

## **TECHNOLOGICAL TRENDS IN CHROMIUM UNIT PRODUCTION AND SUPPLY**

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### **ABSTRACT**

The production of chromium units as ferrochromium alloys is dominated by the submerged arc furnace. Submerged arc smelting of ferrochromium is now a mature technology where improvements to decrease costs are becoming increasingly difficult. Thus some ferrochromium producers are introducing new technologies to be more cost effective and to produce better products. These developments are continuing and this paper charts the course of the more important of these and probable future trends. Included are D.C. plasma smelting, pre-heating and pre-reduction processes, and processing units such as the rotary kiln, rotary hearth furnace and fluid-bed reactor. The possible elimination of electrical energy is raised in a section on coal/oxygen based, smelt-reduction processes with some examples. Finally, the question of 'direct stainless steel' is discussed with its implications for the future supply of ferrochromium.

### **INTRODUCTION**

The smelting of chromite ores is dominated by the electric submerged arc furnace and it has become entrenched as the recognised production unit for ferrochromium alloys. Nevertheless, it does have some significant limitations in the smelting of chromite. These limitations, coupled with the fact that as a technology it can be regarded as having reached the 'mature' phase of its evolutionary development, require ferrochromium producers and their main customers, the stainless steel producers, to take a hard look at more cost and quality effective production and supply of chromium units.

The objective of this paper is to outline some of the current and possible future developments in high carbon ferrochromium and charge chrome production, the reasons for these developments and their perceived strengths and weaknesses; and to look also at possible threats to ferrochromium production in the supply of chromium units to stainless steel producers by other means.

## SUBMERGED ARC FURNACE TECHNOLOGY

The main features of a submerged arc furnace smelting chromite are shown in Figure 1. These include:

- 3-phase 3-electrode A.C. operation
- Soderberg electrodes
- choke feed with overburden of chromite, reductants and fluxes
- energy generation by electric resistance heating controlled by secondary voltage and electrical resistivity of burden and slag
- electrical resistivity of burden determined mainly by size and type of reductant, e.g. coke (low resistivity) versus coal (high resistivity).
- electrical resistivity of slag determined by its composition.

Close control of the charge composition and its sizing, and of the slag composition, are essential for effective operation of the submerged arc furnace. For example, three important slag properties are determined by its composition:

- slag viscosity : determines physical separation and recovery of metal from slag, and high viscosity slags can cause foaming problems in furnace operation.
- slag resistivity : helps determine electrode penetration and power input to the furnace with more resistive slags allowing deeper penetration, higher voltage operation and greater power inputs.
- slag liquidus : determines overall operating temperature and degree of superheat to the melt.

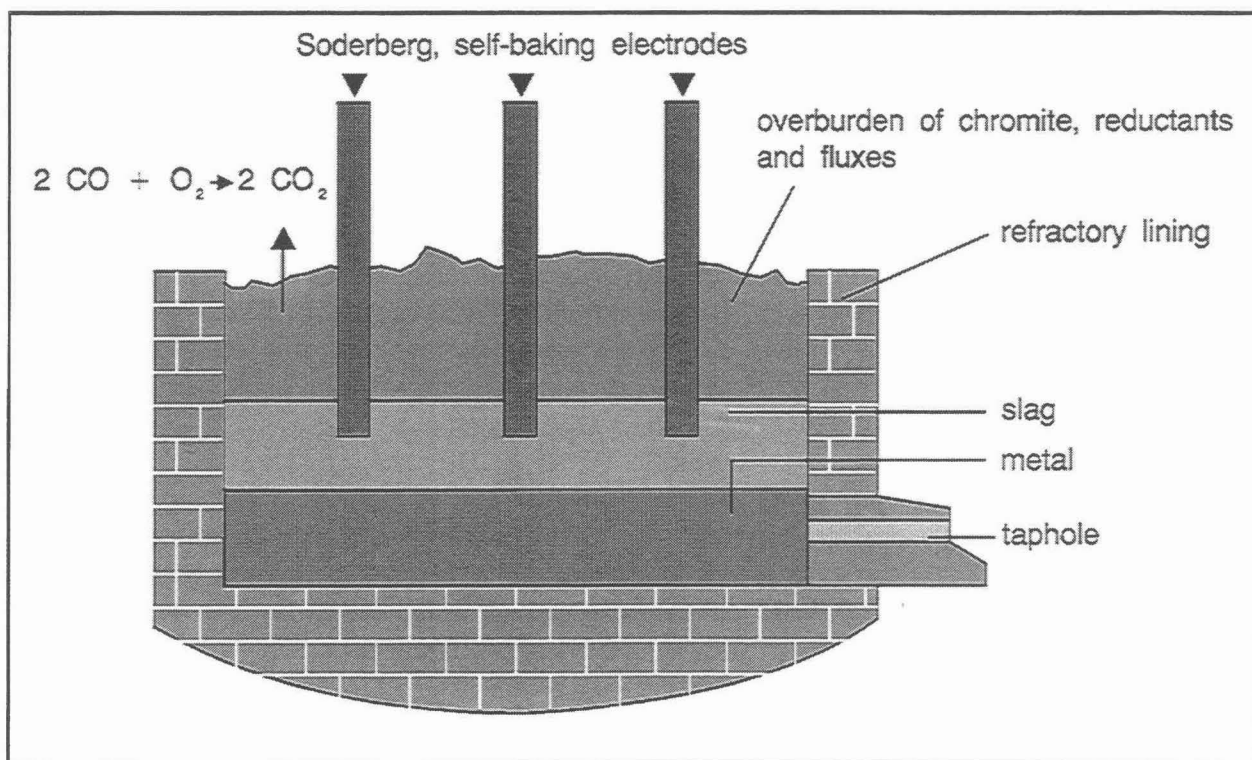


Fig. 1: Cross section of 3-phase AC sub. arc furnace

The strengths of the submerged arc furnace for smelting chromite may be defined as:

