Thermochimica Acta, 127 (1988) 25–35
Elsevier Science Publishers B V , Amsterdam – Printed in The Netherlands

THE EFFECT OF ADDITIVES ON THE REDUCTION OF CHROMITE BY GRAPHITE: AN ISOTHERMAL KINETIC STUDY

J S J VAN DEVENTER

Department of Metallurgical Engineering, University of Stellenbosch, Stellenbosch, 7600, (South Africa)

(Received 16 June 1987)

ABSTRACT

Mixtures of chromite, graphite and various additives were reacted isothermally under argon, and the loss in mass was recorded continuously The additives used, SiO_2, Al_2O_3, K_2CO_3, Na_2O_2 CaO, MgO, Fe and Cr, all influence the Boudouard reaction positively Of these, only MgO and Al_2O_3 revealed an inhibiting effect during the carbothermic reduction of chromite The X-ray diffraction peaks characteristic of the additives decreased in intensity during reduction, which could indicate that the additives reacted in some way In most of the reduction products olivine (MgO Al_2O_3), Fe, Fe_3C and $(Cr,Fe)_7C_3$ could be identified It appears as though MgO plays an inhibiting role in the decomposition of the chromite spinel A decrease in the particle size of the chromite accelerated the reduction kinetics when CaO was used as additive, but no difference in the equilibrium conversion was observed The activation energy of 192 kJ mol^{-1} for the reduction reaction without any additives is of the same order of magnitude as that measured by other authors

INTRODUCTION

Chromium is one of the most versatile and widely used elements in steels, pigments, chemicals and refractories [1] There are few materials that can replace chromium satisfactorily using present technology Chromite ore is obtained from major sources in ten different countries, the largest quantities being supplied by the Republic of South Africa and the USSR [2] Agglomerated chromite fines can be prereduced economically prior to smelting in a submerged-arc furnace, as the coal used represents a less expensive form of energy than the electricity used in a furnace [3,4]

Barnes et al [5] investigated the prereduction of the Upper Chromitite Layer (UG-2) in the Bushveld Complex, which has a low chromium to iron ratio They determined the degree of iron metallization versus time and surmised that both chemical reaction and diffusion were rate controlling In a further study on this ore, Searle and Finn [4] established that iron and chromium species diffuse from the interior of a particle to the surface, where reduction takes place and metallization occurs The chromite spinel may crack along crystallographic planes when iron is removed

0040-6031/88/$03 50

Barcza et al. [6] proposed a mechanism for the reduction of Transvaal chromite which involved the diffusion of carbon across the layer of reaction product. The findings of Searle and Finn [4] and Rankin [7] that carbon monoxide is the reducing agent contradicts the mechanism suggested by Barcza et al. [6].

Rankin [7,8] investigated the mechanism of reduction of chromite from the Bushveld Complex. At temperatures up to 1200 °C the reduction products were Fe and Cr_2O_3, and at temperatures greater than 1200 °C the reduction products were Fe, $(Cr,Fe)_7C_3$, Fe_3C and $MgAl_2O_4$. During reduction the initially formed Fe was transformed to Fe_3C. As the outer zone of the grains became depleted in iron and chromium, the concentration of aluminium and magnesium increased and $MgAl_2O_4$ formed, which contained a considerable amount of chromium. Barcza et al. [6] observed some reduction of SiO_2 in gangue, and confirmed this by adding SiO_2 to their reaction mixtures. In none of the other papers published on the reduction of chromite has any attention been paid to the effects of additives or gangue constituents.

It is the objective of this paper to explore the influence of such additives on the reduction of chromite by graphite. X-ray diffraction was used to identify reaction products.

EXPERIMENTAL

The chromite ore used in this study was from the Kroondal mine in the Bushveld Complex in South Africa, and was similar to that used by Rankin [7,8]. After size reduction and screening the 53–106 μm fraction was selected for use in most experiments. Other size fractions were used to investigate the effect of particle size. The chromite was separated from the gangue components by magnetic separation followed by heavy-medium separation with di-iodomethane. Unliberated silicate minerals were removed by leaching the product in aqueous hydrofluoric acid. This purified chromite contained 20.8% FeO, 6.6% Fe_2O_3, 9.3% MgO, 15.3% Al_2O_3 and 46.9% Cr_2O_3 by mass. The formula for the chromite spinel was calculated as $(Fe_{0.56}Mg_{0.44})(Cr_{1.19}Al_{0.58}Fe_{0.16})O_{3.88}$, which was close to the stoichiometric formula $(Fe,Mg)(Cr,Al,Fe)_2O_4$ [7]. X-ray fluorescence was used to determine this composition.

