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The Solid-state Reduction of Chromite

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The work described in this paper establishes the technological feasibility of the use of an externally heated shaft furnace for the reduction of composite chromite pellets.

In the search for alternative routes for the production of Fe–Cr–C alloys, an effort was made to utilize the off-gas of a coal–oxygen smelter for the prereduction of chromite.

The kinetics of the solid-state reduction of composite chromite pellets were established, and the mechanism of reduction was studied. It was found that, although the solid-state reduction of composite chromite pellets occurs via a CO gaseous reduction step, the presence of finely divided carbon in close proximity to chromite is imperative in order to promptly restore the reduction potential of the gaseous phase around the oxide particles.

Accordingly, the off-gas of a ferrochromium smelter cannot be used directly to prereduce its charge. However, the off-gas can be utilized solely as a fuel to provide the energy for the solid-state reduction of composite chromite pellets in the reduction chamber of an externally heated shaft furnace.

A mathematical model, based on experimentally determined kinetic data on chromite reduction and heat-transfer analyses, was developed to describe such a process. The validity of certain assumptions made, and the boundary conditions employed in the model, were confirmed experimentally with a bench-scale shaft furnace. The model predictions with regard to the behaviour of the shaft furnace were in good agreement with the experimental findings.

Introduction

The major problem in the development of non-electrical processes for the production of ferrochromium is the simultaneous generation of substantial quantities of CO-rich off-gas. However, unlike iron ores, chromium ore cannot, for all practical purposes, be directly reduced by such off-gases.

The inability of CO gas, in the absence of solid carbon, to reduce chromite at a rate commensurate with that experienced in the solid-state reduction of composite chromite pellets has never been explained satisfactorily. Moreover, the possibility of solid-state reduction of chromite directly by solid carbon has generally been dismissed[1,2].

For the application of the prereduction of chromite in practice, it is essential that the agent and mechanism of the solid-state reduction of chromite are understood, so that the CO-rich off-gas can be fully utilized. Consequently, some aspects of the kinetics of the solid-state reduction of chromite were investigated in an attempt to ascertain a mechanism for the reduction by which the experimental findings of the present investigation, as well as those of previous researchers, could be explained satisfactorily.

The results of this part of the study strongly supported the theory that the solid-state carbothermal reduction of chromite is essentially indirect, i.e. by CO gas, and that the direct reduction of chromite by solid carbon is much less important. However, the presence of finely divided carbon in close proximity to the oxide is essential to maintain the low oxygen potentials in the gaseous phase that are required for the progress of reduction.

The impracticality of maintaining a sufficiently low oxygen potential within chromite particles during reduction by a reducing gas ruled out, on chemical grounds, the feasibility of the direct utilization of a CO-rich off-gas for the prereduction of chromite. Efforts were therefore focused on the use of the combustion energy of the gas in the combustion chamber to preheat and prereduce composite chromite pellets in the reduction chamber of an externally heated shaft furnace.

A computerized mathematical model was developed to simulate the rise in the temperature and the degree of reduction within the charge of such a furnace as a function of time. The results of these simulation tests aided the design of a bench-scale shaft furnace that was used to experimentally verify the predictions of the model.

This paper discusses the results of some experiments on the solid-state reduction of composite chromite pellets, and describes the mechanism proposed for the progress of reduction. The simulation model for the reduction of composite chromite pellets in an externally heated shaft furnace is then addressed. Finally, the bench-scale shaft furnace and verification experiments are described briefly.

The Kinetics of the Solid-state Reduction of Chromite

Some factors that significantly affect the kinetics of the reduction of chromite were investigated in an effort to ascertain the most likely mechanism of reduction.

Thermogravimetric Analysis

A number of experiments were carried out in a thermogravimetric analyser (TGA), where samples of dried briquettes or pellets with a mass of 10 g were heated under an inert atmosphere at 1300 °C for 2 hours.

Excess stoichiometric carbon

Composite pellets containing various quantities of carbon were reduced in the TGA. However, the rate of reduction of composite pellets was not significantly affected by the carbon content of the composite pellets.

