# REACTIONS AND PHASE RELATIONSHIPS IN A DC ARC PLASMA FURNACE PRODUCING FERROCHROMIUM

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## INTRODUCTION

In December 1983, metal was tapped from the world's first commercial plasma furnace for the production of ferrochromium; a 16MVA DC transferred arc furnace installed at the Krugersdorp works of Middelburg Steel and Alloys. Some of the research and development work which led to its installation was presented in a paper at INFACON 86 [1]. A more detailed description of the furnace and its operation is given in a separate paper at this conference [2].

The 16MVA plasma furnace achieved full design performance early in 1986. Now, three years later it no longer exists. This may appear paradoxical but the simple reason is that its operation since 1986 was so successful that it was decided to uprate it to 40MVA. This entailed a complete rebuild and the new 40MVA furnace may be regarded as a second generation plasma furnace resulting from the 16MVA furnace.

In February 1987, the 16MVA furnace was shut-down temporarily in order to investigate and replace the lining, which was of some concern particularly in the vicinity of the taphole. Immediately prior to shut-down, the furnace was tapped as fully as possible. As it was operated with a constant heel of metal which could not be tapped, together with banks of slag and partly reacted charge to protect the sidewall refractories, there was a considerable amount of material left in the furnace. It was decided, therefore, to investigate the furnace contents during the 'dig-out' operation in order to obtain information upon the condition of the lining, the composition of metal, slag and unreacted material remaining, and thus upon some of the metallurgical reactions taking place.

This paper does not include all the information from the 'dig-out' but concentrates upon aspects of the chemistry and metallurgy of the metal and slag remaining in the furnace. This leads to interpretations concerning the reactions taking place in the furnace and highlights some of the apparent differences between this, an open-bath operation, and the established submerged arc furnace production of ferrochromium. The paper does not pretend to answer fully the apparently complex reactions involved but hopes rather to generate further questions and create a deeper interest in what is taking place within such a furnace. If it does this, it will have served its purpose.

## DIG-OUT PROCEDURE, SAMPLING AND ANALYSIS

Three cross-sectional traverses were established across the furnace during the dig-out operation. Each sample taken could, therefore, be accurately located within the furnace by means of the relevant traverse, the horizontal distance along the traverse and the vertical distance to the furnace hearth.

As the dig-out progressed, photographic records were made of exposed cross-sections. These showed the relative dispositions of metal, slag and refractory, refractory wear, and metal or slag penetration into the refractories. From the photographic records, scale profiles were produced of various cross-sections through the furnace.

The dig-out samples were inspected macroscopically and chemically analysed. Selected samples were then chosen for sectioning and metallographic examination. Scanning electron microscopy (SEM) for phase identification was carried out where necessary.

Selected for discussion in this paper are 9 metal and 10 slag samples. They have been selected because they are not generally representative of the composition of metal and slag normally tapped from the furnace and thus might provide a deeper understanding of the reactions taking place in the furnace.

The locations of these samples have been projected onto a typical cross-sectional profile, as derived from measurement and photography. These are shown in Fig. 1. The locations of the samples are not shown in plan view because this was not found to be significant with respect to the results and discussion as presented in this paper.