1. Relatively easy to control provided the charge is well classified to maintain a permeable overburden and allow escape of reduction gases, and provided also that the charge composition is well calculated and remains constant to maintain steady state electrical conditions and target slag composition.
2. Self regulating, with power input determining rate of consumption of overburden.
3. Some preheating and pre-reduction of the overburden by the hot, ascending reaction gases.

Weaknesses are:

1. Requires lump ore or agglomerated ore fines for maximum operating efficiency and maximum chromium recovery. This is an important factor, for example, in South Africa where approximately 70 per cent of the chromite mined is produced as fines. Agglomeration by pelletising or briquetting is costly and may not be entirely effective in furnace operations.
2. High cost coke is required as a reductant mainly to achieve correct electrical resistivity in the burden. Coal can be used in part to adjust resistivity but there may be problems with evolution and combustion of volatiles above the burden, with consequent overheating of the furnace superstructure.
3. Furnace operation and metallurgical control is dictated by the quality and physical form of the charge, and by the slag composition.
4. Slow and diluted response to deliberate changes in charge composition.
5. Chromium recoveries range from poor (65%) with high fines usage, to moderate (80%) (Figure 2).
6. Waste-gas utilisation not practical unless the furnace is closed.

There have, however, been some recent developments to improve the efficiency of submerged arc furnaces. These include:

1. Computerised control to optimise power inputs.
2. Closed top operations with utilisation of off-gas energy.
3. Pelletised and pre-oxidised fines feed.
4. Optimising slag compositions for maximum chromium recovery. For example, minimising MgO:CaO ratio in the slag improves chromium spinel dissolution thus enabling more complete chromium reduction and improved chromium recovery. Similarly, changing from basic to acid slag practice also increases spinel dissolution and chromium recovery but there are penalties in the control of silicon and sulphur in the alloy, and in decreased taphole refractory life.

Despite improvements in submerged arc furnace operations, it is evident that this is a technology which is in its 'mature' or even 'old age' phase (Figure 3). Newer technologies are necessary to address the disadvantages of the submerged arc furnace, in particular the area of ore fines utilisation, high cost reductants and chromium recoveries.

One attempt at addressing these problems is the D.C. arc or 'plasma' furnace.