Flowrate of nitrogen gas

In the first few experiments, an unperforated alumina crucible was used. The rate of reduction was not affected by an increase in the flowrate of N_2 gas. However, when a perforated alumina crucible was used, an increase in the gas flowrate resulted in a significant increase in the rate of reduction, as shown in Figure 1. The N_2 flowrate is expressed as the ratio between the volume flowrate of the gas (l/min) and the mass (g) of the sample (F/M). The higher degrees of reduction attained at higher N_2 flowrates are due to the fact that the N_2 carried the gaseous product(s) of reduction away from the reaction site. A very high reduction rate would therefore be expected if the test could be carried out in a vacuum. A test run in a graphite-resistance vacuum furnace was therefore conducted, and is described later.

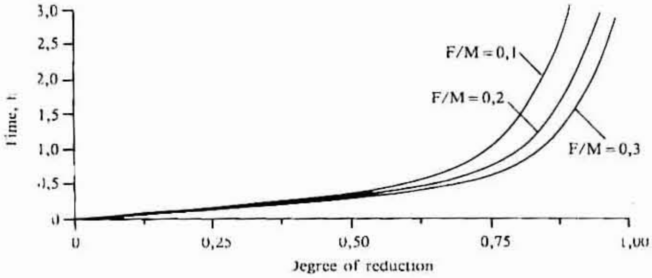

FIGURE 1. Effect of N_2 gas flowrate on the reduction at 1300 °C

Compactness of the charge

The rate of reduction of hand-rolled pellets, pellets compacted at 100 kg/cm^2, and pellets compacted at 1000 kg/cm^2 were compared. It was found that the compactness of the samples adversely affects the reduction rate of chromite.

CO_2 treatment of green pellets

Although the addition of binder (1 per cent sodium silicate by mass) by itself did not noticeably affect the rate of reduction, the CO_2 treatment employed to harden the pellets had a significant influence on the kinetics of reduction, as illustrated in Figure 2.

This is an important phenomenon, since it is known that sodium carbonate, which is formed by the reaction of CO_2 with sodium silicate, has a catalytic effect on the Boudouard reaction[3,4].

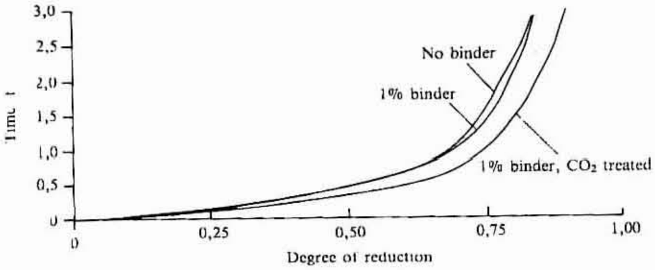

FIGURE 2. Effect of CO_2 treatment of green pellets on the reduction at 1300 °C

Simulation of the Reduction of Chromite in Composite Pellets

In the attempt to fully understand the mechanism of reduction of chromite, efforts were directed towards the simulation of the conditions, on a macro basis, that prevail within a pellet during the course of reduction.

Reduction of chromite in separate layers

To simulate the situation around a carbon particle in a composite pellet, two chromite disks, separated by a layer of graphite as shown in Figure 3, were heated in a crucible for 2 hours in the TGA. Polished sections were made from both disks, and the depth of the reduced layers was compared under the microscope.

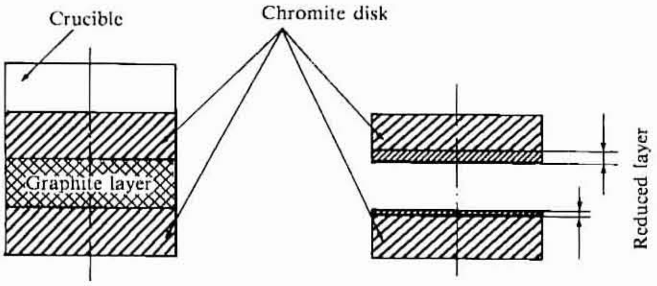

FIGURE 3. Schematic diagram of reduction of chromite in separate layers

The upper disk had a reduced layer about three times the thickness of that of the lower disk (Figure 3), notwithstanding the fact that the contact area with graphite was the same in each case. This may be explained by the following sequence of events.