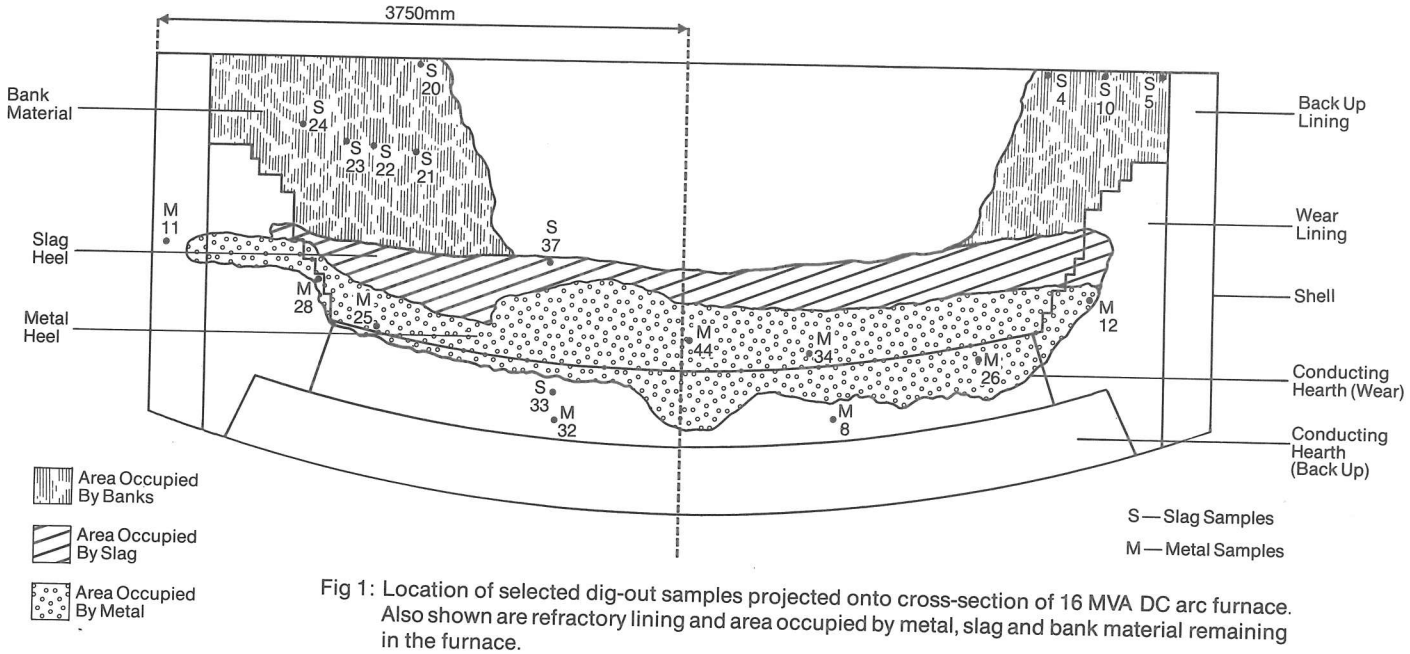


Fig 1: Location of selected dig-out samples projected onto cross-section of 16 MVA DC arc furnace. Also shown are refractory lining and area occupied by metal, slag and bank material remaining in the furnace.

## METAL AND SLAG TAPPED FROM THE DC ARC FURNACE

Before considering the results of the dig-out it is important, as a reference, to be aware of the composition and microstructural features of the metal and slag tapped from the DC arc furnace under normal production conditions.

Two compositions of metal are produced and these may be referred to as low-silicon and high-silicon metal or alloy. Typical compositions are:

| mass % | low-Si metal | high-Si metal |
|---|---|---|
| Cr | 53.5 | 52.0 |
| Si | 1.0 | 4.0 |
| C | 8.5 | 7.5 |
| S | 0.020 | 0.010 |
| P | 0.010 | 0.010 |
| Cr:Fe | 1.5 | 1.5 |

The differences in composition are achieved by changes in charge recipe, slag composition and furnace operation. The Cr:Fe ratio of 1.5 reflects the Cr:Fe ratio of the input chromite.

Metallographic and SEM examination of the low-silicon metal shows that it consists predominantly of the $(CrFe)_7C_3$ carbide with minor amounts (less than 10 vol %) of a high chromium ferrite, or sigma phase, containing 33% Cr, 54% Fe and approximately 12% Si, Fig. 2. The preponderance of carbide and small amount of sigma phase reflects the high carbon content of the metal. The metal is highly fractured and porous.

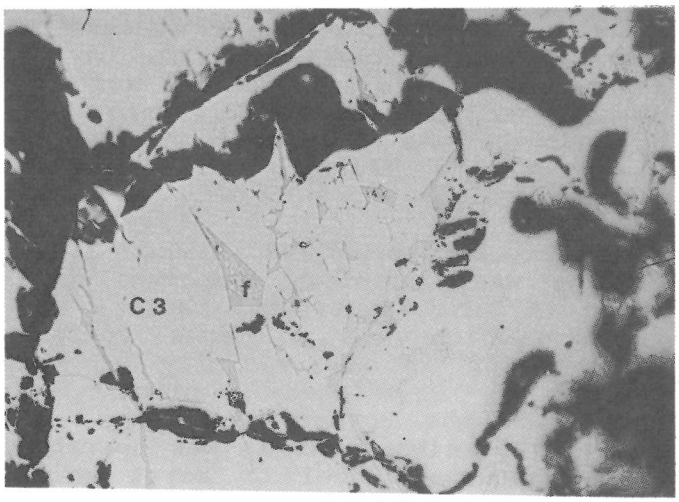


Fig. 2 : Low-silicon metal tapped from the DC arc furnace showing mainly $(CrFe)_7C_3$ (C3) with some interstitial sigma phase (f); black areas are cracks and porosity

The high-silicon metal is fairly similar in microstructure to the low-silicon metal, although the sigma phase is replaced by an iron-chromium silicide $(FeCr)_3Si$ containing 3% Cr, 82% Fe and 14% Si.