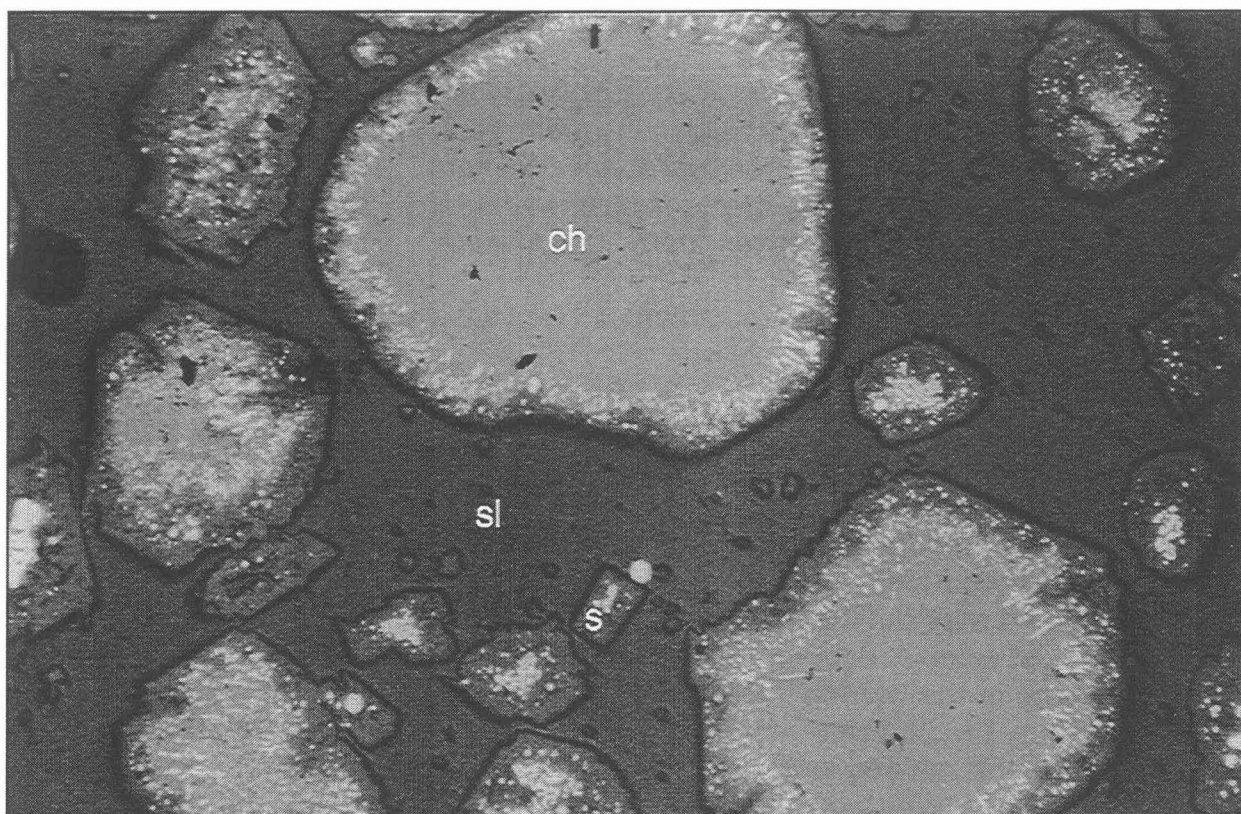


Fig. 2: Section of slag from sub. arc furnace smelting ferrochromium showing poor chromium recovery from partly reduced chromite spinels (ch) containing metallics (white), with secondary recrystallised spinels (s) and glassy slag (sl)

Mag. 100x

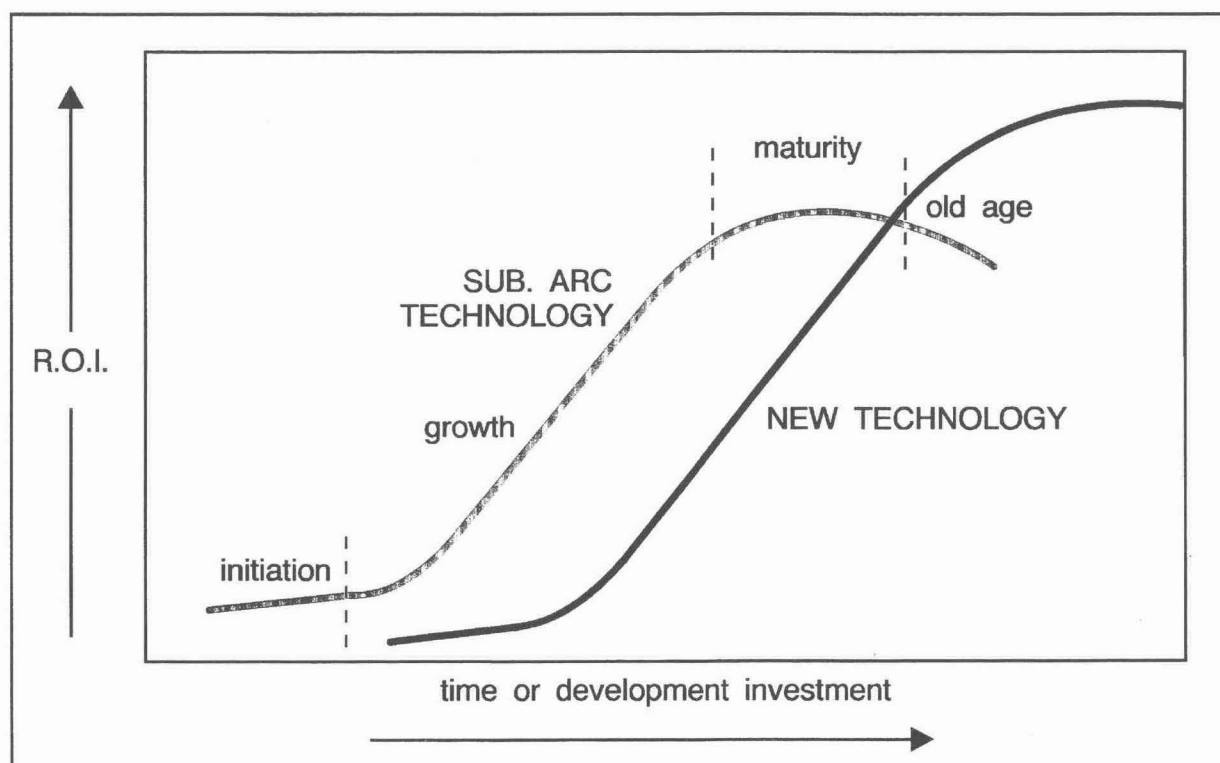


Fig. 3: Growth and decline of technologies in terms of return on investment

## DC ARC OR DC PLASMA TECHNOLOGY

Various organisations have carried out developmental work in the use of D.C. arc or plasma technology for smelting chromite to ferrochromium. These are not all detailed in this paper but in the author's experience some of the more noteworthy are:

1. Tetronics in the U.K. with their transferred, precessing arc using a non-consumable electrode [1].
2. SKF in Sweden with their non-transferred arc heaters. These were incorporated in their Plasmasmelt Process which became a commercial operation in Malmo [2] but unfortunately only operated for a short time before being closed down as a result of the recent decline in the ferrochromium market.
3. The South Carolina Research Authority, SCRA, joint development with Macalloy in the United States, using transferred arc with hollow graphite electrodes [3].