High purity graphite with a particle size between 53 and 90 μm was used as reductant. Different quantities of analytically pure SiO_2, Al_2O_3, MgO, CaO, Na_2O_3, K_2CO_3, Fe and Cr were used as additives.

Reduction experiments were conducted in a thermogravimetric (TG) balance, which was flushed with purified argon at a rate sufficiently high so as not to affect the rate of reduction. A 50% excess of graphite (0.48 g), based on the 21.42 mass percent removable oxygen contained in the chromite spinel, and chromite (2 0 g) were mixed intimately with or without additives and placed in a recrystallized alumina crucible in the furnace of the TG balance The furnace was heated to a constant temperature before the start of a run

Some reduction products were subjected to X-ray diffraction for identification of the phases A Philips diffractometer with graphite monochromator was used, the radiation being Cu K_α Phases were identified by reference to the ASTM X-ray powder data file

RESULTS AND DISCUSSION

The fractional conversion X of chromite during reduction is defined here as

$$X = \frac{\text{cumulative mass of oxygen removed from sample at time } t}{\text{mass of removable oxygen in sample at } t = 0}$$

The removable oxygen is considered here to be associated with FeO, Fe_2O_3 and Cr_2O_3 in the chromite, which is 21 42 mass % Since experiments were carried out in the range 1240–1400 °C, the exit gas should consist essentially of CO [9,10] This was confirmed during the reduction of UG2 chromite [4,5] Hence

$$X = \frac{\Delta m M_{\mathrm{O}}}{m Z M_{\mathrm{CO}}}$$

where Δm = registered mass loss of sample, m = initial mass of chromite, z = mass % of removable oxygen in chromite and M = molecular mass

Results from TG experiments were easily reproducible with an average deviation of 4 5% Figure 1 shows the effect of temperature on the reduction of chromite by graphite The initial slopes of these curves have been replotted in Fig 2 as an Arrhenius plot The slope of this best fit line may be used to calculate the activation energy of 192 kJ mol^{-1}, which is of the same order of magnitude as the 181 kJ mol^{-1} measured by Barnes et al [5] These values are lower than the 256 kJ mol^{-1} observed for the gasification of graphite by CO_2 [11]

X-ray diffraction of the products obtained after 120 minutes of reduction at 1400 °C revealed the formation of Fe, Fe_3C, $(Cr,Fe)_7C_3$ and olivine (MgO Al_2O_3) Rankin [7] observed a similar range of products when graphite was used as reductant When carbon monoxide in the presence of graphite was used as reducing agent, similar reduction products were observed [7] Nafziger et al [3] observed a variety of carbides, metal, olivine, pyroxene (MgO SiO_2) and oxides (such as MgO and Al_2O_3) as products during the reduction of two U S chromites It may therefore be expected

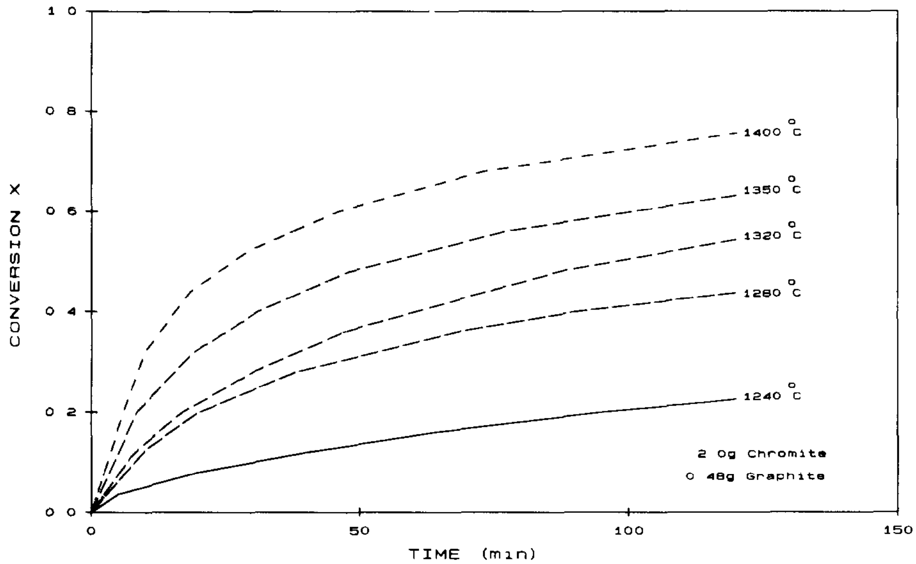

Fig 1 The effect of temperature on the reduction of chromite

that different chromites may yield different reduction products, and as a corollary, that different additives may influence the reduction process