The slag used for the high-silicon metal is less basic than for the low-silicon metal, with a basicity ratio, MgO + CaO : $SiO_2$ (mass %), of 1.3 compared with 1.6 respectively.

Microstructurally the slags differ greatly. Slag from the low-silicon metal production is similar to a submerged arc furnace slag with large, partly reduced chromite spinels evident in a glassy slag matrix, Fig. 3.

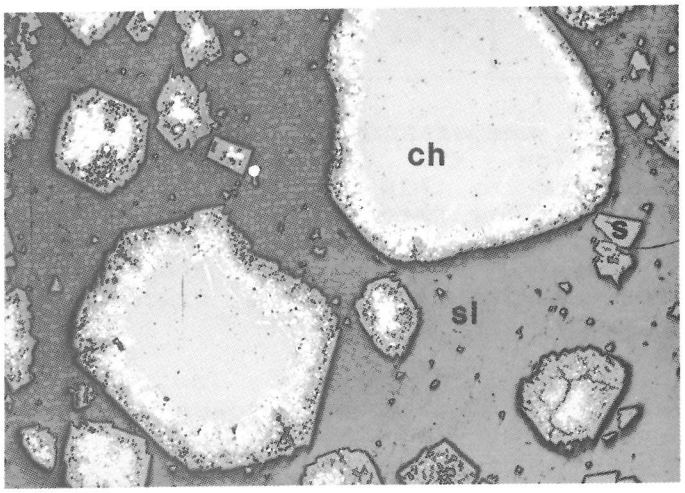


Fig. 3 : Slag from low-silicon metal production showing partly reduced chromite spinels (ch), metallics (white), recrystallised spinel (s) and glassy slag (sl).

100x

The metallised perimeter surrounding central unreduced cores of chromite are very evident in Fig. 3. Evident also is a recrystallised secondary spinel of $MgO.Al_2O_3$ which occurs both as rims on the chromite grains and as discrete well-formed crystals in the glassy slag.

In contrast, slag from the high-silicon metal production contains chromite spinels in a highly advanced state of reduction with metallic blebs accumulating in the centre of the former grains which are now largely altered to $MgO.Al_2O_3$, Fig. 4. Small, well-formed recrystallised spinels are evident also in the glassy slag matrix.

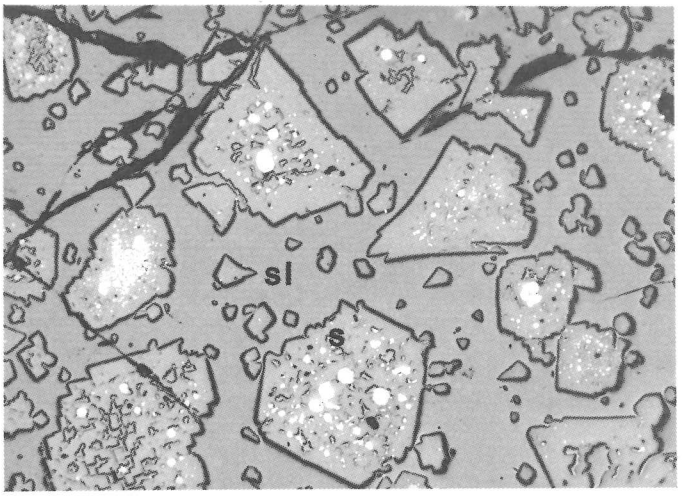


Fig. 4 : Slag from high-silicon metal production showing advanced state of reduction with metallic blebs (white) in remnant spinel grains converted to secondary $MgO.Al_2O_3$ spinel (s) in glassy slag (sl)

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It is evident, therefore, that the high-silicon metal slag has been far more highly reduced than the low-silicon metal slag. Chromium recoveries to metal will be correspondingly greater provided the metallics are released from the slag.

## METAL AND SLAG FROM THE DIG-OUT

In this section, the results of the dig-out are presented and are discussed separately for the metal and slag samples.

### Metal Samples

The compositions of the metal samples are given in Table I

From Table I, it is evident that there are large variations in the composition of the metal in the furnace. This is particularly true for the chromium content and the compositions in Table I are given in order of decreasing chromium content.

