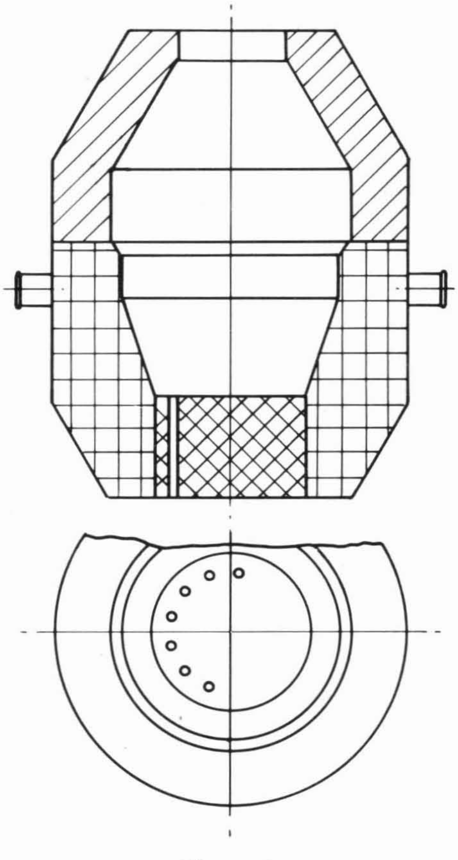
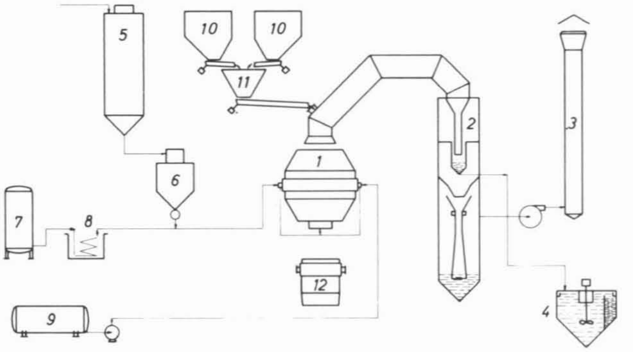


Figure 1
The converter

---

*Gesellschaft für Elektrometallurgie m.B.H., West Germany.



1. Converter vessel
2. Washer
3. Stack for cleaned gas
4. Settler
5. Lime silo
6. Pressure vessel for lime feed
7. Oxygen tank
8. Oxygen vaporizer
9. Propane tank
10. Bunker for additional feed material
11. Bunker scale
12. Tapping ladle

Figure 2
The flowsheet for the process

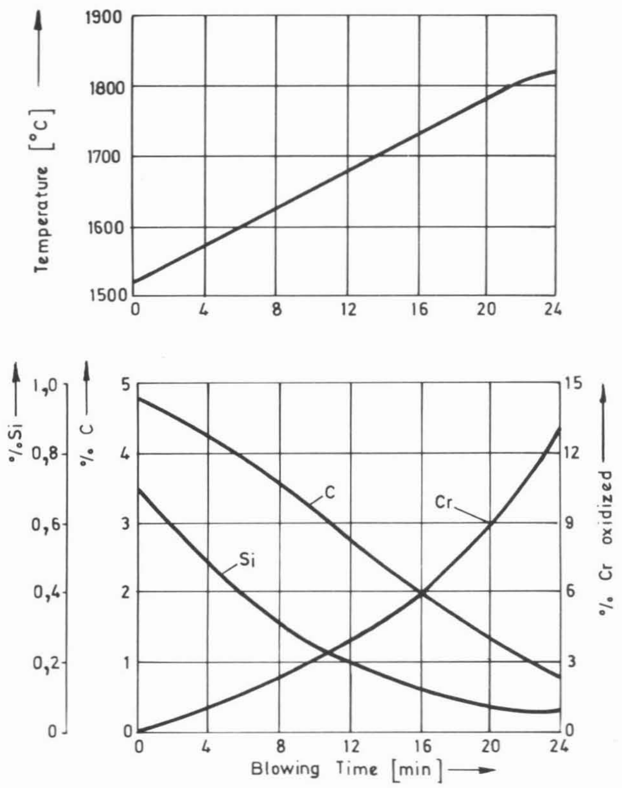


Figure 3
Temperature, carbon, and silicon contents, and chromium oxidation as functions of blowing time.