Figures 3–8 illustrate that the additives K_2CO_3, Na_2O_2, SiO_2, Fe, Cr and CaO all accelerate the carbothermic reduction of chromite at 1400 °C X-ray diffraction of the products after 110 minutes of reduction with 10 and 15%

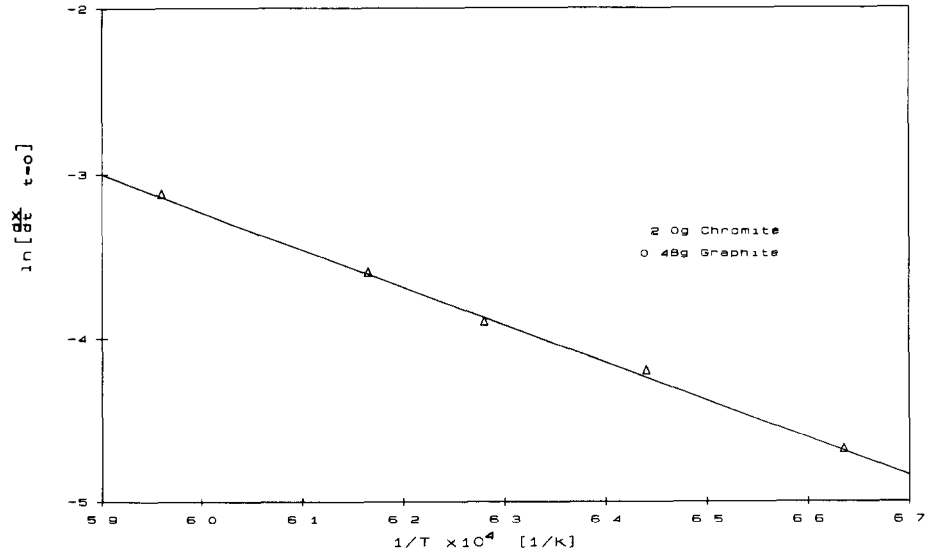

Fig 2 Arrhenius plot of the initial rate of reduction of chromite

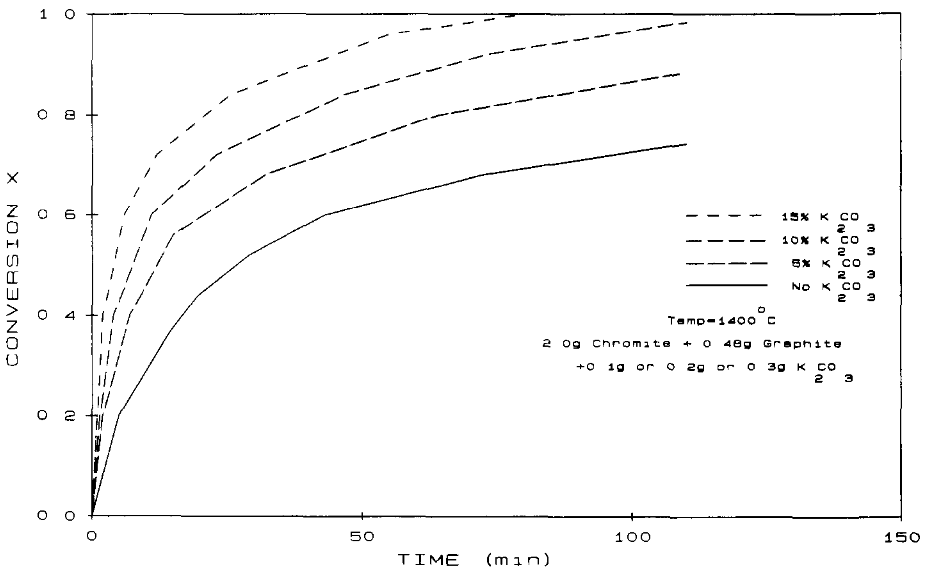

Fig 3 The effect of additions of K_2CO_3 on the reduction of chromite

additives showed low intensity peaks of K_2CO_3, Na_2CO_3, SiO_2, MgO SiO_2 and CaO No peaks due to Cr could be identified The major phases were similar to those identified when no additives were used, i e Fe, Fe_3C, $(Cr,Fe)_7C_3$ and olivine Examination of the products after 20 minutes of reduction showed X-ray diffraction peaks of K_2CO_3, Na_2CO_3, SiO_2 and