The upper surface of the lower chromite disk is in contact with graphite, and is partially metallized. The gaseous product of the reduction reaction, CO_2, is converted to CO gas in the graphite layer by the Boudouard reaction, and the lower surface of the upper chromite disk is consequently not only in contact with graphite (as for the lower disk), but also with purified CO gas. The mere fact that the reduced layer in the upper disk is about three times as thick as that in the lower disk provides convincing evidence that those oxide particles which have not been in close proximity with carbon have been reduced by CO gas.

The results of these experiments, although only qualitative in nature, strongly support the premise that those particles of ore which are not in contact with carbon are reduced by carbon monoxide gas. This conclusion has far-reaching implications, and had to be substantiated by experimental evidence that pellets can be reduced, at a reasonable rate, by carbon monoxide gas in the absence of carbon.

Gaseous reduction tests

The reduction of the chromite particles in a composite chromite pellet that are not in close proximity to the carbon particles was simulated in the small reactor, as shown schematically in Figure 4.

A mixture of chromite and graphite in the bottom of an alumina crucible was used to generate a CO–CO_2 gas mix *in situ*. This gas mix was regenerated to CO on its upward passage through the graphite layer that covered the chromite–graphite mixture. An alumina ring was cast over the graphite layer to hold the sample (a chromite pellet) apart from the solid reductant but in the stream of the regenerated gas. The reactor, with the pellet located at its gas outlet, was heated in the TGA at 1350 °C for 2 hours.

The fluid dynamics around a stationary spherical particle in a moving fluid has been described in the literature[5]. When the fluid velocity is low, the streamlines depicting the flow distribution around the particle are symmetrical, as shown in Figure 4. The velocity is zero at points A and C on the surface of the particle, and has its maximum value at points B and D. Consequently, little reduction is expected on the surface of the pellet at points A and C, owing to the rapid formation of a stationary CO–CO_2 gas film at these points. However, a much higher degree of reduction is expected at points B and D, where the prompt, fresh supply of the gas ensures that the reducing potential of the gaseous phase is maintained at these points.

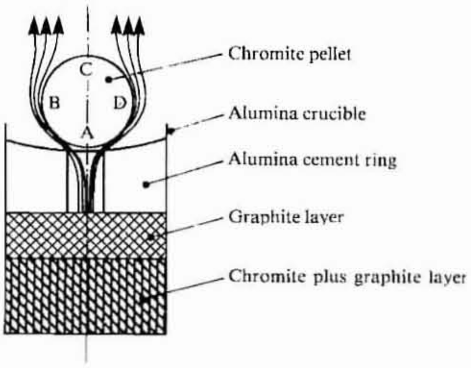

FIGURE 4. Section of the experimental arrangement for the reduction of chromite pellets by purified CO gas stream

These predictions were verified by optical microscopy[6]. Figure 5 shows a section of the side of a chromite pellet that was reduced in a small stream of CO gas for 2 hours at 1350 °C.

The ability of CO, in the absence of solid carbon, to reduce chromite at a reasonable rate was shown by these experiments. It was now important to establish whether carbon could reduce chromite at a reasonable rate in the effective absence of CO gas under similar experimental conditions. For this purpose, reduction tests were carried out in a vacuum.

Reduction experiments in a vacuum resistance furnace

A crucible containing two chromite disks separated by a layer of graphite was heated to about 1300 °C within a period of 2 hours under a pressure of about 4 mm Hg in a small vacuum resistance furnace (VRF).

The direct reduction of chromite by solid carbon could occur by either of two possible reactions:

$$2\,Cr_2O_3 + 3\,C \rightarrow 4\,Cr + 3\,CO_2 \qquad [1]$$
$$Cr_2O_3 + 3\,C \rightarrow 2\,Cr + 3\,CO. \qquad [2]$$

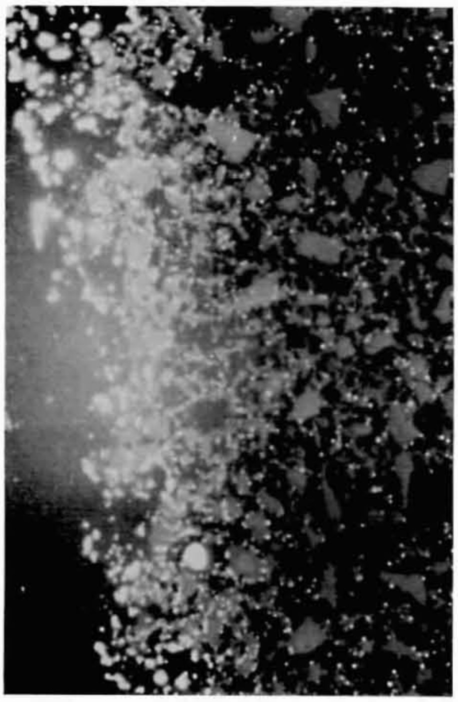

FIGURE 5. Section of the side of a chromite pellet reduced in a CO gas stream (1350 °C, 2h). Magnification 40x. Light regions, metallized; grey regions, unreduced; dark regions, void