The most successful development in this field, however, has been the collaborative programme between Mintek and the former Middelburg Steel and Alloys (MS&A). This commenced in the late 1970s, accelerated rapidly in the early 1980s and resulted in the world's first commercial D.C. arc furnace in 1984. The furnace was rated at 16 MVA and operated until 1988 when it was reconstructed and uprated to 40 MVA. It is still the only D.C. arc furnace in the world producing ferrochromium alloys.

The furnace's main features are shown in Figure 4. These include:

1. Single central hollow graphite electrode.
2. DC transferred arc from the graphite electrode (cathode) to the copper bus tube (anode) at the base plate of the furnace via a conducting refractory hearth.
3. Fine materials feed through the hollow electrode.
4. Open-bath smelting operation.
5. Closed furnace with single gas off-take.

Many of the weaknesses of the submerged arc furnace are the strengths of the D.C. arc furnace. For example:

1. Operates with ore fines without prior agglomeration.
2. Uses cheaper reductants such as anthracite or coal, and allows a wider choice of reductants so that sulphur and phosphorus inputs can be minimised.
3. Achieves higher chromium recoveries (>85%). (Figure 5).
4. Changes in charge composition are reflected rapidly in slag and/or metal composition.
5. Greater freedom in metallurgical control; for example, because slag resistivity is no longer a limitation, high CaO slags, with conductivities too high for submerged arc furnace operation, can be used for production of extra low sulphur alloys.
6. Closed top operation is simplified with single electrode only, and collection and utilisation of waste-gas energy becomes a better proposition.
7. Better control of, and greater range in, product composition; for example, alloys with ultra low contents of S and P (by reductant choice and slag compositional control) and silicon levels from less than 1% to 3-4% can be produced on request.

