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THE EFFECT OF GANGUE COMPONENTS ON THE REDUCTION OF MANGANOSITE BY GRAPHITE: AN ISOTHERMAL KINETIC STUDY

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ABSTRACT

Mixtures of manganosite (MnO), graphite and various gangue components were reacted isothermally under argon, and the loss in mass was recorded continuously. Manganosite reduced first to Mn_5C_2, which then reacted with the remaining manganosite to form metallic manganese. Additions of haematite (Fe_2O_3) revealed no significant effect on the reduction of MnO by graphite, while CaO, MgO and Al_2O_3 accelerated the reduction slightly. The reaction was enhanced significantly by additions of K_2CO_3. Silica (SiO_2) retarded the reduction appreciably, possibly because of the formation of β-$MnSiO_3$. The influence of these impurities on the Boudouard reaction was observed during the isothermal gasification of graphite in an atmosphere of CO_2.

INTRODUCTION

Manganese is commonly used in the steel industry as an alloying element to impart desirable physical properties to steel. In almost every instance manganese is added to the steel as a ferroalloy, which is produced in a submerged-arc furnace by reduction of manganese ore [1]. Manganosite (MnO) is formed during the early stages of the complex transformations which occur when manganese ore is reduced to ferromanganese [2]. Koursaris and See [1] established that two routes exist for the reduction of manganosite to form carbide and metal in a furnace, namely, (a) reduction of solid manganosite by solid carbon, and (b) reduction of manganosite dissolved in the slag by a carbon-saturated alloy.

Although the reduction of manganosite is the most important reaction in the production of ferromanganese, very little is understood about the nature of the process. Rankin and Van Deventer [3] provided evidence that the reduction of manganosite by graphite proceeds by way of carbon dioxide as a gaseous intermediate. The activation energy of this reaction was found to be 241 kJ mol^{-1}, and this was similar to the measured activation energy for the gasification of graphite by CO_2, namely 257 kJ mol^{-1} [3].

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TABLE 1

Typical analysis of Mamatwan ore

Constituent	Mass%	Constituent	Mass%
Mn_2O_3 [a]	55.8	MgO	3.1
Fe_2O_3	6.1	SiO_2	4.5
CO_2	14.9	CaO	12.9
H_2O	0.7	K_2O	0.2
Al_2O_3	0.2	other	1.6

[a] Total manganese content of ore expressed as Mn_2O_3.

Manganese ores contain iron oxides and gangue minerals in addition to manganese oxides and carbonates. These gangue minerals may have an effect on both the nature of the reduction products and the kinetics of reduction. A typical composition of South African Mamatwan manganese ore is given in Table 1.

It is the objective of this paper to explore the influence that these gangue components have on the kinetics of reduction of manganosite by graphite. X-ray diffraction analysis was used to identify reaction products. Analysis of the gas evolved from the reduction will be used to calculate the product composition.

THEORETICAL CONSIDERATIONS

Downing [4] constructed a Pourbaix diagram for the Mn–O–C system in which the pure phases Mn_2O_3, Mn_3O_4, MnO, Mn_7C_3, C and Mn are considered. Rankin and Van Deventer [3] discussed this diagram, but showed that Mn_5C_2 (and not Mn_7C_3 as expected from the diagram of Downing) was the stable carbide product.

The minimum temperature required for reduction to take place can be calculated from free energy data. Figure 1 has been calculated from free energy data [5] and illustrates the temperature dependence of the P_{CO}/P_{CO_2} ratio for the Boudouard reaction and the reduction reaction. Values are shown for different activities of Mn and MnO. The minimum reaction temperatures for different values of the activities a_{Mn} and a_{MnO} are shown in Fig. 2.

For pure manganosite the minimum reaction temperature decreases as a_{Mn} decreases, i.e. as Mn dissolves in another element such as iron or carbon. For pure manganese metal the minimum reaction temperature increases as a_{MnO} decreases, i.e. as MnO forms a solution with other oxides. Figure 1 shows that the fraction of carbon dioxide in the gas evolved from the carbonaceous reduction of manganosite is expected to be negligible. This fraction will decrease with an increase in temperature at constant activities of MnO and Mn.