The design of the equipment was started in the Spring of 1972, and operation began in April 1973. For the staff to become familiar with the equipment, a series of heatings was initially made to reduce the carbon content from about 5 per cent to just under 3 per cent. Subsequently, our efforts were concentrated on producing ferrochromium with a maximum carbon content of 1 per cent, and Figure 3 shows the removal of carbon and the oxidation of chromium and silicon as a function of blowing time for such a representative heat of 8 tonnes input. Under optimum conditions, up to 11 tonnes of liquid metal can be charged, depending on the thickness of lining consumed.

The vessel was charged with 8 tonnes of liquid ferrochromium containing the following:

C 4,8%
Si 1,0%
Cr 64,0%
S 0,08%.

After a blowing time of 24 minutes, i.e. 3 minutes per tonne, the metal was tapped. The final analysis was as follows:

C 0,82%
Si 0,05%
Cr 65,08%
S 0,04%.

The top curve of Figure 3 shows the temperature rise as a function of blowing time. It can be seen that the temperature increases linearly during the first 80 per cent of the blow. Till then the temperature has risen by about 250°C to 1770°C.

The heat losses then increase so that the rise in temperature is reduced. The total temperature increase for the whole blowing period amounts to about 300°C.

The bottom curve of Figure 3 shows the removal of carbon and the oxidation of chromium and silicon. (The left-hand vertical scale shows the percentage of silicon and carbon in the melt, and the right-hand vertical scale shows the percentage of chromium oxidized.) It can be seen that the main portion of the silicon is oxidized at the beginning of the blow and then decreases slowly to a very low value. The removal of carbon occurs slowly down to about the 4 per cent level, and then drops linearly down to about 2 per cent. Below a carbon content of 2 per cent, the rate of removal decreases owing to the decreased carbon activity in the metal.

The curve for chromium shows the percentage of chromium charged to the converter that has been oxidized. It is practically an inverse curve for the recovery. It can be seen that the gradient of this curve increases during the blowing time. At the end of the oxygen blow, 12,8 per cent of the chromium charged has been oxidized. This amount represents only the chemical losses (i.e., oxidation). It is obvious from the curves for carbon and chromium that further blowing to lower carbon values would result in a rapidly decreasing chromium yield.

It was soon realized that efforts would have to be directed towards two major aspects:

(a) optimization of chromium recovery, and
(b) optimization of lining life.

The conditions prevailing during the blow demand a compromise between chromium recovery and lining wear for the following reasons.

(i) From the thermodynamic point of view, a high temperature is necessary to minimize the chromium oxidation. However, a higher operating temperature results in more rapid erosion of the lining.
(ii) It was found that the chromium oxide in the slag and the slag basicity were virtually constant for all heats. This means that a low slag volume (i.e., minimum fluxing additions) favours a higher chromium recov-

ery but a high lining wear, because the lining itself then acts as the 'fluxing agent'.

Sulphur removal is affected greatly by the basicity and the viscosity of the slag. A practice involving a minimum addition of lime in the initial phase of the blow to satisfy lining-life performance, followed by a final addition of lime during the end of the blow to satisfy sulphur removal, has been used. In this way, at the end of a three-month training period, the following results were achieved:

(1) a chromium recovery of approximately 85 per cent when blowing down to a maximum carbon content of 1 per cent,
(2) excellent sulphur removal (from between 0,08 and 0,12 per cent to between 0,03 and a maximum of 0,05 per cent), and
(3) encouraging performance as far as lining life is concerned.

It is doubtless possible to lower the sulphur content still further, but this would result in a higher slag volume and hence a lower chromium recovery.

The above represents the results obtained up to July 1973, when this paper was written. Since then, the technique has been improved *by reducing the chromium-rich slag with silicochromium*. During the reduction step, argon is blown instead of oxygen for about five minutes, and lime is added to produce a basic slag for lining protection and desulphurization. By this procedure, the chemical recovery could be increased for the product of 1 per cent carbon (max.) from 87,2 to 97 per cent and for 2 per cent carbon (max.) from 93,5 to 98 per cent. The effective recovery is about 3 to 4 per cent below the chemical one owing to physical losses originating from metal trapped in the slag, ejections from the converter, and losses during casting and crushing.