If reduction proceeded by one of these mechanisms, the rapid removal of the gaseous phase from the reaction site should cause high degrees of reduction at those surfaces of the chromite disks that were in contact with graphite. However, very few partially metallized particles were detected by optical microscopy on the upper face of the lower chromite disk, although more were found on the lower face of the upper disk.

The fact that very minor reduction occurred in this experiment cannot be explained by reaction [1] or [2]. However, the results can be satisfactorily explained by assuming that reduction progresses according to the following mechanism:

$$Cr_2O_3 + 3\,CO \rightarrow 2\,Cr + 3\,CO_2, \qquad [3]$$

followed by the Boudouard reaction,

$$3\,CO_2 + 3\,C \rightarrow 6\,CO, \qquad [4]$$

resulting in the overall reaction

$$Cr_2O_3 + 3\,C \rightarrow 2\,Cr + 3\,CO. \qquad [5]$$

It appears that a little CO gas, formed by carbon and some residual oxygen, reduces very few chromite particles on the upper face of the lower chromite disk according to reaction [3], and the CO_2 evolved is regenerated to CO on its upward passage through the graphite layer according to reaction [4]. The ascending CO, in turn, reduces a few chromite particles on the lower face of the upper chromite disk and generates some CO_2. This CO_2, unlike that generated within composite pellets, does not come into contact with other carbon particles, and hence is not regenerated to CO. After the readily available residual oxygen has been exhausted, no more CO gas is available to cause reduction on the contact points of the chromite disks with carbon.

These results strongly support the theory that the carbothermal reduction of chromite is essentially indirect, i.e. by means of CO gas, and direct reduction of chromite by solid carbon is of much less importance.

Kinetics of the Reduction of Composite Chromite Pellets

The investigation resulted in a clearer picture of the mechanism of the solid-state reduction of chromite, which made it possible to proceed to a more quantitative description of the reduction process.

The rate-controlling mechanism of the gas–solid reactions [3] and [4] can be determined from single particles. Since gas–solid reactions are necessarily heterogeneous in nature, the instantaneous rate of reaction will depend on the specific surface area of the interface between the reactants at a particular time. Numerous rate-controlling models exist for mass transport and chemical reaction steps in different single-particle geometries[5,7,8]. Perhaps the simplest, and yet the most widely applicable, model is that for the case of a topochemical reaction where diffusion in the product layer is the rate-controlling mechanism and an unreacted shrinking-core model applies.

The application of a single-particle gas–solid reaction model to a multi-particulate system, such as composite chromite pellets, must be exercised with extreme care because the formation of mixed oxides and freshly reduced metal particles may affect the rate of the gas–solid reaction.

It is important to note that, according to the Ellingham diagram, oxygen potentials of the order of 10^{-12} atm. are required for the reduction of chromite. Although CO gas appears to be the principal reducing agent in the reduction of chromite, the close proximity of finely divided carbon and chromite is a prerequisite, because CO_2 produced by the reduction reactions must rapidly be regenerated to CO to avoid the poisoning of the reducing atmosphere. With this in mind, an attempt was made to determine the most likely rate-controlling mechanism in the solid-state reduction of chromite, and to compare the experimental data from the present investigation with the applicable rate equation.

Since CO gas appears to be the principal reducing agent in the solid-state reduction of composite chromite pellets, sufficient supply of the gas (by the Boudouard reaction) in the vicinity of an oxide particle is essential for the reduction reactions to proceed. It is consequently conceivable that the rate of gasification of carbon by CO_2 may be the rate-controlling step in the solid-state reduction reaction, at least in the early stages of reduction. This possibility was examined in more detail.

