

The Melting Behaviour of Chromite Ores and the Formation of Slag in the Production of High-carbon Ferrochromium

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Chromium losses to slag occur mainly in the form of metal drops and small particles of ore. Chromium recovery always depends on the melting behaviour and reducibility of the ore.

A number of techniques were employed to investigate this behaviour. It was found that the melting property is relevant to the reducibility, and that both the structure of the ores and the properties of the gangue minerals substantially affect the reduction and melting rates. Chromium reduction is an auto-catalytic process. Disintegration of the ores often occurs when reduction is nearly complete, which may accelerate the formation of slag. Early slagging interrupts the carbon transfer and retards the formation of metal. In order to improve chromium recoveries, the melting rate should correspond to the reduction rate. It is suggested that the prevention of early slagging would improve the smelting operation. It is also necessary to develop a more economic process.

Introduction

Attempts to improve the recovery of chromium production have focused on the smelting process. In some cases, losses of chromium to the slag in the form of metal drops, small particles of ore, or soluble chromium oxide may be considerable. It is well known that the reducibility and melting behaviour of chromite ores are the important factors affecting the chromium yield, and more and more attention is therefore being paid to investigations of the characteristics of chromite ores.

A number of papers on chromium reduction have been published in recent years¹⁻¹⁰. There are two main viewpoints on the reduction mechanism. One is based on liquid-solid phase reaction. It is considered that the ore may melt and reduction may take place in the slag. The other is based on most reduction taking place in the solid state. Although the chromite grains keep their solid form, the structure of the ore changes. The first mechanism suggests that appropriate additions of flux and the quick formation of slag may assist smelting. The second, however, advocates that prereduction of chromite ore is an essential way to improve production. Owing to these conflicting standpoints, completely different operations may be adopted.

It is well known that the structure of chromite ores is very complicated and their reduction behaviour varies greatly. Factors such as composition and structure, the constituents of the gangue, the grain size of the spinel, the density of the grains, and the cleavage fracture exert a substantial influence on the smelting and reduction behaviour. The objective of this investigation was to interpret the relationship between the melting properties

and the reducibility of chromite ores, to investigate the dependence of these properties on the structure and chemistry, and to find ways to decrease chromium losses to the slag.

The reduction and melting behaviour of several chromite ores was studied by a number of techniques, including thermogravimetry (TG), differential thermal analysis (DTA), high-temperature microscopy (HTM), ore microscopy, X-ray diffraction, and pilot smelting. This paper briefly gives the results of these investigations, and discusses the mechanisms of reduction and slag formation.

Melting Behaviour

Chromite ores comprise mainly spinel and various other minerals. Though the Cr, Fe, Al, and Mg contents differ considerably, the melting points of different spinels remain in the same high-temperature range. The gangue components are enstatite, quartz, olivine, and other minerals. Although the melting points of the gangue minerals are lower than those of the spinel, since the proportion of these minerals is small, the melting behaviour of the ore without the addition of reductants and flux remains the same as that of the spinel. This test concentrated on the effects of carbon and flux additions.

The tests were conducted in a high-temperature microscope with a 20 kVA graphite-tube furnace. Graphite and fluxes were passed through a 200-mesh screen. The ores tested passed through an 18-mesh screen. It was expected not to break the spinel-gangue bonding of the ores during sizing. The samples were pressed into 6 x 6 columns. The chemical analyses of the tested ores are given in Table I.

TABLE I
ANALYSES OF THE TESTED SAMPLES, WT %

Source	Cr ₂ O ₃	MgO	SiO ₂	Al ₂ O ₃	FeO	CaO
Albania	40	21	11	8	13	0,4
Turkey	42	19	8	9	14	0,4
India	50	11	5	12	15	0,5
S. Africa	41	13	7	11	23	0,5
Madagascar	43	16	10	10	14	0,8
Tibet	51	16	5	10	13	0,3

The smelting mechanism is described in terms of two temperatures: T1 is defined as the start of melting, at which the top of the samples becomes spherical, while T2 is defined as the melting temperature, at which the height of the samples is reduced by half.