On the basis of their chromium content the samples may be divided into three sub-groups:

- chromium contents substantially greater than normal with Cr:Fe ratios much greater than that of the chromite ore input (samples M25 to M8)

Table I: Composition of metal samples from the furnace dig-out

| sample no. | composition (mass %) | | | | Cr:Fe |
|---|---|---|---|---|---|
| | Cr | Si | C | S | |
| M25 | 68.0 | <0.1 | 8.3 | 0.03 | 2.9 |
| M26 | 65.7 | <0.1 | 8.1 | <0.01 | 2.5 |
| M12 | 64.5 | <0.1 | 8.5 | 0.02 | 2.4 |
| M8 | 59.1 | 0.6 | 8.0 | 0.05 | 1.8 |
| M28 | 56.9 | 0.2 | 6.6 | 0.06 | 1.6 |
| M44 | 51.9 | 3.3 | 7.9 | 0.01 | 1.4 |
| M34 | 51.2 | 4.5 | 7.6 | 0.01 | 1.4 |
| M11 | 47.4 | 0.3 | 4.3 | 0.2 | 1.0 |
| M32 | 30.0 | 1.6 | 6.3 | 0.01 | 0.5 |

- chromium contents similar to that of normal production, with Cr:Fe ratios close to that of the chromite input (samples M28 to M34)
- chromium contents, and Cr:Fe ratios, much lower than normal (samples M11 and M32).

Considering first the low chromium sub-group, the two samples are themselves distinctly different and must be accounted for differently.

Sample M11 is typical of metal that has been produced by the selective, or preferential, reduction of chromite through sub-stoichiometric addition of reductant in an open-bath chromite smelting operation. This mechanism has been referred to previously as a means to producing a high Cr:Fe ratio slag which can be smelted subsequently to a high chromium alloy [1]. A low chromium, medium carbon alloy with a high sulphur content, typical of M11, results from such selective reduction. Evidently, therefore, circumstances in the DC arc furnace were at some time, or at some location, favourable for this mechanism to occur and this is highly significant. The fact also that this metal penetrated close to the furnace shell before freezing (see Fig. 1) can be attributed partly to a refractory defect in that area but also to the low liquidus temperature of approximately 1440°C for this metal composition, compared with approximately 1590°C for the normal tapped metal. Due to its low liquidus, compared with the much higher temperatures of the smelting operation, the degree of superheat imparted to this metal will be very large. When metal of this composition is produced, therefore, there are real dangers of it penetrating deeply into refractories which are cracked or flawed.

Sample M32 from the low chromium sub-group has an even lower chromium content than M11 but it has greater contents of carbon and silicon, and low sulphur. This composition indicates that it has not been produced by selective reduction. The sample was taken from a joint between the furnace hearth bricks and evidently is the result of ferrochromium penetration and reaction with the conductive stainless steel cladding of the bricks.

The second sub-group of samples, having close to normal chromium contents, requires little further comment except that M28 has evidently undergone silicon refining and also some carbon refining. This may be expected if an initially high silicon, high carbon alloy comes into contact with a high level of chromium oxide and iron oxide activity, such as in a poorly reduced slag or unreduced chromite.

In the first sub-group, chromium contents are generally well in excess of 60% and Cr:Fe ratios far exceed the 1.4 to 1.5 of the input chromite. Silicon levels are very low, generally less than 0.1%, indicating again a secondary reaction of the original silicon in the alloy with unreduced oxides. Carbon levels have, however,

not been affected and are at, or close to, stoichiometric proportions.

These high chromium alloys can be accounted for by the subsequent reduction of the high Cr:Fe slags produced by the selective reduction mechanism already referred to. Significant also is the fact that there is a tendancy for the high chromium alloys to occur towards the base or periphery of the metal heel whereas the main body of the heel consists of the normal composition of metal (see Fig. 1). This effect probably results from the relative liquidus temperatures of the alloys combined with the vertical and radial thermal gradients in the furnace. Liquidus temperatures of the high chromium alloys are 1670°C, or almost 80°C higher than the normal alloys and relatively close to the smelting temperature. Thus only a slight decrease in temperature will result in solidification of this alloy composition and its descent through the greater mass of lower liquidus alloy, with apparently insufficient time for dissolution in the molten heel, to form a solid heel at the hearth. The lower temperatures at the hearth will restrict dissolution of the alloy into the main mass of metal. Insufficient samples of the heel were available to determine whether there was a gradational or a sharply demarcated change to the normal alloy composition.

Two alternative possibilities to account for the presence of high chromium metal in the furnace are offered. Firstly, a selective reduction test campaign was carried out in the furnace prior to its shut-down and these alloys may have resulted from any residual high Cr:Fe slag remaining in the furnace. However, normal smelting operations were resumed in the furnace for a further 2 to 3 weeks before final shut-down and one would have expected the high Cr:Fe slag to have been diluted with the incoming charge. Thus this is considered to be the least likely explanation.