The first campaigns consisted of between 30 and 50 heats with a tar—dolomite lining. In the initial phase, only two heats a day were made, and this means that the converter was allowed to cool down. Meanwhile, the lining life could be increased up to 200 heats with a magnesite-enriched tar—dolomite lining. Further improvement is definitely possible by the application of a pure magnesite lining. The exchangeable bottom will stand between 70 and 80 heats, and further improvements are possible.

I should like to emphasize the following points.

(a) Our Weisweiler works produces ferrochromium carburé (carbon content typically 5 per cent) because this carbon content is most heavily in demand in the Federal Republic of Germany. From the standpoint of overall economics, this may not represent the optimum conditions, and we are prepared to go so far as to say that material of higher carbon content may be quite suitable for the OBM process and will not automatically result in a lower chromium recovery.

    It is obvious that the silicon content in the feed metal should be as low as possible. The abovementioned data refer to a feed with a maximum silicon content of 1 per cent. With higher silicon contents, the recovery, as well as the lining life, will be badly affected. It seems possible, however, that ferrochromium with higher silicon contents, say up to 5 per cent, can be treated by a varied procedure including a change of slag at a stage when the silicon content has been blown down to about 1 per cent, since, according to thermodynamics, the chromium losses are almost negligible at 1 per cent silicon in the metal. Nevertheless, the detrimental effect of a higher silicon content on the lining life will have to be accepted even if a larger amount of lime is added at the beginning.

(b) A very important factor is the transport of liquid ferrochromium from the furnace to the converter. If the metal temperature at the start of the blow is too low, excessive oxidation of the chromium will occur. The temperature of the metal as tapped from the furnace is fixed, and it is therefore important to fulfil the following conditions if heat losses are to be minimized:
    (i) a short furnace launder should be used,
    (ii) the transfer ladle should be adequately preheated, which would also prevent skull formation, and
    (iii) the transfer of metal from the furnace to the converter should take place as quickly as possible.

(c) The metal tapped from the furnace should be adequately deslagged before being transferred to the converter, so that the volume of slag in the converter is kept to a minimum.

APPLICATION TO THE MAKING OF STAINLESS STEEL

Generally speaking, the following basic techniques are being employed in the production of stainless steel, although certain variations of these processes are not uncommon:

(1) electric-arc furnace,
(2) electric-arc furnace + vacuum decarburization,
(3) electric-arc furnace + refining by converter, such as the oxygen converter employing the top-blowing practice or AOD technique or others.

In principle, all three basic processes have one primary object in common: the use of high-carbon ferrochromium, for example, material with carbon and silicon contents of approximately 5 to 8 per cent and 3 to 5 per cent respectively, or approximately 4 to 6 per cent and 1,5 to 2 per cent respectively.

Although the electric-arc-furnace process by itself is well capable of satisfying such a requirement, development over the past few years in the decarburization of stainless steel by vacuum and oxygen-converter practice has demonstrated the superiority of these techniques in regard to such factors as chromium recovery, productivity, and final carbon content provided that certain measures are taken.

It is not intended in this paper to discuss the pro's and con's of these stainless-steel processes. Instead, the remarks are confined to the suitability of medium-carbon ferrochromium for the specific needs of these processes. For example, in regard to vacuum treatment, the starting carbon content is normally limited to 0,8 per cent, but preferably a maximum of 0,5 per cent. This necessitates a preblow in the electric-arc furnace. The following calculation for the production of a ferritic steel with a chromium content of 18,5 per cent will serve to illustrate the advantage offered by a medium-carbon ferrochromium. It is assumed that 30 per cent of the total chromium input is charged as scrap and the balance as high-carbon ferrochromium (chromium content 65 per cent). As a result, the following melt-in carbon will be obtained (at a carbon recovery of 100 per cent and the addition of 210 kg of ferrochromium per tonne of stainless steel with 18,5 per cent final chromium content):

	C in FeCr %	C introduced into stainless steel heat by FeCr %
(A)	1,5	Approx. 0,3
(B)	5,5	Approx. 1,1
(C)	7	Approx. 1,5

It is obvious that, under condition (A), such a heating could be transferred direct to the vacuum-treatment station without preblow unless other factors necessitate such a step.