The effect of flux additions, which corresponded to the additions made in commercial production, on the melting temperature of chromite ores was almost negligible under a non-reducing atmosphere. Both the samples, with and without flux additions, were not melted below 1800°C. Microscopic examination of the samples showed that, although the fluxes and gangue resulted in the formation of a liquid phase, the chromite spinel hardly dissolved in the slag. The shapes of the ore grains remained almost the same as before the test. Only the grain surfaces appeared somewhat recrystallized. Therefore, the melting behaviour of the ores defined in this paper indicates only the fluidity of the ores under certain conditions, and does not indicate the homogeneity of the melt.

With the addition of carbon, the behaviour was completely different since, above 1200°C, carbon starts reacting. The structure of the chromite changes substantially, and the metal and some oxygen separate from the spinel. The formation of an initial slag and metal phase changes the ratio of solid to liquid phases (mainly the ratio of residual spinel at liquid phases), and that changes the melting temperature and rate.

Table II shows the results of the test. It was found that the difference between the values of T1 and T2 (delta T) for the tested ores varied substantially. Some ores melted rapidly, and some slowly. At T1, the charge materials started softening, and some ore grains had already been reduced. At T2, most of the ore was reduced and the initial slag possessed some fluidity. Hence, delta T may indicate the reducibility of the ore. It was found that, for a certain ore, the smaller the value of delta T, the more easily the reduction would take place. Therefore, it is acceptable that delta T and T1 should represent the smelting behaviour.

Reduction Behaviour

Since smelting behaviour is always associated with reducibility, this work combined the investigation of both aspects.

TABLE II
MELTING TEMPERATURES OF CHROMITE ORES WITH CARBON AND FLUX ADDITIONS (IN DEGREES CENTIGRADE)

Source	TO*	T1	T2	Delta T
Albania	1698	1400	1415	15
Turkey	1790	1420	1470	40
India	1795	1460	1470	10
S. Africa	1790	1440	1450	10
Madagascar	1605	1480	1560	80
Tibet	1650	1455	1480	25

* With carbon only

The materials for the test, including the graphite and ores, were passed through a 180-mesh screen. The heating rate was 10°C/min, and the maximum temperature was 1450°C.

Figure 1 shows the DTA curves for four chromite ores. The chromium reduction is a strongly endothermic reaction, which gives a clear endothermic peak. It was found that the variation in the curves, such as the inflection point, peak area, peak height, width, and slope, corresponded to the reduction characteristics of the ores.

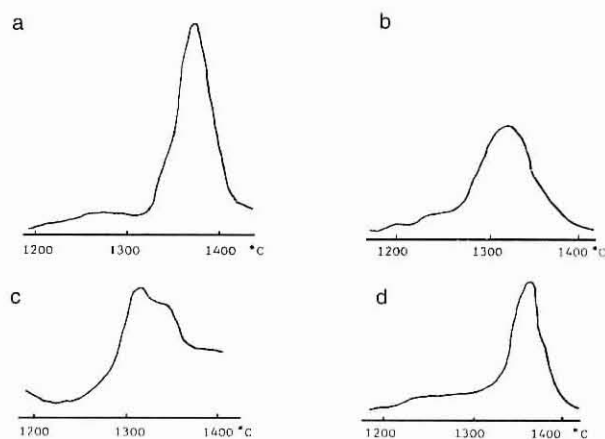


FIGURE 1. DTA curves for chromite ores with carbon additions
a. India b. Albania c. Madagascar d. South Africa

Most of the reduction reaction started at around 1200°C. At first, the curves rose slowly and smoothly. No peak appeared at that stage. At 1300 to 1400°C, strong reactions took place and an endothermic peak appeared. Two temperature measurements were obtained from the curves: the first is that of the initial reduction, and the second is that of strong reduction. The curves for some ores peaked rapidly and then immediately returned to the base-line. Usually, the readily reducible ore gives this type of curve. The curves for the other ores peaked more slowly, and did not return to the base-line even at higher temperatures. Obviously, these reactions were somehow retarded by a certain rate-control step. Ores that are difficult to reduce often yield this type of curve. Therefore, the peak width, especially the tail part, represents the reducibility of the ore.