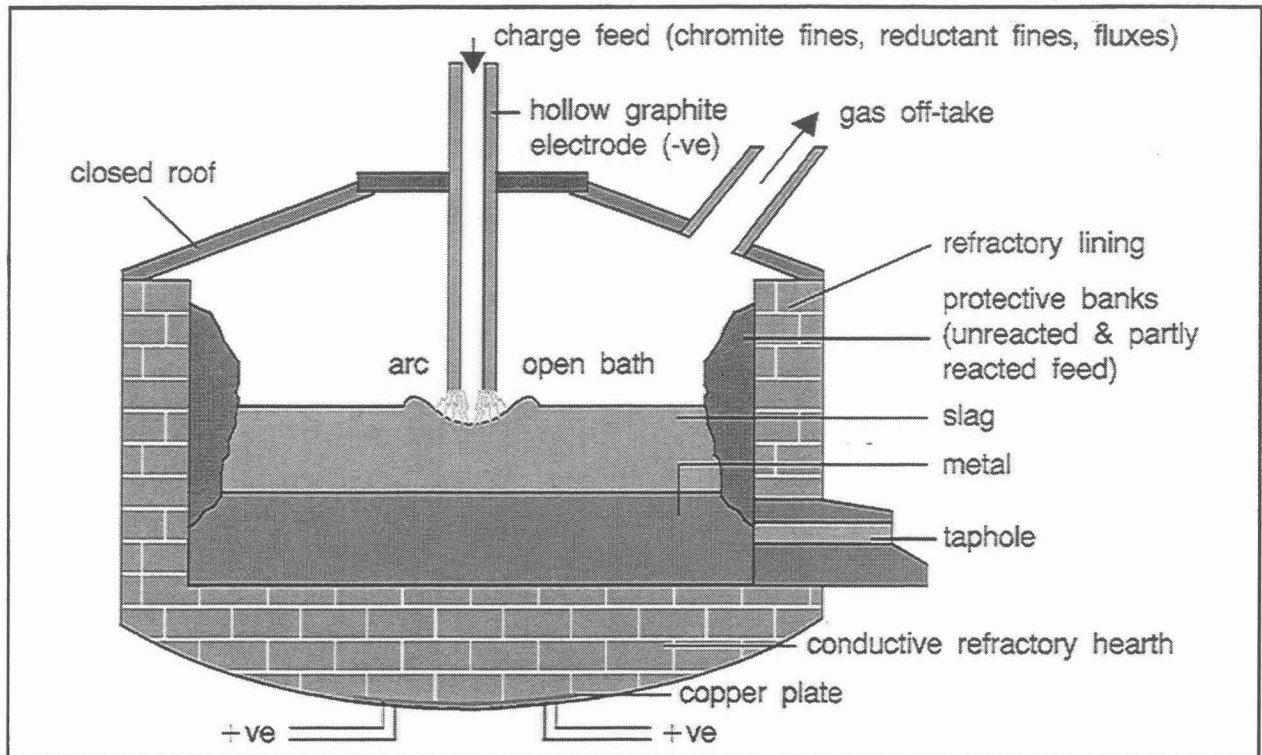


Fig. 4: Cross section of DC transferred arc furnace

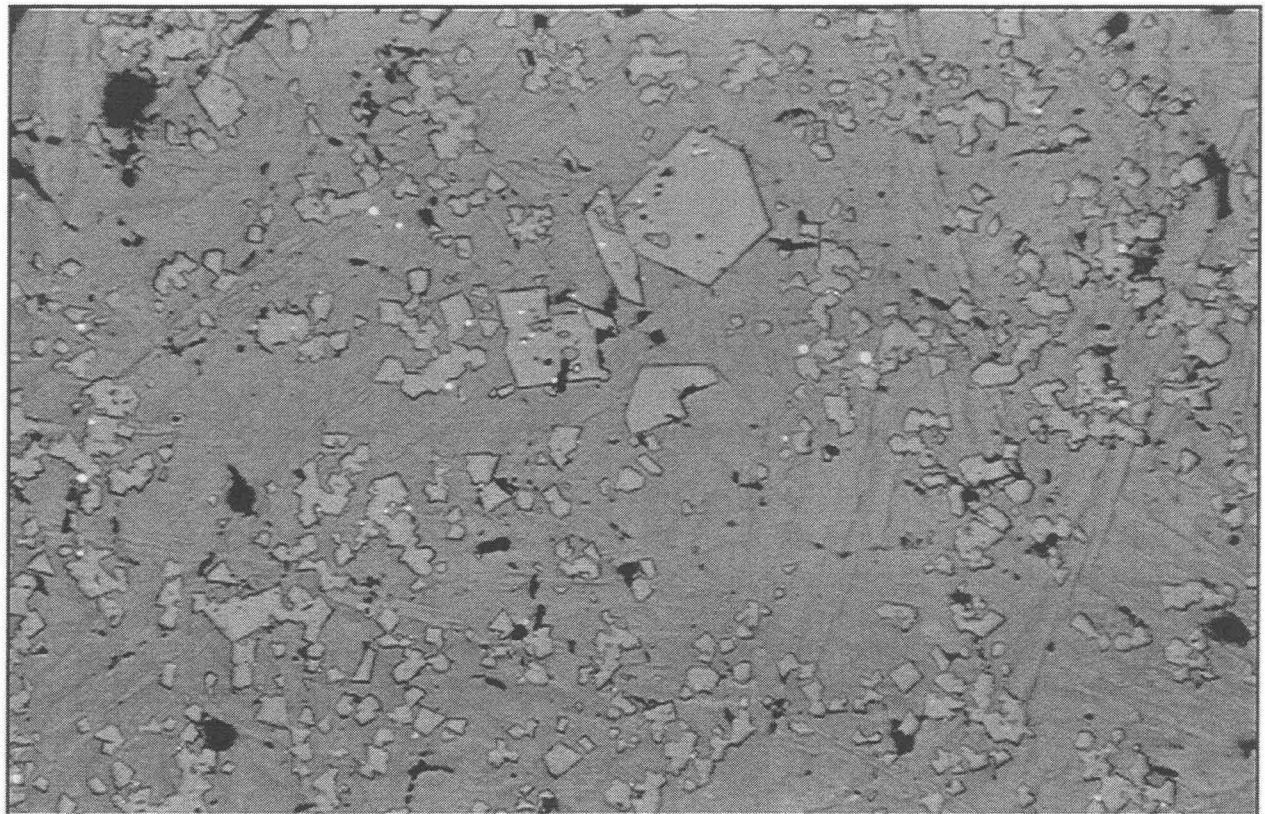


Fig. 5: Section of slag from DC arc furnace showing no evidence of residual partly reduced chromite spinels. The section contains essentially secondary spinel crystals ( $\text{MgO} \cdot \text{Al}_2\text{O}_3$ ) with some small metallic prills in a glassy slag

Mag. 100x

The D.C. arc furnace also has the ability to produce chromium-bearing alloys other than high-carbon ferrochromium or charge chrome. For example:

1. Selective reduction of low Cr:Fe chromite ores can be carried out to produce a low chromium high iron (but high sulphur) alloy and a slag with an increased Cr:Fe ratio. This slag may be subsequently processed to high carbon ferrochromium with a greater chromium content than was possible with the original ore.
2. Production of medium-carbon ferrochromium (3-4% C) by reacting charge chrome fines with chromite ore fines, the ore being reduced by the silicon and carbon contained in the charge chrome. By-product is a low-grade chromium slag with a high Cr:Fe ratio for processing to high chromium alloy.

There are, however, some important control factors to consider and some disadvantages in D.C. arc operation:

1. Strict operational control is necessary requiring reliable and comprehensive instrumentation, data logging and process control systems. For example, feed:power balance is critical; excess power (or insufficient feed) leads to superheating of the bath with grave implications for refractory and furnace integrity, while insufficient power (or excess feed) causes freezing of the bath, electrode blockages and tapping problems.
2. Stray arcing can be a problem.
3. Taphole maintenance is more critical than in a submerged arc furnace.
4. Lower thermal efficiency than a submerged arc furnace due to greater radiation loss from the open-bath operation and higher temperature gases leaving the system.

The most important area for development work on the D.C. arc furnace is to improve its thermal efficiency by using the energy in the furnace off-gases. This leads to the next technological improvement which is addressed in the following section.

## PREHEATING

Some preheating is inherent in submerged arc furnace operation with the hot furnace gases ascending through the overburden.

In addition, Outokumpu have incorporated a degree of pre-heating by directing the hot off-gases through overhead bins containing the charge and by using the furnace gases to preheat a pelletised chromite feed.

The most effective application of pre-heating is, however, likely to be linked to the D.C. arc furnace.

