

## The Reduction of Synthetic Iron Chromite in the Presence of Various Metal Oxides – A Thermo-analytical Study

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The reduction of  $\text{FeCr}_2\text{O}_4$  by activated carbon in Ar and CO atmospheres was studied by various thermo-analytical techniques. The results indicated that the CO atmosphere enhances the reduction reaction, since the enthalpy of the reaction was determined as  $197 \text{ kJ}\cdot\text{mol}^{-1}$   $\text{FeCr}_2\text{O}_4$  in Ar and  $158 \text{ kJ}\cdot\text{mol}^{-1}$   $\text{FeCr}_2\text{O}_4$  in CO.

The influence of the stoichiometry on the reduction of the spinel was studied by investigating the reduction of  $(\text{Fe}_{0.4}, \text{Mg}_{0.6})(\text{Fe}_{0.4}, \text{Cr}_{0.6})_2\text{O}_4$  under similar conditions. The enthalpy values indicated that the reduction reaction became less endothermic:  $532 \text{ kJ}\cdot\text{mol}^{-1}$  and  $233 \text{ kJ}\cdot\text{mol}^{-1}$  in Ar and CO respectively.

A kinetic investigation indicated that the reduction reactions of  $\text{FeCr}_2\text{O}_4$  and  $(\text{Fe}_{0.4}, \text{Mg}_{0.6})(\text{Fe}_{0.4}, \text{Cr}_{0.6})_2\text{O}_4$  were preceded by an initial reaction that was associated with the reduction of iron, and probably by the decomposition of the CO that formed during the reaction, on the surface of the Fe and/or spinel. This reaction is described by the kinetic model

$$\{1 - [1 - \alpha]^{0.33}\}^2 = kt,$$

with an activation energy of  $129 \text{ kJ}\cdot\text{mol}^{-1}$ . The second process is described by the model

$$\{[1/(1 - \alpha)]^{0.33} - 1\}^2 = kt.$$

The activation energies for the various reactions were very similar.

The presence of metal oxides did not influence the kinetics of the initial reaction although different intermediate species were formed.

### Introduction

The prereduction of chromite ore has been investigated extensively over the past few years. Most of the studies have been aimed at describing the reduction process in terms of a kinetic model, normally deduced from isothermal thermogravimetric measurements, and from X-ray-diffraction and energy-dispersive X-ray analyses, and were carried out using chromite ore with coal or char as solid reductant or carbon monoxide as gaseous reductant<sup>1-6</sup>. The chemical composition of chromite ore differs from sample to sample, and an average composition for the sample is normally presented. These various compositions cause the various types of ore, which have the same chromium content, to behave differently owing to variations in the chemical stability, melting point, etc. Impurities that are introduced through the binding material, coal, or even gangue can influence the mechanism of the reduction reaction. It is therefore not surprising that a great variation exists in the kinetic parameters as determined from thermogravimetric analysis.

A fundamental study of the reduction reaction was therefore conducted on the influence of the chromite spinel composition and its impurities, in the form of metal oxides, on the reduction kinetics.

### Experimental

#### Sample Preparation

The chromites  $\text{FeCr}_2\text{O}_4$  and  $(\text{Fe}_{0.4}, \text{Mg}_{0.6})(\text{Fe}_{0.4}, \text{Cr}_{0.6})_2\text{O}_4$  were prepared as follows, according to the general method used by Rogers<sup>7</sup> for the synthesis of  $\text{FeV}_2\text{O}_4$ .

- (i) A 2:1 stoichiometric mixture of  $\text{Cr}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  was stirred in petroleum ether for 18 hours and then vacuum dried. For the synthesis of  $(\text{Fe}_{0.4}, \text{Mg}_{0.6})(\text{Fe}_{0.4}, \text{Cr}_{0.6})_2\text{O}_4$ , the stoichiometric amounts of  $\text{Fe}_2\text{O}_3$ ,  $\text{MgO}$ , and  $\text{Cr}_2\text{O}_3$  were used. This produced a homogeneous mixture, which is essential for complete conversion to spinel.
- (ii) The mixture was heated in a tube furnace at  $1300^\circ\text{C}$  under a 1:1 CO /  $\text{CO}_2$  dynamic atmosphere. The temperature, as well as the atmospheric conditions, was maintained for 15 hours.
- (iii) The spinel was cooled to ambient temperatures in the CO /  $\text{CO}_2$  atmosphere, and was subsequently checked for unreacted starting materials by X-ray powder diffraction.
- (iv) Steps (ii) and (iii) were repeated until no starting materials were detected.