Mineralogy of the Reduction Products

Special attention was paid to microscopic examination of the tested samples. It revealed the features of the samples at different reduction stages, together with the reduction mechanisms.

It was found that the initial reduction took place at the surface or in the outer layer of the grains, and at cleavages or fractures. Figure 2 shows the initial reduction feature. It can be seen that there are a number of thready, bead-like, and globular drops of metal at these places. The formation of metal phase substantially changes the structure of chromite spinel, and causes recrystallization. The solid-phase volume of the reduction products is less than that of the original spinel. It was observed that, at the initial reduction stage, the shapes of the ore grains were almost unaltered, and much fracturing and porosity appeared. The porous layer and fractures compensate for the decrease in

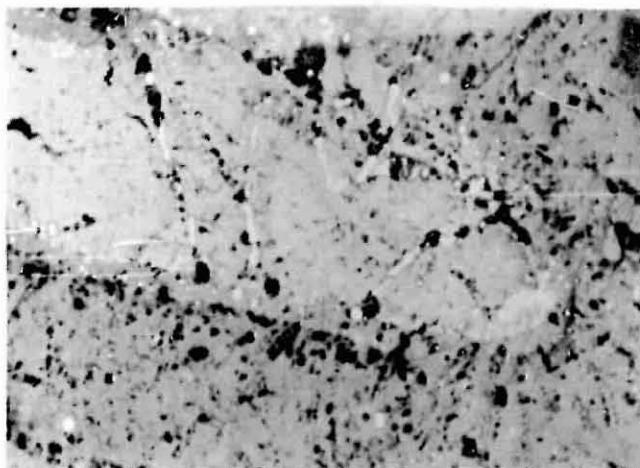


FIGURE 2. Initial metallization on grain surfaces and cracks

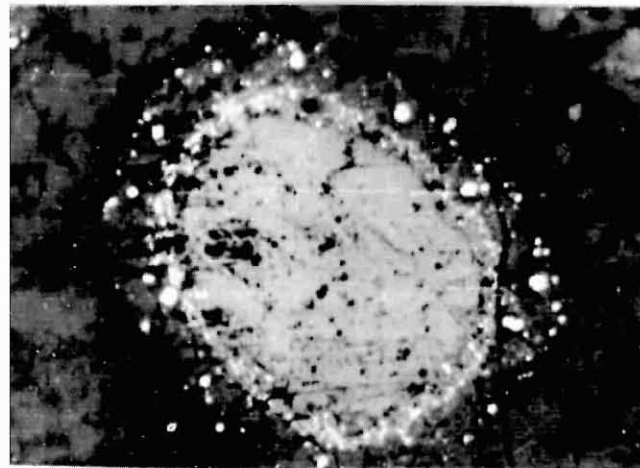


FIGURE 4. A feature of the topochemical reaction

volume. With the growth and coalescence of the metal drops, the chromite spinel disintegrated accordingly. This may speed up the transportation of carbon and the formation of metal. The surface reflectivity of the spinel also weakened appreciably.

Two typical reduction features of chromite ores were observed.

- (1) Extensive reduction. In this case widespread fine particles of metal were observed all over the grain surfaces. Most of the metal grains had just started growing (Figure 3).
- (2) Topochemical reduction. Figure 4 shows that the reduction moved from the exterior of the grain to the ore. In the outer layer, growing metal drops and recrystallized spinel were the main phases. However, the chromite spinel within the core remained almost unchanged.