The alternative, therefore, is that selective reduction may be locally inherent in this type of operation given the way in which the furnace is operated to build up banks of partly reacted material on the sidewalls for refractory protection. Selective reduction with sub-stoichiometric carbon quantities could occur within these sidewall banks, with reduction later of the resulting high Cr:Fe material when changes in the bank geometry and size occur.

Metallographically, there are significant differences between many of these samples and the tapped metal. For example, although $(CrFe)_7C_3$ is still the dominant carbide, the $(CrFe)_{23}C_6$ carbide may also occur. This carbide was detected through SEM analysis as rims around the larger $(CrFe)_7C_3$ crystals and as discrete smaller crystals in a ferrite matrix, Fig. 5.

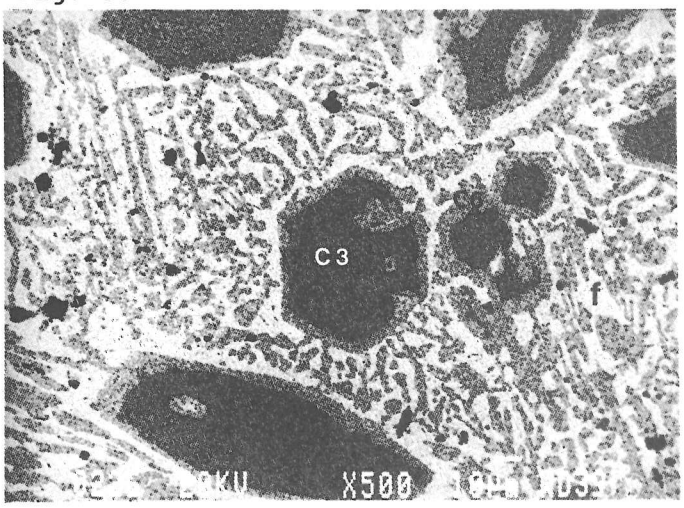



Fig. 5 : Evidence of $(CrFe)_{23}C_6$ (C6) as rims around large $(CrFe)_7C_3$ crystals (C3) and as discrete crystals in a ferrite matrix (f)

100x

The $(CrFe)_{23}C_6$ was detected only in those alloys containing markedly sub-stoichiometric amounts of carbon (M28 and M11) and not in the higher carbon alloys.

The amount of ferrite (FeCr) phase is also related to the carbon content of the alloys, increasing as carbon decreases. This is illustrated in Figs. 6 and 7 where the carbon decreases from 8.3%, (M25) to 6.6%, (M28).

The crystallisation sequence of the alloys can, therefore, be described as follows:

The primary phase to crystallise is $(CrFe)_7C_3$ at its carbon stoichiometry of approximately 9%C. If the alloy contains sufficient carbon to satisfy the entire chromium requirements, chromium will crystallise in this carbide form only, followed by the ferrite phase when no free carbon remains. If, however, the melt is substoichiometric in carbon content, crystallisation of the $(CrFe)_7C_3$ depletes the melt of carbon before chromium crystallisation is complete,

thus forcing the secondary crystallisation of $(CrFe)_{23}C_6$ at approximately 5.7%C and finally ferrite crystallisation.

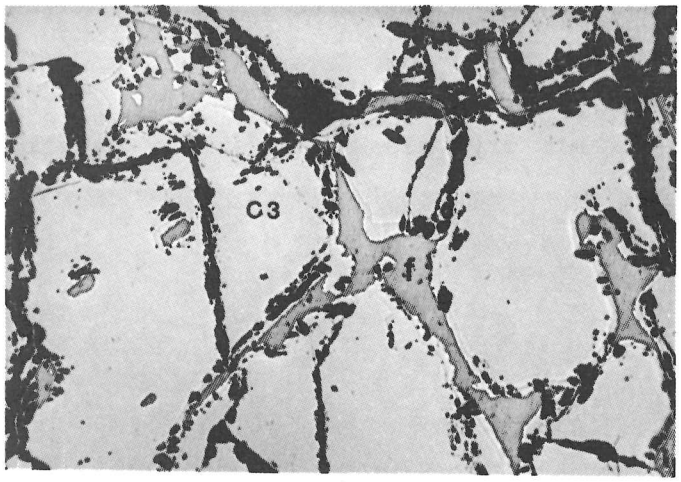



Fig. 6 : Stoichiometric carbon alloy (8.3%C) with large crystals of $(CrFe)_7C_3$ (C3) and small amounts of ferrite matrix (f). 100x