Because the charge to the D.C. arc furnace consists of fine materials, it appears logical to use a fluidised-bed system as the pre-heater. Experimental testwork was carried out by MS&A with Mintek and the development has been continued by Samancor. In 1994, a large pilot operation was successfully completed and the process is ready for commercial application.

It is estimated that preheating of the charge to the D.C. arc furnace in this manner will decrease the electrical energy requirement by approximately 1 MWh/t alloy and increase furnace throughput by approximately 30 per cent.

The effective use of off-gas energy in preheating the charge is a step towards decreasing the use of electrical energy, a high cost component in the production of ferrochromium in many countries.

A further step in decreasing the electrical energy component is to pre-reduce the chromite using cheaper sources of energy prior to final electric smelting. This aspect is addressed in the next section.

## **PRE-REDUCTION**

Significant developments in pre-reduction technology have already been made and others are in progress or will undoubtedly be made in the future, for this is an area in which substantial cost savings may be realised.

Following is a brief survey of existing or potential pre-reduction processes.

### **SDK/CMI Process**

Developed and used originally by Showa Denko (SDK) in Japan and subsequently installed by Consolidated Metallurgical Industries in South Africa in the mid-1970s. This was the first commercial pre-reduction process for chromite.

In the process, chrome ore fines are milled finer, pelletised with coke as reductant, and fired in a rotary kiln to approximately 1400°C. The kiln is heated by a pulverised coal burner. The pellets achieve approximately 60 per cent total metallisation of chromium and iron, and are discharged into a submerged arc furnace for final smelting.

Strengths of the process include:

- decreased electrical energy requirement (approximately 2.2 MWh/t alloy versus 3.8 MWh/t alloy for submerged arc smelting)
- use of low cost coal-based energy
- greater flexibility in furnace slag composition with respect to electrical conductivity due to the decreased proportion of reductant in the charge; thus the CaO content of slag can be higher for desulphurisation of the metal
- higher chromium recoveries than in submerged arc furnace smelting
- use of ore fines.

Weaknesses are:

- costs incurred in milling and pelletising the ore fines
- requirement for coke in the pellets
- only moderate levels of metallisation, mainly the iron component which is more easily reduced
- relatively high carbon contents in the final alloy
- accretion formation in the kiln.

## **CDR Process**

To address some of the apparent weaknesses of the SDK Process, Krupp commenced development of a rotary kiln pre-reduction process in 1984, based partly upon their earlier experience of the Krupp CODIR Process for DRI production.

MS&A and Samancor were jointly involved in batch trials and pilot trials on the process. A commercial plant was installed at the Middelburg Ferrochrome plant in 1990 and named CDR for Chrome Direction Reduction.

Amongst the advantages anticipated for this process over, for example, the SDK Process, are:

- direct use of unagglomerated chromite fines
- self agglomeration of the fines in the high temperature zone (approximately 1500°C) where the charge becomes pasty
- use of low cost coal for both the energy source and the reductant
- high degrees of metallisation (80% to >90%)
- further decreases in the electrical energy required for final smelting to approximately 1,6 MWh/t alloy for cold charging and 1,2 MWh/t for hot charging.

The commercial plant has had some developmental difficulties but these are being progressively resolved and already many of the perceived advantages have been realised.

Difficulties associated with the operation and which are receiving attention include:

- accretion formation and its prevention or elimination
- determining the most suitable refractories, particularly in relation to accretion forming tendency
- effective temperature measurement within the kiln along the reaction zone
- maintaining a constant degree of pre-reduction and agglomeration.

With the high levels of metallisation which are attained, the final furnace treatment becomes mainly a melting rather than a smelting operation. A dedicated furnace for treating the kiln product may be either a submerged arc furnace operating as a slag resistance furnace or a D.C. arc furnace.

## **Rotary Hearth Furnace**

The rotary hearth furnace is potentially capable of pre-reducing chromite and pilot tests have been carried out to investigate it for this application.

The chromite fines are pelletised with coal as reductant, charged as a stationary monolayer onto the moving rotary hearth and discharged after one revolution.

Potential advantages include:

- low cost pellets due to low pellet strength requirement
- use of coal in pellets for the same reason
- rapid metallisation (15-20 minutes) to high levels (80%) at temperatures of 1450°C
- low maintenance cost compared with rotary kilns
- no accretion formation.

The pilot tests, however, demonstrated that there is a strong tendency for the pellets to re-oxidise rapidly due to difficulties in maintaining a sufficiently low  $pO_2$  in the pellet monolayer. Further development work is necessary.

### **Fluidised-Bed**

If the fluidised-bed can be used as a pre-heater for chromite why not a pre-reducer as well? The reason is that pre-reduction of chromite requires temperatures of at least  $1300^{\circ}\text{C}$ , preferably  $1350\text{--}1400^{\circ}\text{C}$ . At these temperatures, with carbonaceous reductants and, therefore, ash components present, incipient fusion and clinkering occurs, resulting in break-down of the fluidised-bed operation.

If the pre-reduction temperature of chromite could be lowered significantly, the fluidised-bed may become an effective unit for this purpose.

In this respect, work which may be of great significance has been carried out by Kawasaki [4] and by MS&A and Samancor into the use of hydrocarbons as reductants. Kawasaki tested methane. MS&A/Samancor have investigated other hydrocarbon-bearing gases, and more significantly, coal volatiles as a hydrocarbon source.