Mineralogical investigation of the samples indicated that no apparent liquid phase had formed below 1350°C, and a great deal of liquid phase had formed above 1450°C.

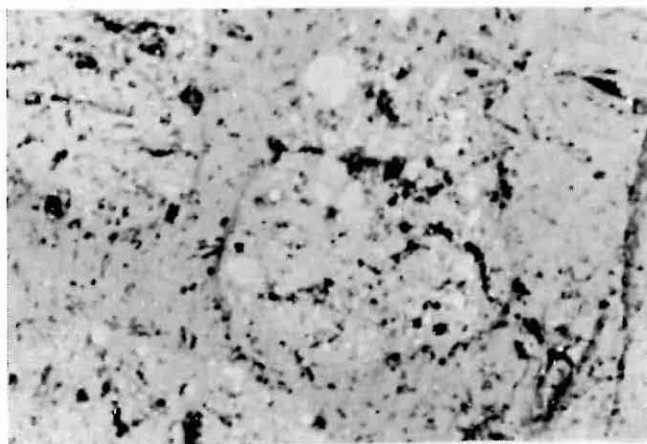


FIGURE 3. Extensive reduction throughout the grain bulk

Formation of Slag

Generally speaking, the final slag tapped with the metal after normal smelting is stable both in chemical composition and in physical properties, but the characteristics of the initial slag are still unknown.

The factors that may affect the formation of slag are as follows:

- (a) the character of the ores
- (b) the chemistry and amount of fluxes and coke used in the smelting
- (c) the furnace parameters and operation.

A number of samples of liquid slag were taken direct from a pilot furnace bath at certain time intervals between tappings in this investigation. The capacity of the submerged-arc furnace was 1000 kVA. The samples were handled carefully to avoid mixing of the metal drops. The variation of slag composition with time and sampling position is given in Table III. It is noted that the slag composition fluctuated within a small range. The Cr_2O_3 contents of the slag sampled at different times are approximate. These figures agree with the reported initial composition⁷ of the slag. It is evident that the reduction of the chromite ore takes place mainly in the softening zone, and not in the slag layer. By the time the mixture of initial slag and charge material moves downwards to the slag layer, the chromium reduction is nearly complete.

There is a small difference in slag composition with time. The tendency of change in chemical composition is obvious. The slag taken 1 hour after tapping contained more SiO_2 . The MgO and Al_2O_3 contents rose with the degree of metal separation from the spinel. The slag-melting point increased with the accumulation of metal in the bath. Furthermore, the SiO_2 content increased in the upper part of the slag layer.

A pilot furnace hearth was sectioned to examine the regular pattern of reactions in the charge materials and the movement inside the furnace. It was found that the softening zone is the most important place where intensive reaction and slag formation take place.

TABLE III
SLAG VARIATION WITH TIME IN THE SMELTING BATH, WT %

No.	Time	Position	SiO ₂	MgO	FeO	Al ₂ O ₃	Cr ₂ O ₃
11	1	U	26,03	29,82	3,02	19,42	6,15
12	1	M	25,75	31,85	3,17	21,51	6,21
13	2	U	24,14	33,36	3,68	23,24	8,26
14	2	M	22,92	32,53	4,17	23,17	9,36
15	3	U	23,20	34,62	2,91	22,37	6,51
16	3	M	21,91	34,97	2,69	25,01	6,01
21	1	U	26,90	33,60	3,27	23,88	6,36
22	1	M	25,77	32,76	4,03	23,42	8,55
23	2	U	26,24	35,03	2,68	23,94	5,45
24	2	M	25,81	35,23	2,74	24,62	5,33
25	3	U	23,67	24,92	3,16	25,50	6,44
26	3	M	22,31	34,03	3,43	26,71	7,31
01	4		24,34	34,97	2,47	24,78	5,09

Note: Samples 11 to 16 were taken near electrode B, while samples 21 to 26 were taken between electrodes B and C. Sample 01 was the final slag. The time indicated is the hours after a tapping. U and M represent the upper or mid positions in the slag layer.