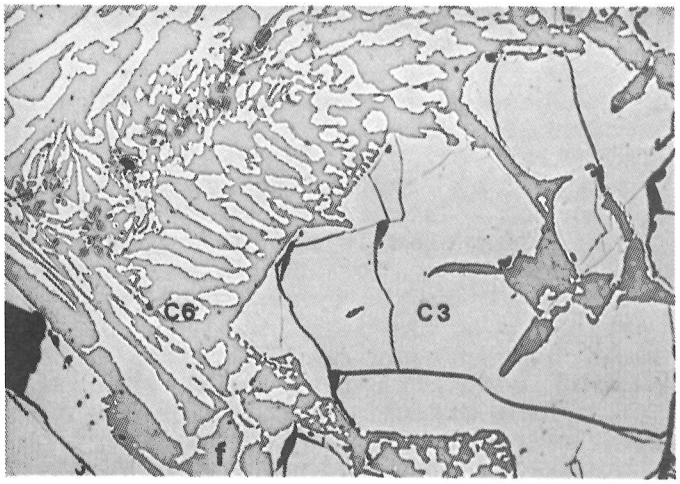
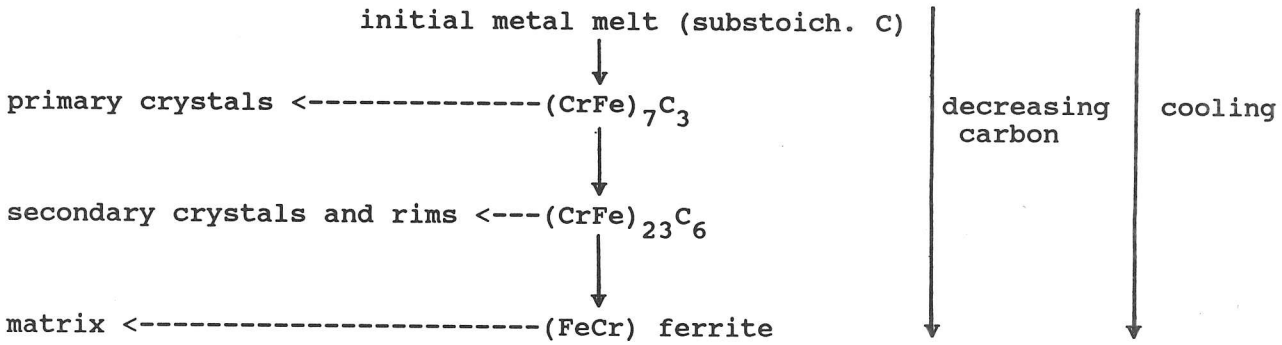



Fig. 7 : Sub-stoichiometric carbon alloy (6.6%C) with large crystals of $(CrFe)_7C_3$ (C3), smaller skeletal crystals of $(CrFe)_{23}C_6$ (C6) and a large proportion of ferrite matrix (f). 100x

The sequence for substoichiometric carbon crystallisation is thus:




## Slag Samples

Extreme variations were evident in both the composition and the microstructure of the 'slag' samples. Some examples of the compositional variations are given in Table II.

Interpretation of the variations in slag composition and their microstructures is extremely complex and a paper of this length cannot address these aspects fully. The results are presented, therefore, with some interpretations but also with the objective of stimulating further thought and discussion upon the reaction mechanisms in this type of ferrochromium smelting operation.

In Table II, an attempt has been made to link the samples broadly into sub-groups based partly upon their composition and basicity ratios, and partly upon their microstructures. The Cr:Fe ratios, although given, are not useful as a means to grouping if the total chromium and iron contents are low, as is generally the case.

Perhaps the most significant of the samples is S10, taken from the top of the banks (see Fig. 1). It has a high $Cr_2O_3$ content and a high Cr:Fe ratio. Its microstructure is shown in Fig. 8.