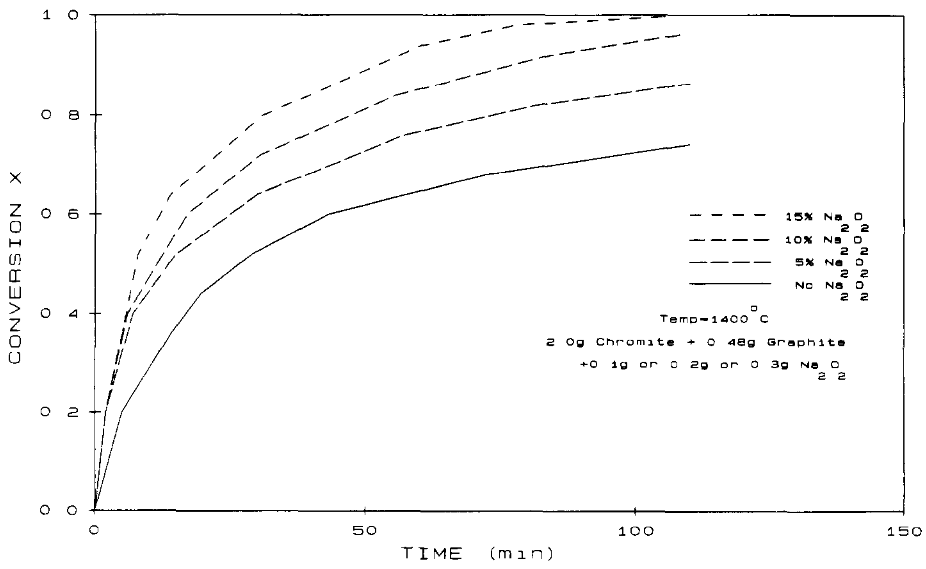

Fig 4 The effect of addition of Na_2O_2 on the reduction of chromite

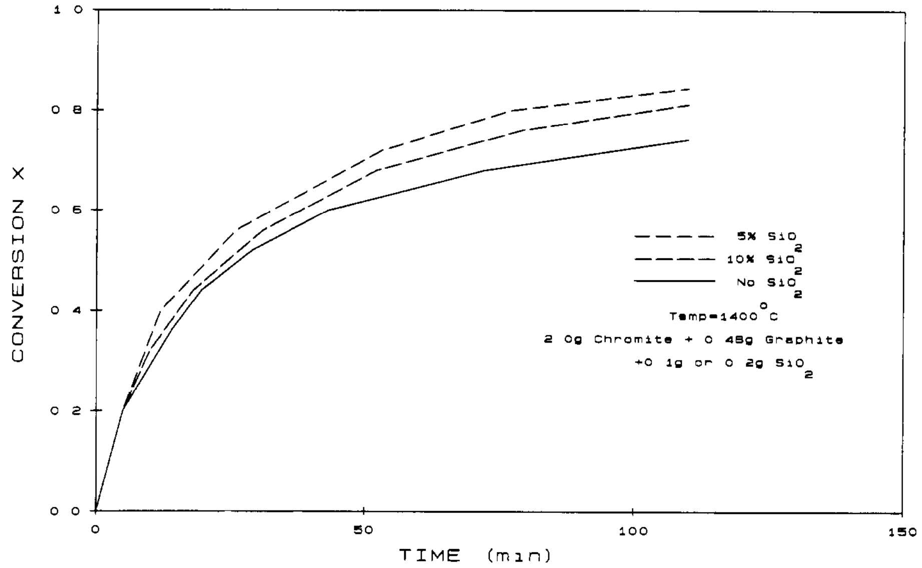

Fig 5 The effect of additions of SiO_2 on the reduction of chromite

CaO which were not as weak as those obtained after 110 minutes of reduction This could indicate that these additives reacted in some way during the reduction process Some non-stoichiometric chromite was present in all samples after 20 and 110 minutes in those samples where SiO_2, Fe, Cr or CaO was used as additive