Discussion

It is generally accepted that the rate and extent of reduction, and the melting behaviour depend mainly on the chemistry and structure of the ore.

Dawson and others^{4,5} who investigated the factors affecting the reduction rate of chromite suggest that the rate and extent of reduction are determined by the chemical composition of the chromite. The reduction of a chromite rich in magnesium and chromium oxides should therefore be more difficult than that of a chromite rich in iron and aluminium oxides.

On the contrary, Hu⁸, in a summary of commercial experience, suggests that the reducibility of chromite ores relates to their ratios of MgO to Al₂O₃: the lower this ratio, the poorer the reducibility.

In reality, data on the production of high-carbon ferrochromium, such as metal productivity and chromium loss to the slag, are always influenced by the origin of the ores used in the smelting. It is very common for ferroalloy producers to take production data as criteria in evaluating chromite ores. Obviously, the chemistry is not the sole factor affecting reducibility.

To evaluate these properties, the following factors should be taken into full account:

- (1) the temperature at which reduction starts
- (2) the maximum metallization at a certain temperature
- (3) the reduction rate.

In this work, both the DTA curves and the HTM results were employed in the evaluation of the reducibility of the ores tested. In spite of the differences in technique, e.g. temperature ranges, states of matter, etc., the conclusions drawn from the two methods agree very well.

Owing to the low temperatures and the absence of flux additions, no slagging occurred during the DTA test. As a result, the DTA curves reveal the tendency of the ore to undergo reduction in the solid state. The HTM, however, showed both the melting behaviour of the chromite ores and the action of the fluxes and reductants. It can be said that the HTM test simulated the chemical reactions and physical changes of the charge materials during smelting.

TABLE IV
VARIATION OF PHASES IN THE CHROMITE ORE VERSUS THE DEGREE OF METALLIZATION DURING REDUCTION

Degree of metallization, %	0	15	41	54
Reducibility of Fe/Cr, %		36/10	90/30	100/48
Spinel, %	79,6	65,7	43,5	32,0
Slag, %	20,4	24,9	30,4	32,4
Metal, %	0	7,3	19,0	25,7
Liquid-to-solid ratio	0,26	0,49	1,14	1,82

Table IV lists the calculated percentages of the phases versus the degree of metallization during the carbothermic reduction of the chromite ores. Presumably, all the metal and slag phases were above their liquidus temperatures, and the spinel remained in the solid state throughout. It is clear that the melting behaviour of chromite ores depends upon both the reducibility and the chemistry of the impurities in the ores. Only when the liquid-solid ratio of the samples is high enough, can the molten state be observed.

Mineral texture is a key factor in melting behaviour. Chromite ores often have a granular, nodular, or tabular form. The textural characteristics of chromite ore involve all its physical properties, chemistry, and crystallography, e.g. grain form and size, density, dispersion of lattice defects, development of cleavage fracture, distribution of cementing gangue minerals, and bonding of spinel grains. Almost all rate-control steps are relevant to these characteristics.

Figures 2 and 4 show typical features of the reduction progress, which may reveal the importance of texture.

Figure 3 shows extensive metallization throughout the grain, with no apparent difference in size and form between the metal particles on the fringe and those in the core. This may indicate that the diffusion rate of the reductant within the grain is as high as, or even higher than, the rate of the reaction kinetics. This feature is often found in readily reducible ores.

In contrast, Figure 4 shows topochemical metallization in a grain section. In this case, the diffusion rate of the reductant is slower than the rate of the reaction kinetics, and the transfer of reductant was thus retarded. Even though a large amount of coalesced metal beads and recrystallized spinel existed in the outer layer of the grain, the reductant had not diffused into the core. Probably dense or recrystallized spinel prevented this, and diffusion may thus have become the rate-controlling step.