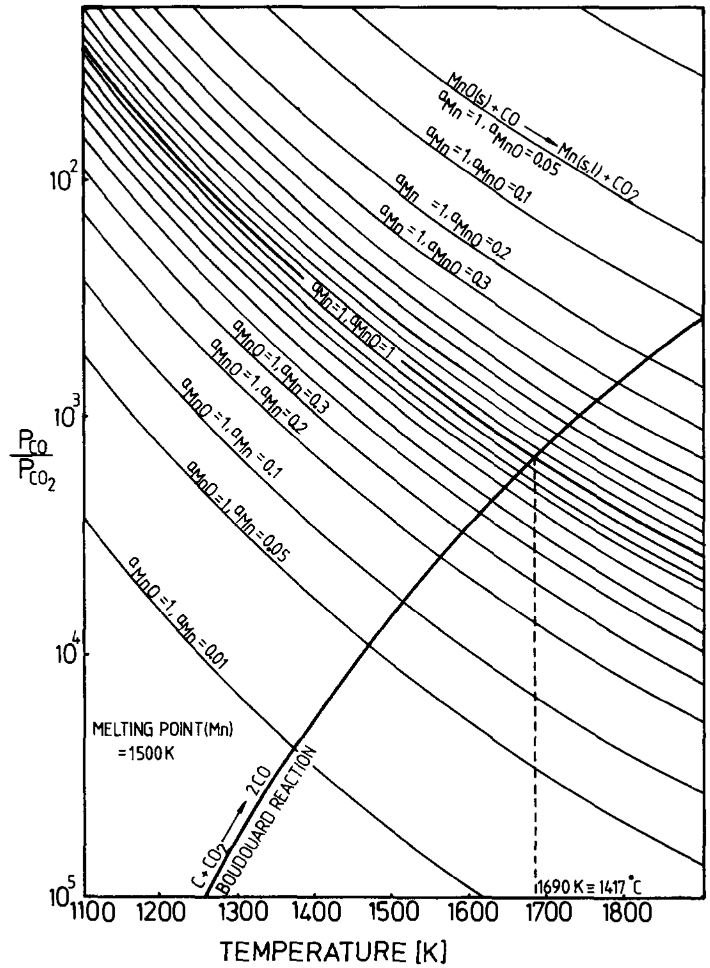

Fig. 1. Thermodynamics of the carbonaceous reduction of manganosite.

The fractional conversion of manganosite during reduction is defined here as:

$$X = \frac{\text{mass of oxygen removed from sample}}{\text{mass of removable oxygen in sample}} \tag{1}$$

If it is assumed that the CO_2 in the gas evolved from the reduction is negligible, then:

$$X = \frac{\Delta m}{m} \frac{M_{\mathrm{MnO}}}{M_{\mathrm{CO}}} \tag{2}$$

where Δm = registered mass loss of sample, m = initial mass of MnO and M_i = molecular mass of component i.