The total reaction time needed was 48 hours.

## Reaction Mixtures

Activated carbon with a particle size < 50 µm, obtained from Merck, was used as the reducing agent. Mixtures were prepared by grinding and mixing the spinel (particle size < 50 µm), activated carbon and, when required, the metal oxide together with a mortar and pestle. The metal oxides used in this study were CaO, MgO, SiO<sub>2</sub>, and Al<sub>2</sub>O<sub>3</sub>.

## Thermal Analysis

Thermogravimetric analysis (TG) and differential-thermal analysis (DTA) were carried out with a Setaram Simultaneous TGDTA 92 analyser. The samples were heated in alumina sample holders from room temperature to 1500°C at a heating rate of 10°C·min<sup>-1</sup>. Sample sizes varied between 50 and 90 mg. Ar, high-purity grade, or CO was used as atmosphere at a flowrate of 50 ml·min<sup>-1</sup>.

Kinetic analysis of the reactions was carried out according to the method described by Zsako<sup>8</sup> and improved by Stander<sup>9</sup>. It is important to note that no mass loss was observed over the temperature range 400 to 1500°C when the carbon that was used for the reduction reaction was heated in an argon or CO atmosphere.

## X-ray Powder Diffraction

All X-ray powder diffraction (XRPD) patterns were recorded on a Seifert MZ-IV instrument using Cu Kα radiation.

## Results and Discussion

### Reduction of FeCr<sub>2</sub>O<sub>4</sub>

The reduction reaction was investigated under various experimental conditions.

#### Carbon monoxide as reducing agent

The TG curve did not show any mass loss, neither did the DTA curve indicate any endo- or exothermic reactions, in the temperature range 50 to 1500°C when FeCr<sub>2</sub>O<sub>4</sub> was heated in a CO atmosphere. This observation is in agreement with the fact that CO is unable to reduce FeCr<sub>2</sub>O<sub>4</sub>.

#### Reduction by carbon in an argon atmosphere

Mixtures containing the spinel, FeCr<sub>2</sub>O<sub>4</sub>, and 10, 16,7, 20, and 30 per cent by mass carbon were heated from room temperature to 1500°C in the thermal analyser in an Ar atmosphere. The samples containing 10 and 30 per cent carbon were heated in a CO atmosphere.

The mixture containing 10 per cent carbon showed an initial mass loss of approximately 7,7 per cent between 600 and 1100°C, which was followed by a mass increase of 2,9 per cent between 1100 and 1450°C when reacted in Ar. X-ray powder diffraction analysis of the product showed the presence of α-Fe, Cr<sub>2</sub>O<sub>3</sub>, and unreacted FeCr<sub>2</sub>O<sub>4</sub>. The mass loss was therefore due to the reduction of iron in the spinel. Renshaw and his co-workers<sup>10</sup> showed that, in such a reaction, the disproportionation of the product CO can occur according to the reaction

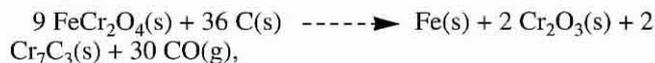


This disproportionation reaction takes place during the initial stages of CO formation, and is catalysed by iron and various iron oxides. The mass gain could therefore be due to the formation of carbon, but it was not possible to verify this experimentally.

The mixtures containing 16,7 and 20 per cent carbon showed mass losses of 26,6 and 32,5 per cent respectively. X-ray powder analysis of the final products showed that the mixtures consisted mainly of α-Fe and Cr<sub>2</sub>O<sub>3</sub>. The calculated mass losses for a reaction that will result in the formation of α-Fe and Cr<sub>2</sub>O<sub>3</sub> as the only solid phases, i.e.



are 11,87 and 10,01 per cent for the 16,7 and 20 per cent mixtures respectively. Although it was difficult to identify a Cr<sub>7</sub>C<sub>3</sub> phase uniquely in the mixture, X-ray powder diffraction suggested that it was present. The calculated mass loss for a reaction that will account for the formation of Cr<sub>7</sub>C<sub>3</sub>, i.e.



is 33,36 per cent for a mixture containing 20 per cent carbon, which is in good agreement with the observed mass loss.