Table II : Composition of slag samples from the furnace dig-out

| sample no. | composition (mass %) | | | | | | | | Cr:Fe | basicity $\frac{CaO+MgO}{SiO_2}$ mass% |
|---|---|---|---|---|---|---|---|---|---|---|
| | met.Cr | met.Fe | $Cr_2O_3$ | FeO | $SiO_2$ | MgO | CaO | $Al_2O_3$ | | |
| S10 | 1.1 | 1.6 | 28.9 | 1.9 | 6.0 | 22.0 | 5.1 | 32.8 | 6.8 | 4.5 |
| S20 | - | - | 6.6 | 4.3 | 8.7 | 23.2 | 5.6 | 52.6 | 1.3 | 3.3 |
| S21 | 0.3 | 2.2 | 13.6 | 3.9 | 3.8 | 22.6 | 4.6 | 47.5 | 1.8 | 7.2 |
| S4 | 6.8 | 6.2 | 9.2 | 1.9 | 16.7 | 19.3 | 8.5 | 30.8 | 1.7 | 1.7 |
| S5 | 6.2 | 2.1 | 15.8 | 4.0 | 22.1 | 12.7 | 13.8 | 22.0 | 3.3 | 1.2 |
| S24 | 0.6 | 0.5 | 9.9 | 5.4 | 25.1 | 15.2 | 24.5 | 18.4 | 1.6 | 1.6 |
| S22 | 1.5 | 1.2 | 9.8 | 5.1 | 15.8 | 17.9 | 16.4 | 32.8 | 1.6 | 2.2 |
| S23 | 0.8 | 1.1 | 18.9 | 10.0 | 11.8 | 8.2 | 18.6 | 27.7 | 1.5 | 2.3 |
| S33 | - | - | 4.7 | 4.2 | 17.9 | 20.7 | 14.2 | 38.1 | 1.0 | 1.9 |
| S37 | 6.1 | 2.8 | 2.3 | 1.0 | 14.8 | 21.7 | 6.1 | 48.6 | 2.1 | 1.9 |

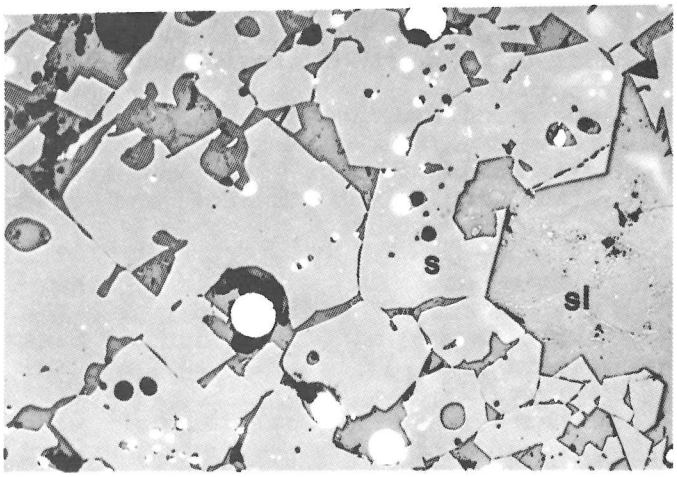



Fig. 8 : Slag with high chromium oxide and high Cr:Fe, showing predominant "secondary" spinel (s), glassy slag phase (sl) and spherical metallics (white)

100x

In Fig. 8, what appears to be a secondary $MgO.Al_2O_3$ spinel is dominant and has intergrown to a large extent. It is set in a glassy slag matrix containing spherical metallics.

SEM analysis of this sample yielded most interesting results. The secondary spinel was found to have the composition 21% MgO, 23% $Al_2O_3$, 0.7% $SiO_2$, 0.6% FeO with 54% $Cr_2O_3$. Here clearly is an extreme example of selective reduction, with all the iron but little of the chromium having been removed from the original chromite spinels, leaving highly altered, chromium enriched spinels.

The metallic spheres are almost entirely iron, with very little chromium, confirming the selective reduction. The glassy slag is essentially a calcium silicate $CaSiO_3$, or wollastonite, with small amounts of MgO and $Al_2O_3$ (5% to 10% each) and virtually no dissolved iron or chromium oxides.

Sample S10, therefore, provides concrete evidence that selective reduction can, and does, occur in the sidewall banks in the plasma furnace during normal smelting operations. Subsequent reduction of this material with its very high Cr:Fe ratio of 6.8 would produce an alloy containing approximately 78% Cr, although there would undoubtedly be some dilution with more iron-rich material to give a final alloy which may well correspond with the high-chromium compositions discussed earlier in this paper.

Samples S20 and S21 are characterised by very high alumina contents, low silica and high basicities. Their theoretical liquidus temperatures are very high, in excess of 2000°C, and it is highly unlikely that they were ever fully molten. Their microstructure appears similar to S10 but SEM analysis showed very little chromium remaining in the secondary spinel which now has the composition 26% MgO and 72% $Al_2O_3$; i.e. fully reduced.

Samples S4, S5 and S24 show microstructures which are similar to each other but very different to the previously described samples. Two of these samples were taken from near the top of the sidewall banks and one from well within the banks (see Fig. 1). Their microstructure is shown in Fig. 9.