The rate of carbon gasification by a CO–CO_2 gas mix was shown by Turkdogan[9] to be directly related to the mass of carbon:

$$-k\,W_c = \left[\frac{\mathrm{d}W_c}{\mathrm{d}\theta}\right]_{\theta \to 0} \quad , \qquad [6]$$

where:

W_c is the mass of carbon,
k is the rate constant for gasification, and
θ is time.

Integration of this equation, by the use of appropriate boundary conditions and other calculated data[6], led to the development of a rate equation that relates the degree of reduction, R, to the reduction time, θ, by the rate constant, k:

$$-k\theta = \ln\,(1 - 0{,}493\,R). \qquad [7]$$

The experimentally determined kinetic data for the isothermal reduction of composite chromite pellets in the temperature range 1300 to 1450 °C were cast into the form of equation [7], and are shown in Figure 6.

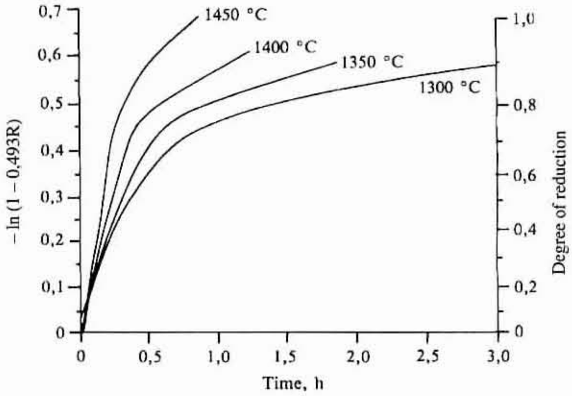

FIGURE 6. Kinetics of isothermal reduction of composite pellets according to equation [7]

If the initial stages of reduction shown in Figure 6 are approximated by a linear relationship, these results can be interpreted as an indication that reduction, in the early stages, is controlled by the carbon-gasification reaction. In this case, it may also be inferred from Figure 6 that the supply and consumption of CO gas around an oxide particle attains equilibrium in about 15 to 20 minutes, after which the reduction rate is no longer controlled by the Boudouard reaction. Should these conclusions be correct, the following would be expected in the initial stages of reduction.

(a) A high CO_2 concentration would occur in the outlet gas as a result of the slow rate of carbon gasification. This phenomenon has indeed been observed by previous investigators[10,11].
(b) The reduction of composite chromite pellets in an oxidizing atmosphere is possible in principle, but long reduction times can cause reoxidation of the reduced particles, as was found by Nunnington and Barcza[12].
(c) Since the gasification of carbon by CO_2 is much slower than gasification by oxygen[3], the reduction of composite pellets should be more favourable in air than in CO_2, as was observed by Nunnington[11].
(d) Because the Boudouard reaction is enhanced by certain catalysts such as alkali carbonates[3,4], the presence of sodium carbonate in composite chromite pellets should increase the reduction rate. This was found to be the case, as shown in Figure 2.
(e) Since freshly reduced iron particles greatly accelerate the Boudouard reaction[3], the addition of iron oxides to chromite should increase the reduction rate of chromite, as was found by Kouroki *et al.*[13]. However, the gaseous product of the reduction of iron oxide, CO_2, would slow down the reduction rate of chromite in the final stages[6].
(f) An increase in the concentration of CO (by external injection) should enhance the rate of reduction, as was found by Algie and Finn[14].

It follows from equation [7] that the initial slopes of the reduction curves in Figure 6 are the reaction-rate constants, k. From these values, an Arrhenius-type plot was drawn, and the activation energy of the reaction during the early stages of reduction was determined as 125 kJ/mol.

Since the metallic droplets coalesce to form a metallic rim around the chromite grains in the final stages of reduction, product-layer diffusion appeared to become the rate-controlling mechanism at this stage. This postulate could not be substantiated by further evidence, and therefore the experimental reduction data were re-examined in terms of an equation proposed by Ginstling and Brounshtein[15]. It appeared that the initial stage of reduction is followed by a transitional stage, after which a linear dependence is again observed. On the assumption that this approximation is justified, the reaction constants were calculated, and the activation energy of the reduction of chromite in the final stages was determined to be 238 kJ/mol.