Figure 5 shows a section of lumpy ore sampled from the softening zone of the hearth of a high-carbon ferrochromium furnace. The surface was covered by a layer of liquidus metal formed during the reaction. Towards the interior, bulk dispersed metallization and spinel recrystallization were clearly apparent, similar to those shown in Figure 4. It seems that the initially formed metal phase often coalesces and grows towards the exterior. Similar phenomena have been recorded elsewhere⁴. Without doubt, the transfer of carbon through the metal phase is inevitable. All the TG, DTA, and HTM studies on the melting behaviour of chromite ores showed that solid-state reduction predominates and promotes the slagging process. In the initial stage, slag formation may assist the transfer of carbon from the coke to the ore particles to some extent. When the slag accumulates, it may become a barrier to the transfer of carbon.

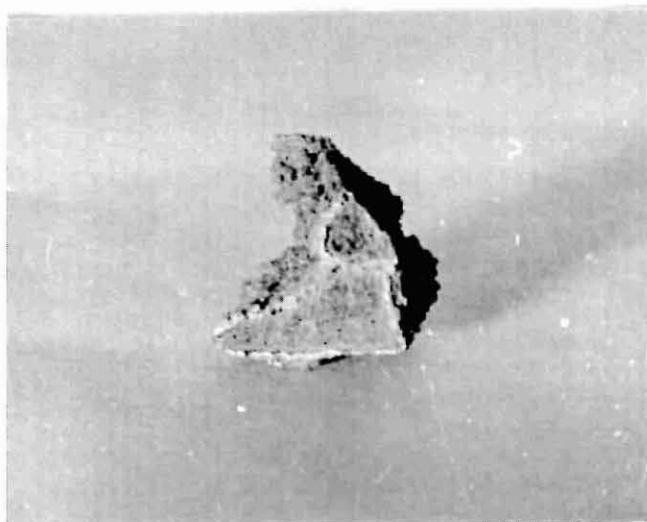


FIGURE 5. A lump of chromite ore covered with a layer of metal

Carbon activity in carbon-saturated alloys is unity – the same as graphite is. Also, carbon transfer in the liquid metal is faster than in the other phases. As a result, carbon-saturated metal plays the role of carbon carrier in the mass-transfer processes, as well as the role of the reductant that takes part directly in the reaction between the liquid and solid phases.

However, if the transfer of carbon to the liquid metal is somehow obstructed, the carbon in the alloys will be consumed and the activity will be less than unity. The reduction rate will thus be retarded.

Carbon is transferred into the chromite particles by surface diffusion, boundary diffusion, and volume diffusion. Surface diffusion is the most rapid mechanism.

As illustrated by the DTA curves in Figure 1, the initial reduction rate is very slow. The rate later accelerates, and rapid reduction occurs. The dependence of rate variations on the structure of the ore can be interpreted as being the result of an autocatalytic process.

A different type of mechanical force appears around lattice defects. Such a force will cause the carbon atoms to diffuse towards the defects. There are a great number of lattice defects on the surface and at the boundaries of chromite grains, but the defects in the bulk of the grains are somewhat fewer. Accordingly, both diffusion and nucleation are hindered by the interior structure of the grains. Metallization in the bulk of the grains substantially increases the number of lattice defects. Evidently, metallization produces numerous pores and cracks. The new phases and defects catalyse the reaction, and may promote diffusion and nucleation. In addition, the reaction product (CO-gas) and spinel recrystallization produce enormous stress within the bulk of the particles, which is strong enough to break the chromite ore. Subsequently, the formation of new surfaces accelerates the carbon transfer and the rate of kinetic reaction.

It is accepted that ores of higher iron content react more readily. The thermodynamics of the reduction of iron oxide in chromite spinel is more favourable than that of chromium oxide. Iron reduction creates numerous vacancies and defects, which provide free sites for carbon diffusion. Subsequently, the extensive nucleation of products rich in iron catalyses the chromium reduction.