In the AOD process, a melt-in carbon content of 1,5 per cent does not give rise to any particular concern. However, the blowing time is extended, and this prolongs the exposure of the lining to the melt and detrimentally affects lining life. Although considerable progress has been reported on this aspect, it is expected that medium-carbon ferrochromium may offer an attractive alternative.

In many instances in the past, the performance of stainless-steel operations was evaluated on the basis of the costs of the raw materials. It is felt, however, that more attention must be given to the effect of the charge on all factors constituting production costs, productivity, and availability. The carbon, silicon, and sulphur contents of the various ferrochromium alloys will have to be evaluated more carefully for their effect on the abovementioned factors.

At the moment, we are not in a position to report any conclusive results on the use of a medium-carbon ferrochromium in stainless-steel production. A comprehensive trial study has been initiated, and we hope to be in a position to discuss the results once they become available.

REFERENCES

1. ELJUTIN, W.P., PAWLOW, J.A., and LEWIN, B.E. Production of ferroalloys electrometallurgy. Berlin, VEB-Verlag Technik, 1953. p. 206.
2. BORONESKI, K., *et al.* Raffination von Ferro-Chrom carburé-Legierungen mit Sauerstoff. *Tech. Mitt. Krupp*, vol. 21, no. 4, 1963. p. 123.
3. SACHARUK, P.A. Entkohlung des Ferro-chroms durch Sauerstoffblasen im Konverter. *Stal in Deutsch*, vol. 5, 1961. pp. 470—472.
4. FRANK, K.D. Zur Herstellung von Ferro-Chrom mit niedrigem Kohlenstoff-Gehalt. RWTH Aachen, Institut für Metallhüttenwesen und Elektrometallurgie, 1954.
5. HUBBARD, H.N., and LANKFORD, W.T. The development and operation of the Q-BOP process in the United States Steel Corporation. American Iron and Steel Institute, 81st General Meeting, May 1973.

DISCUSSION

Question from the audience:

When you started the experiments with oxygen-blowing, I believe you had previously weighed several alternatives from which you chose the bottom-blowing one. Is that so?

Mr Franke:

We knew that the results of top blowing performed by other companies were not too encouraging. Only the appearance of the bottom-blowing OBM converter encouraged us to find out whether this new converter was better suited to the decarburization of ferrochromium.

Question from the audience:

Can you quote the dust collected per blowing in one tap?

Mr Franke:

Dust amounts to about 200 kilograms per heat at an average size of 8 tonnes of metal. The dust is recovered in the form of sludge. The raw gas contains about 8 g/Nm^3 and still contains 30 mg/Nm^3 after cleaning.

Question from the audience:

As you mentioned in your paper, is the slag basicity almost constant?

Mr Franke:

We have found that, irrespective of the slag volume, the chromium content of the slag is fairly constant. It varies between, say, 45 and 60 per cent, with an average of 50 per cent. The only way to avoid excess chromium oxidation is to keep the slag volume as low as possible. Concerning the basicity ($CaO:SiO_2$), a figure of 1,5 to 1,7 will automatically arise, either by the addition of lime or, if no lime is added, by the lining acting as a flux element. It is correct that a higher basicity would result in a lower chromium oxide content in the slag; but the absolute chromium loss would be increased since the slag volume will be bigger.

Question from the audience:

Can one use gases other than propane?

Mr Franke:

Of course; one can use butane for instance. Whether one can use natural gas depends on its nitrogen content. It should be free of nitrogen because the nitrogen will be completely absorbed by the metal.

Question from the audience:

Can you say anything about the temperature drop during the reduction step when only argon is blown instead of oxygen?

Mr Franke:

The drop in temperature during the reduction step amounts to about 80°C. As the diagram shows, the temperature at the end of the oxygen-blowing amounts to about 1820°C, so that, at the final reduction step, the temperature has fallen to about 1740°C.