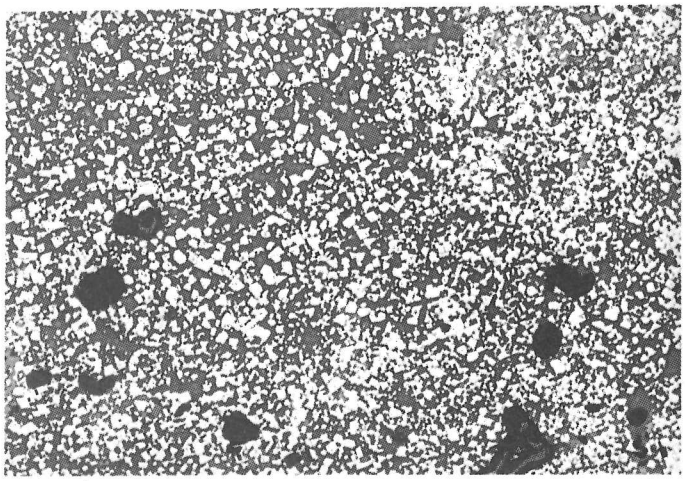


Fig. 9 : Slag showing numerous fine secondary spinels in a glassy slag matrix

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Fig. 9 is taken at the same magnification as Fig. 8 and it is evident that the secondary spinel crystals are very fine grained. No partly reacted or highly reduced original chromite spinels, as seen in the tapped slags are evident. SEM analysis, however, showed that in this case the secondary spinels contain large amounts of both chromium and iron oxide, 35%-45% $Cr_2O_3$ and 25%-32% FeO. This is difficult to reconcile with the secondary, recrystallised, spinel structure unless it is possible that the $Cr_2O_3$ and FeO were first dissolved in the slag from the original spinels, were then not reduced to metal due to lack of reductant, and then re-substituted within the finely crystallising secondary spinel lattice as the slag cooled. The glass matrix is again a calcium silicate with some MgO and $Al_2O_3$ and very little chromium and iron oxides.

It is significant that although S4 and S5 were taken in the vicinity of S10, both in vertical section (see Fig. 1) and in horizontal plan, they do not show evidence of selective reduction, emphasising that the selective reduction mechanism can be highly localised depending upon reductant availability.

Samples S22 and S23 were taken fairly close to each other deep within the banks. Basicities are high in both cases, 2.2 and 2.3 respectively, but there are some compositional differences particulary in relation to chromium and iron oxide contents. Cr:Fe ratios are similar to the input chromite, evidence that there has been no selective reduction.

Samples S33 and S37 come from very different sources, S33 from within altered hearth brickwork and S37 from the top of the slag heel. Although their basicities are greater than the tapped slag, microstructurally they are similar to one another and to the highly reduced tapped slags from the high-silicon metal operation (see Fig. 4), showing that they have been nearly completely reduced.

## CONCLUSIONS

From this investigation of metal and slag samples from the 16MVA DC arc furnace dig-out it has been shown that:

- there can be very large differences between the composition and microstructure of the metal and slag within the furnace and that which is tapped
- within the furnace itself, there are extreme variations in the metal, slag and partly reacted bank material
- metal compositions occur with chromium contents lesser than and greater than that of the tapped metal : this is attributed to localised selective reduction, where a low chromium alloy is produced first, leaving a 'slag' with increased Cr:Fe ratio which may subsequently be reduced to a high chromium alloy
- large differences in the liquidus temperatures of the alloys, combined with temperature gradients in the furnace, result in differential solidification and emplacement of these alloys before they can be dissolved within the main molten metal heel
- refining of silicon, and in some cases carbon, from the alloys occurs where high chromium and iron oxide activities, such as in unreduced slag, contact the metal; in lower-carbon alloys, $(CrFe)_{23}C_6$ occurs together with $(CrFe)_7C_3$

- slags similar to the slags tapped from the furnace are evident, but there are also slag compositions and microstructures which cannot be adequately explained in terms of the generally accepted reduction reaction sequence from chromite to ferrochromium
- secondary, or recrystallised, spinels in these unusual slags range from the expected $MgO.Al_2O_3$ composition to highly chromium-rich and iron-depleted compositions and to compositions containing significant amounts of both iron and chromium

The dig-out has highlighted the complexity of some of the reactions taking place in the DC arc furnace; if similar dig-out operations occur in the future, the opportunity should be taken to obtain additional samples in order to clarify further the reactions involved in this type of ferrochromium smelting operation.

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