A mass loss of 39,7 per cent was obtained for the reduction of the spinel FeCr<sub>2</sub>O<sub>4</sub> in the presence of 30 per cent carbon (Figure 1). The differential thermogravimetric (DTG) curve indicated that the overall reaction consisted of at least three overlapping reactions. It was also not possible to correlate the experimental mass loss with a general chemical reaction. The calculated mass loss for the reaction



amounted to 35,03 per cent.

#### Reduction by carbon in a carbon monoxide atmosphere

The samples containing 10 and 30 per cent carbon were heated in a CO atmosphere, and the reduction reactions were compared with those obtained in an Ar atmosphere.

The sample containing 10 per cent carbon showed a 17 per cent mass loss when heated to 1500°C. It was not possible to correlate the experimental mass loss with a general chemical reaction; this suggests incomplete reaction. This result, when compared with that obtained in Ar, indicated that the CO atmosphere enhanced the reduction reaction. The TG curve for the sample containing 30 per cent carbon indicated a mass loss of 38,7 per cent, similar to that observed for the reaction in Ar.

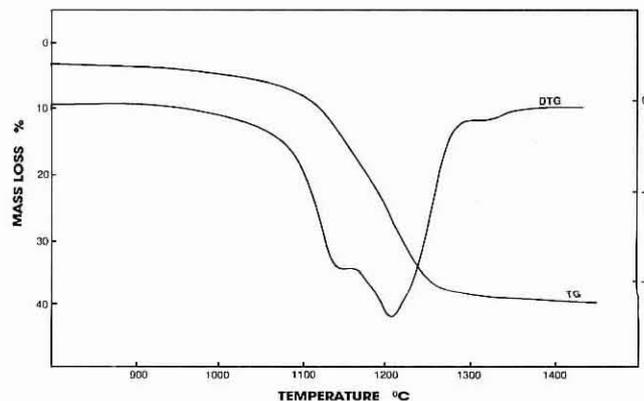


FIGURE 1. TG and DTG curves for the reduction of FeCr<sub>2</sub>O<sub>4</sub> with 30 per cent carbon in an argon atmosphere

The reactions in the two atmospheres were compared quantitatively by a comparison of the various reaction enthalpies as calculated from the DTA curves (Figure 2, curves A and B), as well as the kinetic behaviour of the reactions. Although the DTA curves were very similar, the reaction in CO was found to be less endothermic ( $158 \text{ kJ}\cdot\text{mol}^{-1} \text{ FeCr}_2\text{O}_4$ ) than in Ar ( $197 \text{ kJ}\cdot\text{mol}^{-1} \text{ FeCr}_2\text{O}_4$ ). Similar kinetic behaviour was observed for the reaction in both atmospheres. Figures 3 and 4 show the degree of reduction of  $\text{FeCr}_2\text{O}_4$  expressed as the total reduction of the spinel to the metal, carbides, and lower metal oxides, as a function of the temperature in Ar and CO respectively. It is interesting to note that both reactions, as well as the reduction of  $(\text{Fe}_{0.4}, \text{Mg}_{0.6})(\text{Fe}_{0.4}, \text{Cr}_{0.6})_2\text{O}_4$  in the two atmospheres, were preceded by an initial reaction between 600 and  $1000^\circ\text{C}$ , which seems to constitute about 6 to 10 per cent of the total reaction. This reaction was accompanied by the partial reduction of iron, and is associated with the decomposition of CO as described above. This reaction was described without exception, by the Jander equation,

$$(1 - [1 - \alpha]^{0.33})^2 = kt.$$

The activation energy was  $129 \text{ kJ}\cdot\text{mol}^{-1}$  and the frequency factor was  $1.55 \times 10^5 \text{ min}^{-1}$ . This reaction is followed by the reduction of the spinel, which seems to be diffusion controlled and is described by the equation

$$\{[1/(1 - \alpha)]^{0.33} - 1\}^2 = kt.$$

The activation energies and frequency factors were the same for the reaction in both atmospheres, i.e.  $765 \text{ kJ}\cdot\text{mol}^{-1}$  and  $6.93 \times 10^{25} \text{ min}^{-1}$  respectively. This activation energy is most probably a combination of various effects, of which diffusion may constitute a major part.