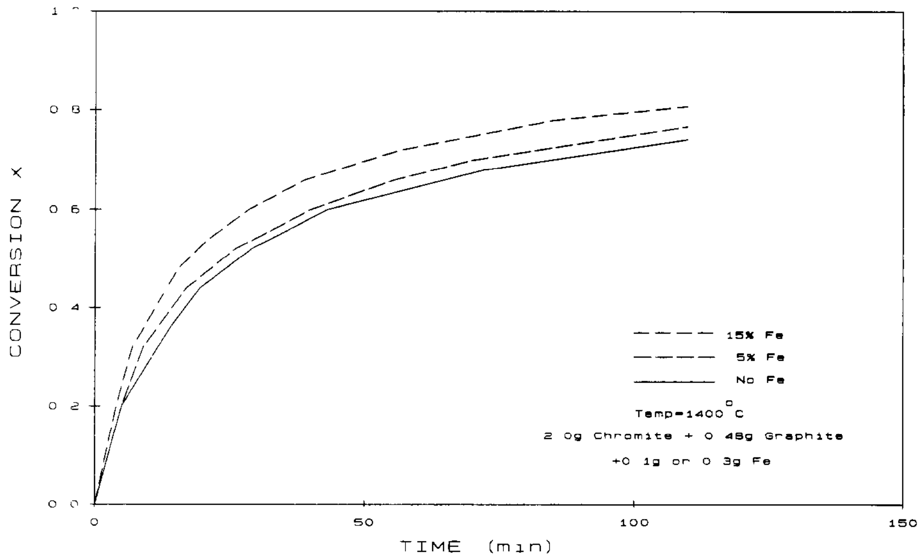

Fig 6 The effect of additions of Fe on the reduction of chromite

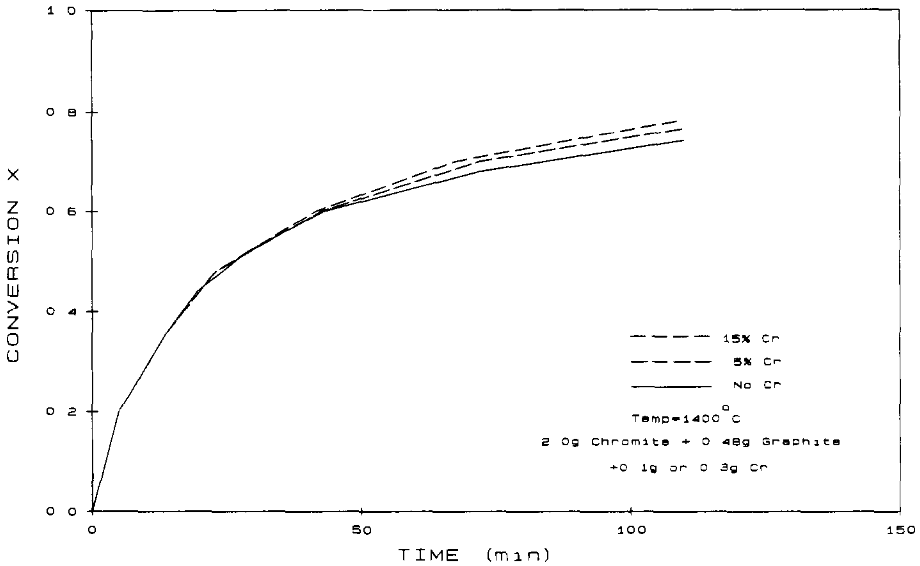

Fig 7 The effect of additions of Cr on the reduction of chromite

It was shown earlier that K_2CO_3, Na_2CO_3, CaO, SiO_2, Al_2O_3 and MgO all catalyse the Boudouard reaction to a larger or lesser extent [11,12] While Turdogan and Vinters [13] showed that iron catalysed the Boudouard reaction when iron was impregnated in graphite, little other work has been published on the effect of metals on the gasification of carbon Some work