Tests have shown that hydrocarbons have a remarkable effect upon lowering the reduction temperature of chromite, particularly if the chromite has been pre-oxidised. For example, at  $1100^{\circ}\text{C}$  a total metallisation of 52 per cent (71% Fe met. and 40% Cr met) has been achieved with liquid petroleum gas (LPG) whereas with coke as reductant but under otherwise similar conditions, only 5 per cent total metallisation is achieved (6.5% Fe met. and 1.0% Cr met).

The mechanism by which this low-temperature reduction takes place is not fully understood and requires deeper investigation. However, if this reaction can be engineered on a large scale using coal volatiles, the implications for chromite pre-reduction processes could be far reaching.

The foregoing section has discussed aspects of pre-reduction as a means of decreasing the electrical energy component in smelting chromite. A further step may be to eliminate it altogether and some developments in this regard are addressed briefly in the next section.

## **COAL/OXYGEN OR SMELT-REDUCTION PROCESSES**

Proposed processes in this category rely upon the combustion of coal with oxygen, or oxygen-enriched air, to provide the entire energy requirement for smelting chromite to ferrochromium.

Notable developments, with varying degrees of success, have been carried out by Kawasaki, NSC, NKK, and Krupp as examples.

The Kawasaki STAR Process is a good example of a shaft furnace type development in this category (Figure 6).

Other developments have included pre-reduction or pre-heating rotary kilns linked to converter-type vessels equipped with coal/oxygen lances for combustion and final smelting of the kiln product, to converter-type vessels only with coal/oxygen injection for total smelting.

While the advantage is seen in eliminating cost of electrical energy, all the processes have in common some major disadvantages and problems to resolve before they can become serious competitors to large-scale ferrochromium production by the more conventional routes and in countries where electrical energy is relatively less expensive.

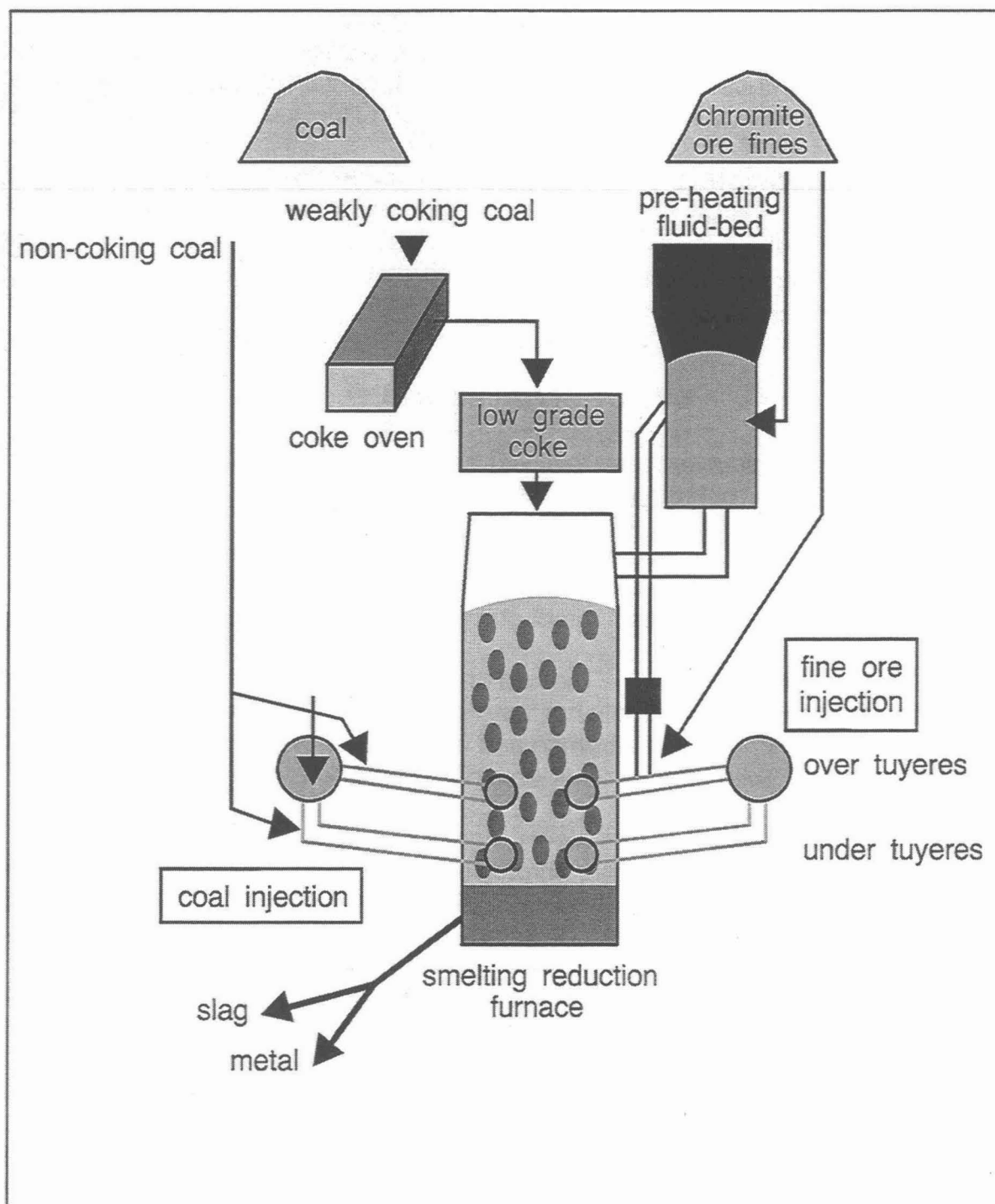


Fig. 6: The Kawasaki Star smelt-reduction process

Some examples of the problems associated with these processes are :