These results indicate that the reduction process is more complicated than either a solid-solid (carbon-spinel) or gas-solid (CO-spinel) reaction. It is, however, clear that both reductants are needed for efficient reaction. The large excess of carbon that is needed for complete reduction can be linked to the formation of intermediates, e.g.  $\text{Cr}_7\text{C}_3$ .

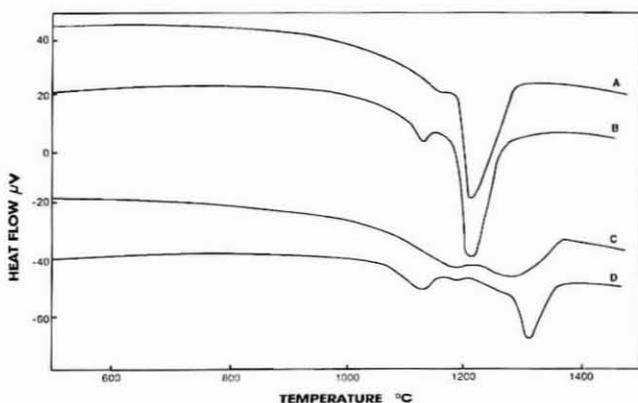


FIGURE 2. DTA curves for the reduction of  $\text{FeCr}_2\text{O}_4$  and  $(\text{Fe}_{0.4}, \text{Mg}_{0.6})(\text{Fe}_{0.4}, \text{Cr}_{0.6})_2\text{O}_4$  with 30 per cent carbon in argon and carbon monoxide

- A  $\text{FeCr}_2\text{O}_4$  Ar atmosphere
- B  $\text{FeCr}_2\text{O}_4$  Co atmosphere
- C  $(\text{Fe}_{0.4}, \text{Mg}_{0.6})(\text{Fe}_{0.4}, \text{Cr}_{0.6})_2\text{O}_4$  Ar atmosphere
- D  $(\text{Fe}_{0.4}, \text{Mg}_{0.6})(\text{Fe}_{0.4}, \text{Cr}_{0.6})_2\text{O}_4$  CO atmosphere

### Reduction of $(\text{Fe}_{0.4}, \text{Mg}_{0.6})(\text{Fe}_{0.4}, \text{Cr}_{0.6})_2\text{O}_4$

The reduction of the spinel was studied under conditions similar to those described for the reduction of  $\text{FeCr}_2\text{O}_4$ .

#### Reduction by carbon monoxide

As for  $\text{FeCr}_2\text{O}_4$ , no reduction of  $(\text{Fe}_{0.4}, \text{Mg}_{0.6})(\text{Fe}_{0.4}, \text{Cr}_{0.6})_2\text{O}_4$  was observed in CO in the absence of solid carbon.

#### Reduction by carbon in argon and carbon monoxide atmospheres

Samples containing the spinel and 10 and 30 per cent carbon were heated in an Ar atmosphere.

The TG curve for the sample containing 10 per cent carbon showed a 17.5 per cent mass loss. X-ray powder analysis of the product indicated only two phases,  $\alpha\text{-Fe}$  and  $\text{MgCr}_2\text{O}_4$ . The observed mass loss was 17.5 per cent. The calculated mass loss for the reaction