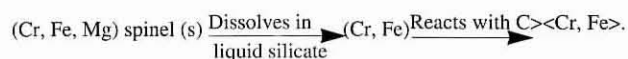
The disintegration of ore and coke during reduction is an important metallurgical phenomenon. In the production of

high-carbon ferrochromium, it is an essential step in the formation of slag.

Coke ash, mainly SiO_2 and Al_2O_3 , comprises 7 to 10 per cent of the slag mass. Variation of the coke addition hardly affects the slag behaviour. However, the melting point of the slag is relatively lower than that of the gangue and the spinel. The ash also contains some Na and K oxides, which may catalyse the carbothermic reduction, and initiate the formation of the liquid-slag phase.

It was observed in this work that lumpy chromite ore grains disintegrate during reduction. In practice, integrated lumps were seldom found in the lower part of the softening zone of the furnace hearth. In the smelting of high-carbon ferrochromium, disintegration often occurs in the middle or final stage of reduction, and results in the formation of metal, grain particles, and slag. Subdivision of lumpy ores promotes slagging, since the surface of the small particles may easily contact molten fluxes and slag. In the case of easily reducible ores, disintegration usually takes place, followed by simultaneous final reduction and slagging. Little residual spinel was found in the slag samples. On the contrary, the disintegration of ores that are difficult to reduce introduces a great quantity of unreduced chromite grains or unseparated metal-spinel particles into the slag. The grains mix with the liquid to form a suspension.

According to the literature^{9,10}, the reduction of chromium proceeds through the following sequence:



If this were so, the chromium content of the slag should be much higher than that of the iron, since the reduction of iron predominates in the initial stage of the reaction. Conversely, the chemistry of high-carbon ferrochromium slags has always shown that the ratio of Cr/Fe in the slag is almost the same as in the charge. Mineralogical investigation of the slag also confirms the constitution of the suspension. It may be surmised that, as soon as spinel grains enter the slag, their opportunity for contacting carbon will be immediately minimized, and final reduction will be interrupted. Reduction in the slag is limited, and thus chromium losses to the slag become inevitable.

With regard to the melting behaviour, density is also an important factor. Porous cementing gangue separates more easily from chromite, especially when its melting temperature is low. Relatively dense, granular chromite often tends to melt. The smelting of chromite that is difficult to reduce, together with the easily meltable gangue, can be really troublesome. In this case, the ore often melts easily and chromite grains become suspended in the slag.

It can be concluded that melting behaviour is governed mainly by reducibility and the properties of the cementing gangue. To eliminate chromium losses to the slag, it is necessary to control the reduction and melting rates for the easy meltable ores, so as to make the melting rates correspond to the reduction rate. A number of ways to adjust the reduction and slagging rates have been investigated, including size control of the raw materials, flux additions, blending of ores with different characteristics, adjustment of the electrical parameters, etc.

The development of new processes, such as plasma smelting and solid reduction of chromite ore, provides a variety of ways to intensify the reduction of chromium.

However, the study of the behaviour of different types of chromite ores and of new processes is still necessary, and will certainly provide more methods to fully utilize the world's chromite resources.

Conclusions

- (1) The melting behaviour of chromite ore under reducing conditions is relevant to the reducibility of the ores. DTA and HTM tests may provide important information on these phenomena.
- (2) Chromite reduction is an autocatalytic process. Both the structure and chemistry of chromite and the gangue properties substantially affect the reduction and melting rates.
- (3) The reduction of chromite takes place mainly in the solid state. The reduction of chromite grains in slag is retarded by interrupted carbon transfer. Accordingly, in order to minimize chromium losses to the slag and prevent early slagging, the melting rate of the chromite ore should correspond to the reduction rate.
- (4) It is necessary to improve the process to intensify reduction and to eliminate early slagging. This will increase the recovery of chromium in the production of high-carbon ferrochromium.

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