Because it appears that the reduction rate of chromite is not controlled by a single mechanism throughout the process, it appears feasible to calculate distinct activation energies for the initial and the final stages of reduction. Since the rate of reduction is high in the initial stages, it may be preferable to prereduce the ore up to the end of the initial stages (60 to 85 per cent reduction, depending on the temperature) in a prereduction reactor, leaving the remainder of the process to be performed in a downstream smelter.

Prereduction of Chromite in an Externally Heated Shaft Furnace

The foregoing studies of the kinetics and mechanism of the reduction showed that the utilization of the off-gas of a downstream smelter for the gaseous reduction of chromite is not feasible. However, this off-gas can be combusted close to its theoretical flame temperature in the combustion chambers of a battery-type furnace, where the atmosphere in the reduction chambers can be controlled. A reduction chamber of such a battery-type furnace features a vertical shaft reactor that is heated from the exterior.

Development of a Computerized Simulation Model

As a first step in the analysis of an externally heated shaft reactor, and as a prerequisite for possible future developments, an attempt was made to simulate the temperature distribution and the progress of reduction within the charge of such a furnace by means of a mathematical model[6].

For this purpose, a moving-bed shaft with a rectangular cross-section was considered. The charge of this furnace, a porous slab of composite pellets, was assumed to be heated only from the two wider sides. A unit volume of the charge, which comes into contact with various hot zones on its downward passage through the furnace, was assumed to consist of n thin slices created by $(n+1)$ temperature-reference planes (nodes).

A computerized mathematical model was developed on the basis of an explicit solution to the finite differential equations that were derived to relate the kinetics of the isothermal reduction of pellets and the transient conduction of heat in a slab-type charge. The model was used to simulate the preheating and prereduction of composite chromite pellets in an externally heated shaft furnace.

Figure 7 depicts a slab-type charge passing at a constant speed through a furnace that is assumed to have a fixed temperature profile along its height, together with the results of the model simulation. The rise in the temperature at the temperature-reference planes within the charge is shown as a function of time in the upper part of Figure 7, while the progress of reduction of the various slices in the charge is illustrated in the lower part.

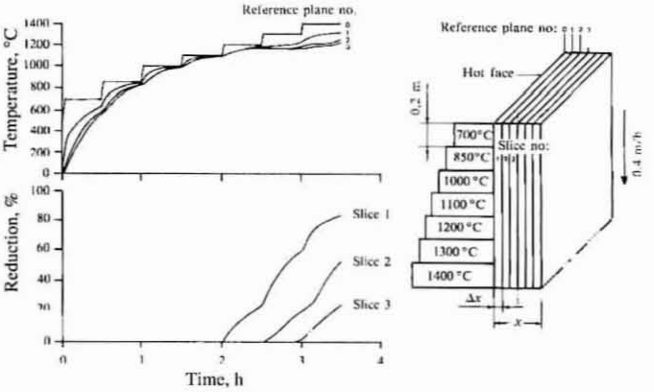

FIGURE 7. Computer simulation of temperature and reduction profiles within a slab-type charge during its downward passage, at constant speed, through a furnace with an assumed temperature profile

The model was subjected to rigorous validation tests, and proved to be highly successful. The results of the model simulations aided the design of a bench-scale shaft furnace, which was used to verify the predictions of the model.

The Bench-scale Shaft Furnace

A schematic diagram of the bench-scale shaft reactor is shown in Figure 8.

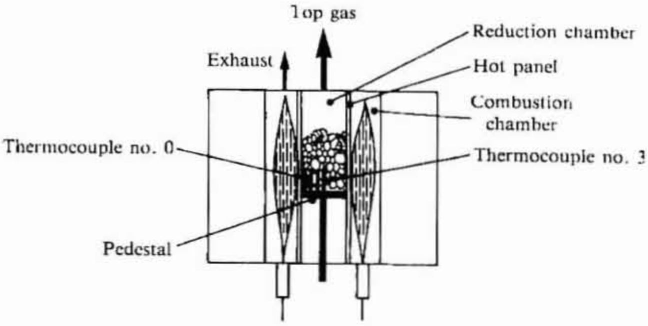

FIGURE 8. Schematic diagram of the bench-scale shaft furnace

Thermocouples were installed in the partition wall to measure the temperature profile along the furnace, and on the pedestal to measure the temperature change within the charge. Two gas burners were used to heat the combustion chambers of the furnace, while a small stream of nitrogen was used (as a dynamic seal) to stop the ingress of air or combustion gases into the reduction chamber.