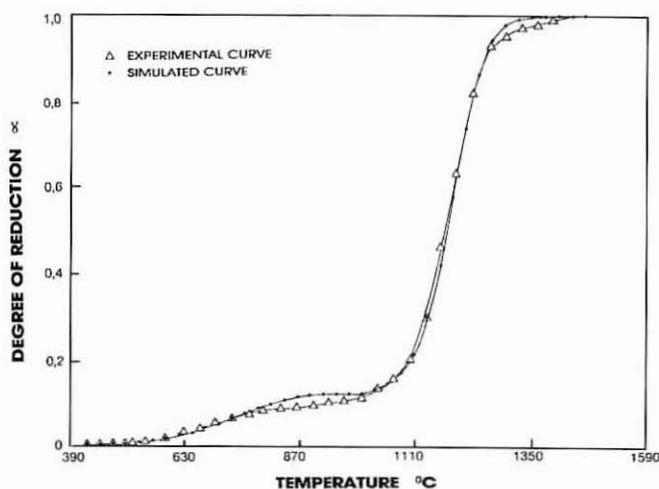
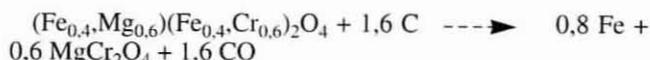


FIGURE 3. Reduction of  $\text{FeCr}_2\text{O}_4$  with carbon (30 per cent) in argon

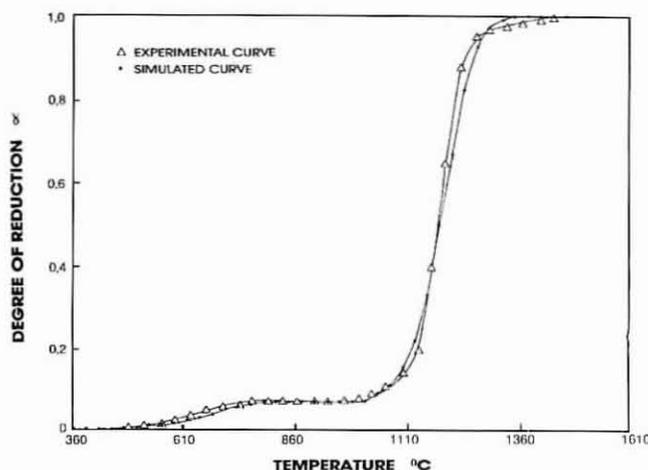


FIGURE 4. Reduction of  $\text{FeCr}_2\text{O}_4$  with carbon (30 per cent) in carbon monoxide

is 19,4 per cent. This reaction was completely different from the reaction that was observed for a similar mixture containing  $\text{FeCr}_2\text{O}_4$ , which was described above. The kinetics of the reduction was described by a two-stage process: the initial reaction as described previously, followed by the reduction of the iron in the spinel (Figure 5). This seems to be described by the same equation, i.e. the Zhuralev-Lesokin-Tempelmann model, but with different kinetic parameters. The activation energy was determined as  $600 \text{ kJ}\cdot\text{mol}^{-1}$  and the frequency factor as  $3,49 \times 10^{19} \cdot \text{min}^{-1}$ . The enthalpy of the reaction was calculated as  $82,5 \text{ kJ}\cdot\text{mol}^{-1}$   $(\text{Fe}_{0,4}, \text{Mg}_{0,6})(\text{Fe}_{0,4}, \text{Cr}_{0,6})_2\text{O}_4$ .

The reaction was very similar in CO. A mass loss of 17,6 per cent was calculated from the TG curve, and the same phases, i.e.  $\alpha\text{-Fe}$  and  $\text{MgCr}_2\text{O}_4$ , were observed. The kinetic model describing the reaction was the same, but the activation energy,  $578 \text{ kJ}\cdot\text{mol}^{-1}$ , was lower than that calculated for the reaction in Ar. The enthalpy of the reaction was  $61,0 \text{ kJ}\cdot\text{mol}^{-1}$   $(\text{Fe}_{0,4}, \text{Mg}_{0,6})(\text{Fe}_{0,4}, \text{Cr}_{0,6})_2\text{O}_4$ . These results indicate that CO may enhance the reaction.