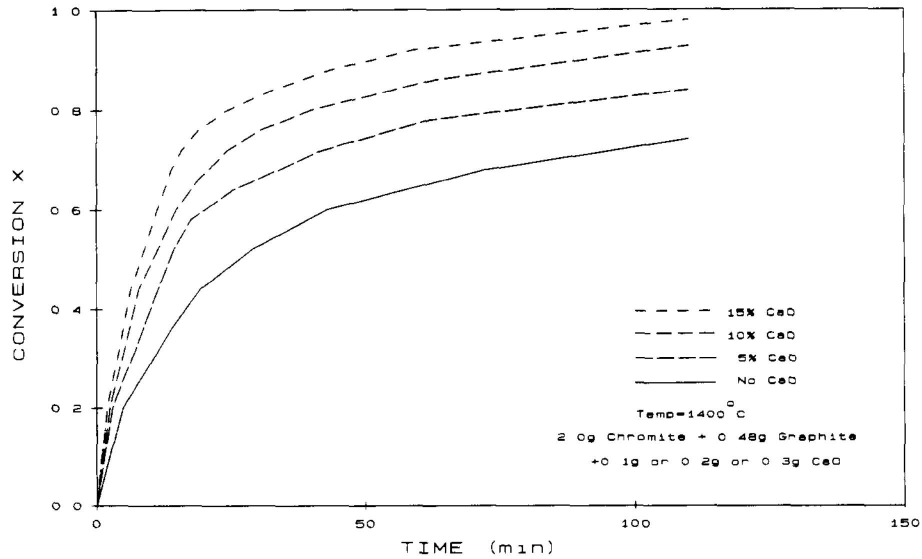

Fig 8 The effect of additions of CaO on the reduction of chromite

has been done, however, on the effect of metals on the carbothermic reduction of oxides Fruehan [14] concluded that the Ni formed during the reduction of NiO catalysed the oxidation of carbon, and Padilla [15] observed that the addition of Sn accelerated the carbothermic reduction of cassiterite It may be expected that metallic constituents such as Cr, Fe_3C or $(Cr,Fe)_7C_3$ could also catalyse the Boudouard reaction Previous workers [4,7] have shown that the reduction of chromite proceeds via carbon monoxide, which may indicate that catalysis of the Boudouard reaction could accelerate the reduction reaction Therefore, all the additives used in this study could be expected to accelerate the reduction of chromite

Such expectations are confirmed by Figs 3–8, although many other explanations could be presented for the enhanced reduction kinetics For example, the positive effect of Ca^{2+}, Na^+ and K^+, and the negative effect of Mg^{2+} and SiO_2 in promoting whisker growth on wustite and therefore catastrophic swelling of iron ore pellets [16] may also influence the reduction of chromite Figure 5 shows that a 5% addition of SiO_2 yielded superior kinetics to the case of 10% SiO_2 This may be explained by the competing effects of an enhanced Boudouard reaction on the one hand, and the formation of the slag phase MgO SiO_2 covering the chromite or graphite on the other It was found earlier [12] that silica retarded the rate of reduction of MnO due to the formation of a slag

Figures 6 and 7 show that the catalytic effects of Fe and Cr are not as significant as those of K_2CO_3, Na_2O_2 and CaO Furthermore, the influence of Cr does not seem to be of any practical importance Figure 8 shows that