Verification Experiments

A number of experiments were performed, but the results of only two will be discussed.

Figure 9 compares the predicted and the experimentally determined temperature and degree of reduction of composite chromite pellets in the reduction chamber of the furnace at wall temperatures of 1200 to 1400 °C.

It can be seen that appreciable temperature gradients exist between the temperature-reference planes due to the presence of a heat sink (reduction) within the charge. The predicted and experimental values of the overall degree of

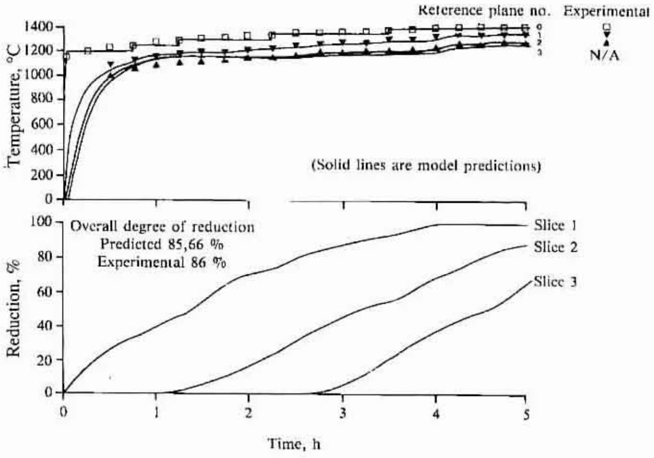

FIGURE 9. Predicted and experimental results – run 2

reduction of the charge were similar (86 per cent) in this experiment.

In another experiment, plain chromite pellets were heated in the furnace. The predicted and the experimentally determined temperature changes within the charge are compared in Figure 10. This diagram shows that the temperature rapidly approaches equilibrium at all points, due to the absence of the reduction reactions within the charge.

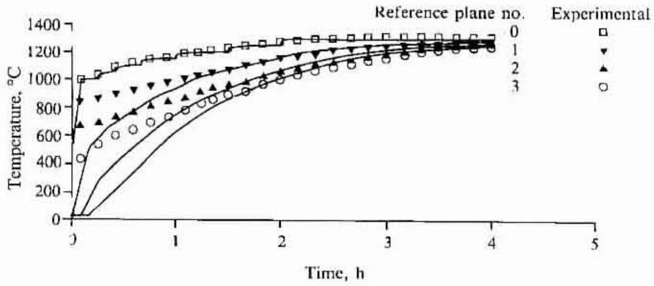

FIGURE 10. Predicted and experimental results – run 10

Conclusions

(1) Although the carbonaceous reduction of chromite occurs via an intermediate gaseous reduction step, the solid-state reduction of chromite by a reducing gas alone is not feasible. This is because the presence of finely divided carbon in close proximity to the oxide particles is necessary in order to promptly restore the reducing potential of the gaseous phase by means of carbon gasification.

(2) Three distinct stages of reduction were observed during the isothermal reduction of composite pellets.
   (a) The initial stage, where the rate of supply of CO gas by gasification of carbon appears to be the rate-determining step. This stage may last from 15 to 30 minutes, and 60 to 85 per cent reduction may be obtained depending on the temperature. The activation energy for this process is 125 kJ/mol.
   (b) The transient stage, where the rates of supply and consumption of CO gas approach equilibrium, and a dense metallic rim begins to form around the oxide particles.
   (c) The final stage, where product-layer diffusion appears to be the rate-controlling mechanism. The activation energy for this process is 238 kJ/mol.

   The mechanism proposed for the initial stages of reduction satisfactorily explains a number of experimental findings.

(3) A battery-type furnace is proposed to prereduce composite pellets in reduction chambers, while the combustion energy of the CO-rich off-gas of a downstream smelter is utilized to heat the charge via external combustion chambers. A computerized mathematical model was developed to simulate the temperature change and reduction of composite pellets in the reduction chamber of such a furnace.

(4) The predictions of the computerized mathematical model were verified experimentally with a bench-scale shaft furnace, thus demonstrating the technological feasibility of the prereduction of composite chromite pellets in an externally heated shaft furnace.

Acknowledgment

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