The TG and DTG curves for the reduction reaction of a mixture containing 30 per cent carbon are shown in Figure 6. The DTG, as well as the DTA curve (Figure 2, curve C), showed that the reaction is different from that of a similar mixture containing  $\text{FeCr}_2\text{O}_4$  reacted in Ar. The reactions of  $(\text{Fe}_{0,4}, \text{Mg}_{0,6})(\text{Fe}_{0,4}, \text{Cr}_{0,6})_2\text{O}_4$  seem to overlap to a larger extent. A rapid mass loss of 34,4 per cent was observed to a maximum temperature of  $1360^\circ\text{C}$ . A further slow mass loss

of 3 per cent was observed between  $1360$  and  $1500^\circ\text{C}$ , which could be due to the sublimation of  $\text{MgO}$ . The enthalpy of the reaction was calculated as  $158 \text{ kJ}\cdot\text{mol}^{-1}$   $(\text{Fe}_{0,4}, \text{Mg}_{0,6})(\text{Fe}_{0,4}, \text{Cr}_{0,6})_2\text{O}_4$ . The reaction was completed at  $1430^\circ\text{C}$  in a CO atmosphere. The influence of the atmosphere on the reaction is clearly illustrated by the DTA curves in Figure 2 (curves C and D). The product consisted of completely metallized material and white  $\text{MgO}$ . The enthalpy of the reaction was calculated as  $69,23 \text{ kJ}\cdot\text{mol}^{-1}$   $(\text{Fe}_{0,4}, \text{Mg}_{0,6})(\text{Fe}_{0,4}, \text{Cr}_{0,6})_2\text{O}_4$ , which is significantly less endothermic than either the reduction reaction in Ar or the reduction of  $\text{FeCr}_2\text{O}_4$  in CO. The kinetic behaviour of  $(\text{Fe}_{0,4}, \text{Mg}_{0,6})(\text{Fe}_{0,4}, \text{Cr}_{0,6})_2\text{O}_4$  was different from that of  $\text{FeCr}_2\text{O}_4$ . Apart from the initial reaction already described, it was impossible to describe the reduction using a single kinetic expression. The same kinetic model,

$$\{[1/(1-\alpha)]^{0,33} - 1\}^2 = kt,$$

seems to describe both the reactions, but the kinetic parameters are different. The initial reaction is followed by a reaction for which the activation energy is  $765 \text{ kJ}\cdot\text{mol}^{-1}$  in both Ar and CO. This reaction is then followed by a reaction with an activation energy of  $730 \text{ kJ}\cdot\text{mol}^{-1}$  in Ar and  $630 \text{ kJ}\cdot\text{mol}^{-1}$  in CO. Figures 7 and 8 illustrate the experimental and calculated curves for the above-mentioned kinetic models and parameters.

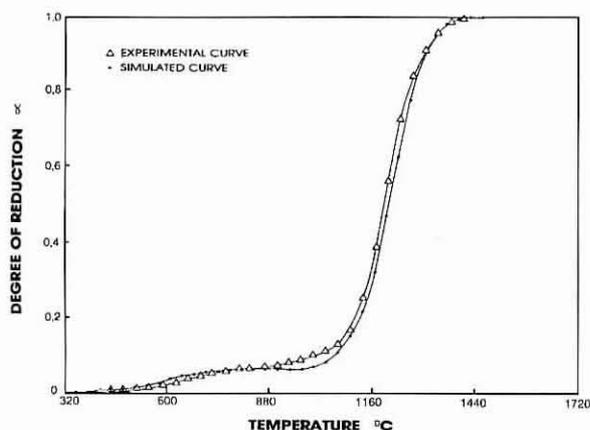


FIGURE 5. Reduction of  $(\text{Fe}_{0,4}, \text{Mg}_{0,6})(\text{Fe}_{0,4}, \text{Cr}_{0,6})_2\text{O}_4$  with carbon (10 per cent) in argon

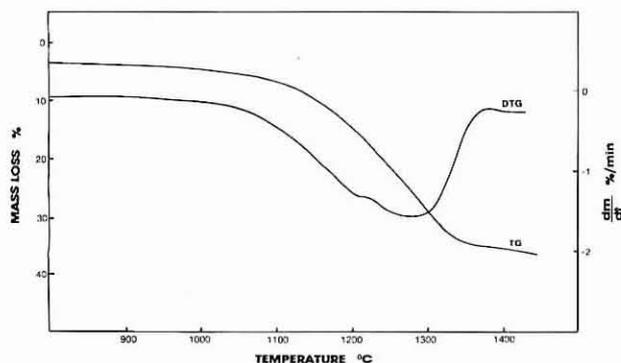


FIGURE 6. TG and DTG curves for the reduction of a mixture containing  $(\text{Fe}_{0,4}, \text{Mg}_{0,6})(\text{Fe}_{0,4}, \text{Cr}_{0,6})_2\text{O}_4$  and 30 per cent carbon in argon