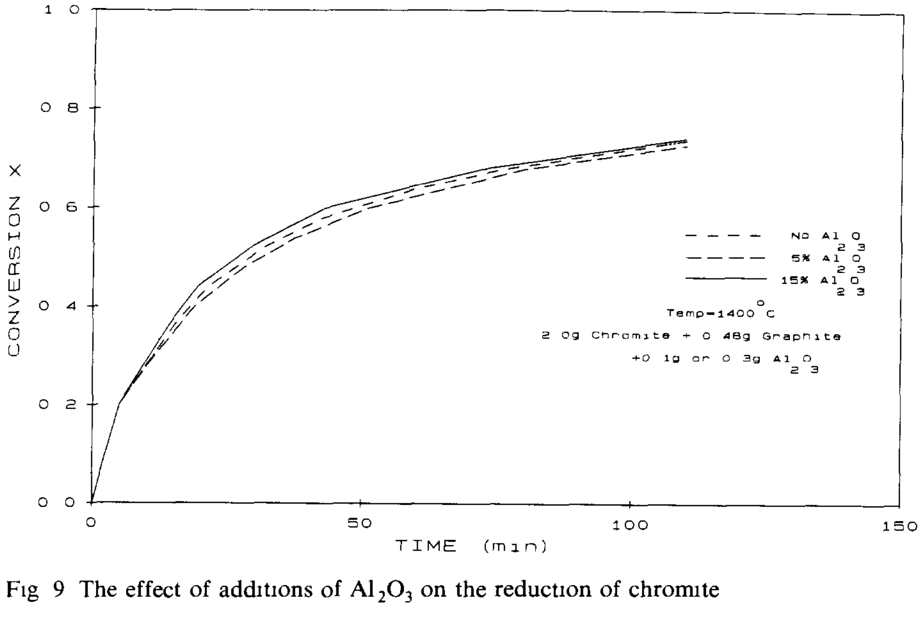

Fig 9 The effect of additions of Al_2O_3 on the reduction of chromite

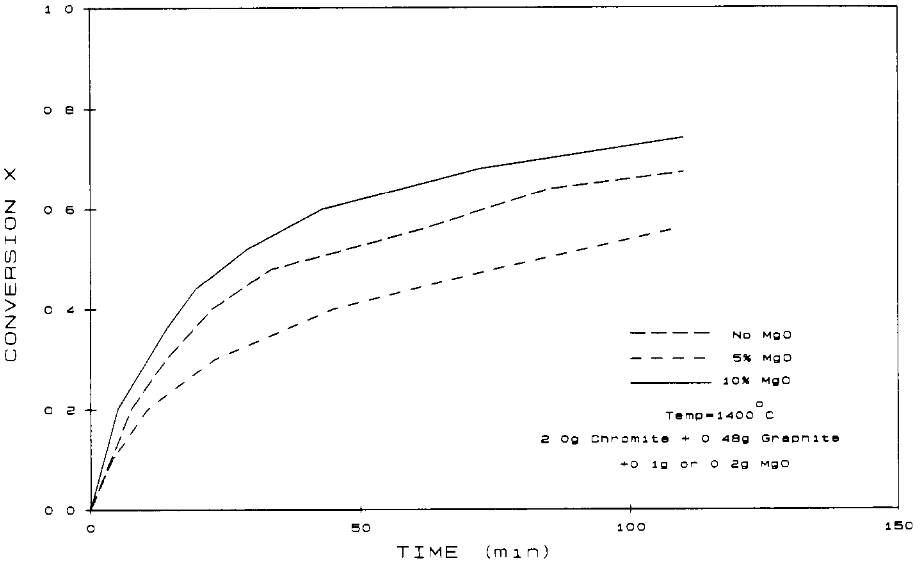

Fig 10 The effect of additions of MgO on the reduction of chromite

the catalytic influence of CaO is almost as strong as that of K_2CO_3 and Na_2O_2 Sundar Murti et al [10] also observed an increased reduction rate of chromite with the addition of CaO This was attributed to the possibility that lime may enter the chromite lattice with the release of FeO and therefore an increased reducibility of the chromite Similar to the observations in the present study, these authors also noticed the disappearance of the CaO peaks on the X-ray diffractogram [10] Although this explanation may be partially true, Sundar Murti et al [10] do not even mention the possibility that CaO may catalyse the Boudouard reaction Also, if CaO enters the chromite lattice it could decrease the reducibility of the chromium oxide Lime was shown to catalyse the carbothermic reduction of MnO [12] and SnO_2 [17] where there was no question of one component being released selectively

Figure 9 shows that Al_2O_3 has a slightly inhibiting effect on the reduction of chromite, especially in view of its positive influence on the Boudouard reaction The significant negative influence of MgO on the reduction of chromite is illustrated in Fig 10 X-ray diffraction of the products after 20 and 110 minutes of reduction revealed a decrease in the peaks of Al_2O_3 and MgO, and an increase in the peaks of olivine It appears as though MgO, and Al_2O_3 to a lesser extent, inhibit the decomposition of the chromite spinel by perhaps hindering the diffusion of iron and chromium in the spinel [18]

Figure 11 shows that a decrease in the particle size of the chromite accelerated the reduction process when CaO was used as an additive It is