1. Oxygen itself requires electrical energy for its production and thus there is still an indirect cost component of electrical energy present.
2. The energy producing reactions are the oxidation of C to CO and CO to CO<sub>2</sub>. The second reaction is the most exothermic and for maximum efficiency, complete combustion of CO to CO<sub>2</sub> should be achieved; i.e. 100 per cent post-combustion. Unfortunately, chromium reduction and prevention of re-oxidation, requires an extremely low pO<sub>2</sub> which cannot be maintained in the presence of CO<sub>2</sub>. Thus only incomplete combustion is possible and the processes are inherently highly energy inefficient. Greater levels of post combustion can be attained by providing a suitable 'barrier' between the chromium reduction reactions and the CO<sub>2</sub>-containing atmosphere. For example, a coke layer or a reducing slag with little turbulence to upset the pO<sub>2</sub> gradient.
3. Even with the most favourable degree of post-combustion, the processes all generate very large volumes of gas containing substantial sensible and chemical heat. It is unlikely that any such processes will be economically viable unless these gases can be used efficiently elsewhere.
4. In the case of converter-type operations, severe refractory problems may be encountered.

### DIRECT STAINLESS STEEL

All of the processes discussed have involved the production and supply of chromium units in the form of ferrochromium or charge chrome.

An alternative approach for the stainless steel customer is to consider the supply of chromium units by some other means which may be more cost effective. This leads us into the realm of the so-called 'direct stainless steel'.

What is direct stainless steel? The terminology is subject to widely differing interpretations, ranging from simple hot transfer of molten ferrochromium to the steel meltshop, to direct smelting of chromite and oxide nickel ores to produce a molten stainless steel 'pig', with various other options between these two extremes.

One definition of a direct stainless steel process is:

"a process for producing liquid iron, chromium (and nickel) units directly from their ores and converting these to stainless steel with no production of intermediate solid forms".

It should be noted that the term 'direct stainless steel' and the definition given, make no statement about how it is to be made. It is rather a statement of a different approach or philosophy to chromium (and nickel) unit supply and may use existing or anticipated smelting and pre-reduction units.

The critical feature, whatever process operation is used, is that it must by definition take place at the stainless steel plant itself. In this sense the concept is a threat to all ferrochromium producers and particularly those not associated with a steelplant.

A wide variety of processes, or combinations of processes, may be suitable for "direct stainless steel" and stainless steel producers who embark upon this route, are likely to each have their own preference best suited to individual conditions or requirements.

Other than the direct transfer of liquid ferrochromium to the meltshop, various possibilities arise:

1. The chromium and iron (and nickel) units may be combined as the ores from the start in the correct proportions for the stainless steel grade, and co-smelted by various alternative process operations. For example:  
     rotary kiln pre-reduction → smelter → converter
2. The ores may be reduced and smelted separately, and then combined at the converter. For example:  
     Corex (or similar) plant for iron  
     mixer → converter  
     pre-reduction kiln + smelter for chromium
3. Pre-reduced chromite (via CDR or SDK-type processes) may be added directly to the iron melt where the carbon and silicon in the iron will reduce most of the balance of the unreduced chromium. Supplemental energy for final reduction and melting will be required. Such a process has been carried out by Kawasaki Steel where pelletised pre-reduced chromite from a rotary kiln is charged to molten iron in a converter. Supplemental heat is supplied by injection and combustion of coke with oxygen.
4. Direct addition of chromite ore to the iron melt allowing silicon and carbon to reduce the chromite. This has been investigated by various producers including NKK, Kobe Steel and Krupp. Potential disadvantages of processes such as these include extra slag volumes from the chromite gangue and a probable poor chromium recovery from the chromite due to the preferential reduction of iron in the chromite.

It has recently been reported [5] that Kawasaki Steel will start to produce stainless steel using a direct chromium ore smelting and reduction process in which chromium ore and ferrochromium are fed directly to a converter containing liquid iron.

## CONCLUSIONS

The high carbon ferrochromium and charge chrome industry is in an era of changing technology and demand patterns. These, separately and collectively will have important implications for its future.

On the technological front we can expect further improvements to existing recent developments such as D.C. plasma smelting and pre-treatment processes, and further developments in coal-oxygen based or supplemental smelting practices. These developments will be driven with the objective of lowering cost-of-production in an industry where at best producers are making only marginal returns.

It is important that ferrochromium producers recognise that they are likely to be faced with a relative decline in demand for their products not because of a decreased demand for chromium but because of changes in the means of supplying chromium more cost effectively to the stainless steel producer in forms other than cold, hard lumps of ferrochromium.

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