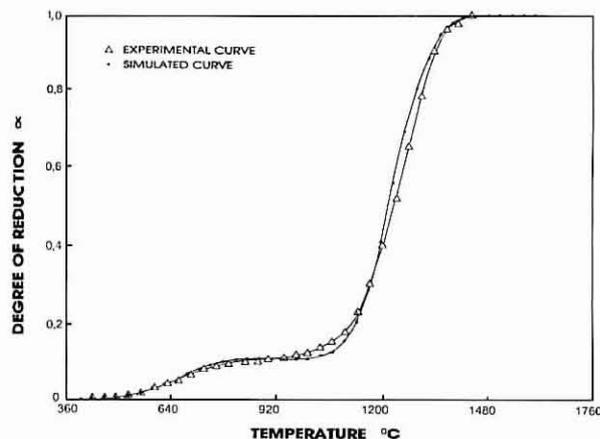


FIGURE 7. Experimental and simulated curves for the reduction in argon of  $(\text{Fe}_{0,4}, \text{Mg}_{0,6})(\text{Fe}_{0,4}, \text{Cr}_{0,6})_2\text{O}_4$  with 30 per cent carbon

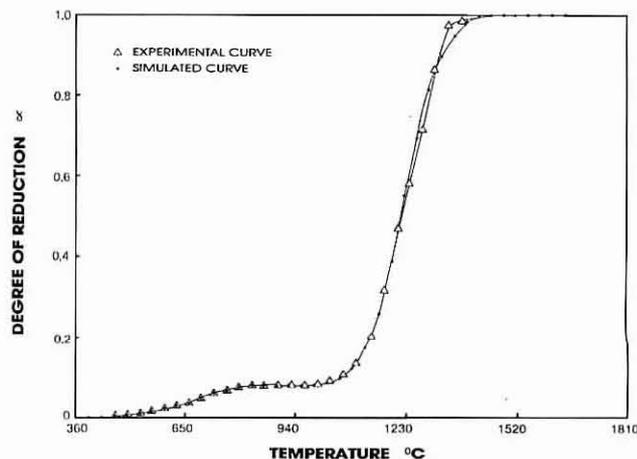


FIGURE 8. Experimental and simulated curves for the reduction reaction in CO of  $(\text{Fe}_{0,4}, \text{Mg}_{0,6})(\text{Fe}_{0,4}, \text{Cr}_{0,6})_2\text{O}_4$  with 30 per cent carbon

### Reduction of FeCr<sub>2</sub>O<sub>4</sub> in the Presence of Metal Oxides

The reduction of the spinel FeCr<sub>2</sub>O<sub>4</sub> was studied in the presence of 20 per cent carbon by mass and 10 per cent metal oxide by mass. The rate of reduction as a function of the temperature is shown in Figure 9. It is clear that SiO<sub>2</sub> had the more significant influence on the reaction. The DTG peak has shifted towards a lower temperature, indicating that the maximum reaction rate is reached at a lower temperature. X-ray powder diffraction of the samples indicated that only the iron was fully reduced, similar to the mixture of spinel and 20 per cent carbon. The various phases present in the samples after reduction are summarized in Table I.

The kinetic analysis of the reduction of the spinel in the presence of various metal oxides did not differ significantly from the kinetics that describe the reduction in the absence of the metal oxide. The reaction is described by two consecutive processes. The first process is described by the Jander diffusional model with an activation energy of 129 kJ·mol<sup>-1</sup> and a frequency factor of 1,47 x 10<sup>5</sup>·min<sup>-1</sup>, as was observed previously. The second process is described by the Zhuralev-Lesokin-Tempelmann diffusional kinetic model.