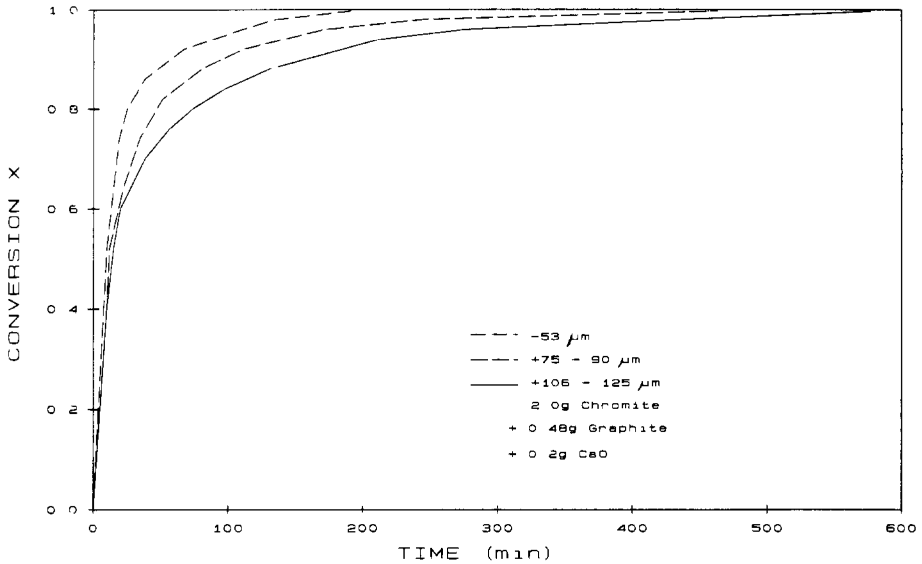

Fig 11 The effect of particle size of chromite on the carbothermic reduction of chromite

interesting to note that all the curves in Fig 11 reach a conversion of 100%, so that the effect of particle size is purely kinetic

CONCLUSIONS

The additives K_2CO_3, Na_2O_2 and CaO enhanced the carbothermic reduction of chromite significantly, while additions of SiO_2 and Fe revealed a more moderate catalytic influence Additions of Cr exerted very little influence on the reduction process Higher additions of silica have a less favourable effect than lower additions due to the formation of a slag phase Whereas Al_2O_3 has a slightly negative effect on the rate of reduction, additions of MgO inhibited the decomposition of the chromite spinel significantly The X-ray diffraction peaks for most of the additives decreased in intensity during the reduction reaction In most of the reduction products olivine, Fe, Fe_3C and $(Cr,Fe)_7C_3$ could be identified An activation energy of 192 kJ mol^{-1} was measured for the reduction without any additives being used

ACKNOWLEDGEMENTS

A M Smith, B S Camby and D N E Smit are duly thanked for their technical assistance The author also thanks the Department of Geology, University of Stellenbosch, for permission to use their XRD and XRF instruments

REFERENCES

1 R H Nafziger, J S Afr Inst Min Metall, 82 (1982) 205
2 D D Howat, J S Afr Inst Min Metall, 86 (1986) 37
3 R H Nafziger, J E Tress and J I Paige, Metall Trans B, 10B (1979) 5
4 M J Searle and C W P Finn, Report No M 96, Council for Mineral Technology, Randburg, South Africa, 1983
5 A R Barnes, C W P Finn and S H Algie, J S Afr Inst Min Metall, 83 (1983) 49
6 N A Barcza, P R Jochens and D D Howat, Electric Furnace Proceedings, 29 (1971) 88
7 W J Rankin, Trans Inst Min Metall Sect C, 88 (1979) C107
8 W J Rankin, Arch Eisenhuttenwes, 50 (1979) 373
9 A R Barnes and C W P Finn, Report no 2070, National Institute for Metallurgy, Randburg, South Africa, 1980
10 N S Sundar Murti, K Shah, V L Gadgeel and V Seshadri, Inst Min Metall Trans Sect C, 92 (1983) C 172
11 J S J van Deventer and P R Visser, Thermochim Acta, 111 (1987) 89
12 J S J van Deventer, Thermochim Acta, 112 (1987) 365
13 E T Turkdogan and J V Vinters, Carbon, 10 (1972) 97
14 R J Fruehan, Metall Trans B, 8B (1977) 279
15 R Padilla and H Y Sohn, Metall Trans B, 10B (1979) 109
16 R Nicolle and A Rist, Metall Trans B, 10B (1979) 429
17 J S J van Deventer, Thermochim Acta, in press
18 S Kouroki, K Morita and N Sano, in L F Houghton (Ed), Proceedings of MINTEK 50, Randburg, South Africa, The Council for Mineral Technology, Randburg, Vol 2, 1987, p 847