The kinetic parameters are summarized in Table II. These results seem to indicate that the kinetics of the reduction during the initial stages of the reaction, the reduction of the iron, was not significantly influenced by the metal oxides. The formation of the different intermediates can, however, influence the kinetics during the later stages of the reduction.

### Conclusions

The reduction of FeCr<sub>2</sub>O<sub>4</sub> and (Fe<sub>0,4</sub>Mg<sub>0,6</sub>)(Fe<sub>0,4</sub>Cr<sub>0,6</sub>)<sub>2</sub>O<sub>4</sub> in Ar and in CO are preceded by an initial process that can be associated with the partial reduction of iron and the decomposition of CO, which formed during the initial stages of the reduction.

CO seems to promote the reduction. This is illustrated by the less endothermic nature of the reactions in CO compared

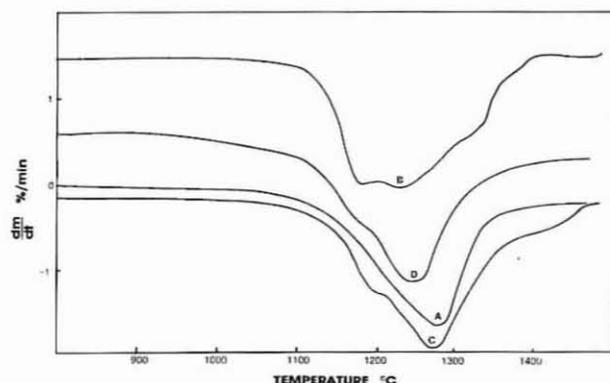


FIGURE 9. DTG curves for the reduction of FeCr<sub>2</sub>O<sub>4</sub> with carbon in argon and in the presence of various metal oxides

A MgO B SiO<sub>2</sub> C Al<sub>2</sub>O<sub>3</sub> D CaO

TABLE I  
INTERMEDIATE PHASE FORMATION DURING THE REDUCTION OF FeCr<sub>2</sub>O<sub>4</sub> IN THE PRESENCE OF METAL OXIDES

Metal oxide	Phases
MgO	MgCr <sub>2</sub> O <sub>4</sub> Cr <sub>7</sub> C <sub>3</sub> α-Fe
SiO <sub>2</sub>	FeCr <sub>2</sub> O <sub>4</sub> Cr <sub>2</sub> O <sub>3</sub> SiO <sub>2</sub> (high-temperature phases) α-Fe
Al <sub>2</sub> O <sub>3</sub>	FeCr <sub>2</sub> O <sub>4</sub> Cr <sub>7</sub> C <sub>3</sub> α-Fe R <sub>2</sub> O <sub>3</sub> (solid solution, R = Al, Cr)
CaO	Cr <sub>2</sub> O <sub>3</sub> Cr <sub>7</sub> C <sub>3</sub> Ca(CrO <sub>2</sub> ) <sub>2</sub> α-Fe

with those in Ar, as well as by the lower activation energies that were observed for the reactions in a CO atmosphere. This, coupled with the observation that the degree of reduction depends on the amount of carbon present, indicates that the reduction mechanism is more complicated than a solid-solid reduction or a gas-solid reaction process only. It seems as if both the reductants are important.

Solid impurities, in the form of metal oxides, did not significantly influence the kinetic parameters of the reduction reaction during the initial stages. The intermediates that form could, however, influence the reaction kinetics.

TABLE II  
KINETIC PARAMETERS FOR THE REDUCTION OF FeCr<sub>2</sub>O<sub>4</sub> IN THE PRESENCE OF METAL OXIDES

Metal oxide	Activation energy kJ·mol <sup>-1</sup>	Frequency factor min <sup>-1</sup>
MgO	730	1,04 x 10 <sup>23</sup>
SiO <sub>2</sub>	720	1,04 x 10 <sup>23</sup>
Al <sub>2</sub> O <sub>3</sub>	730	1,04 x 10 <sup>23</sup>
CaO	720	1,04 x 10 <sup>23</sup>

Kinetic model:  $\{[1/(1 - \alpha)]^{0,33} - 1\}^2 = kt$ .

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