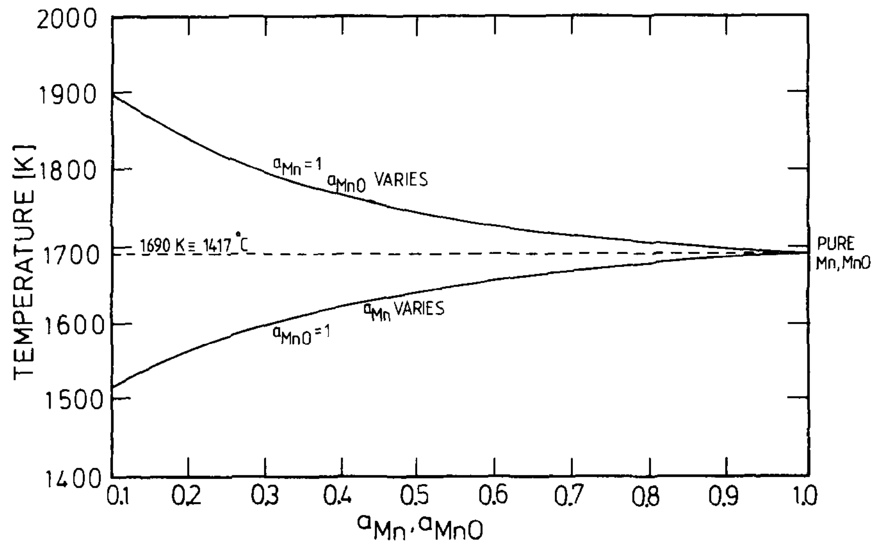

Fig. 2. Effect of the activities of Mn and MnO on the minimum temperature of reduction.

If equimolar quantities of manganosite and carbon react and only CO and Mn metal are formed according to the reaction:

$$MnO + C = Mn + CO \tag{3}$$

then the maximum value of X is unity. However, if the following reaction occurs

$$5MnO + 7C = Mn_5C_2 + 5CO \tag{4}$$

and equimolar quantities of manganosite and carbon are used, then the maximum value of X will be $5/7$.

If it is assumed that manganosite is reduced according to reactions (3) and (4) and that no free carbon is present after completion of the reduction, then the product distribution may be calculated as follows:
The fraction of manganese present as MnO, α_{MnO}, is

$$\alpha_{MnO} = 1 - X \tag{5}$$

The fraction of manganese present as Mn, α_{Mn}, is

$$\alpha_{Mn} = \frac{7}{2}X - \frac{5}{2}\frac{n}{m}\frac{M_{MnO}}{M_C} \tag{6}$$

where n = initial mass of carbon.
The fraction of manganese present as Mn_5C_2, $\alpha_{Mn_5C_2}$, is

$$\alpha_{Mn_5C_2} = \frac{5}{2}\left\{\frac{n}{m}\frac{M_{MnO}}{M_C} - X\right\} \tag{7}$$

EXPERIMENTAL

The manganosite was prepared from manganese dioxide of analytical grade, which was heated for 5 h in a magnesia crucible at 1100 °C under an atmosphere of hydrogen. An X-ray diffractogram of the product revealed only manganosite. Table 2 gives the size distribution of the product. High purity graphite with particle size between 125 and 180 μm was used as reductant. Different amounts of CaO, MgO, SiO_2, Al_2O_3, Fe_2O_3 and K_2CO_3 were added to the reaction mixtures in order to investigate the influence of gangue components on the reduction of MnO. These additives were all of analytical grade.

Reduction experiments were conducted in a vertical tube furnace fitted with a continuous weighing and recording electronic balance, which was described in an earlier paper [3]. Equimolar amounts of MnO (2.00 g) and graphite (0.3386 g) were mixed intimately with or without additives and placed in a small recrystallized-alumina crucible in the furnace at a temperature of 1350 °C. During a run the mass and temperature of the crucible was recorded continuously. The furnace was flushed with purified argon at a rate of 0.7 l min^{-1}, which was sufficiently high not to affect the rate of reduction. Purified carbon dioxide was flushed through the furnace at a flow rate of 1.0 l min^{-1} during gasification experiments. In this case 0.6 g of graphite was intimately mixed with 0.06 g of a particular additive and placed in the furnace.

Gas evolving from reduction experiments was passed through a tube filled with NaOH-impregnated asbestos. This tube was weighed before and after each experiment in order to determine the concentration of CO_2 in the gas. The solid product in the crucible was examined by X-ray diffraction to identify the phases in the reaction product. A Philips diffractometer with a graphite monochromator was used, the radiation being Cu K_α. Samples were also subjected to EDAX (energy-dispersive analysis of X-rays) analyses in a scanning electron microscope.

TABLE 2

Size distribution of the MnO used in experiments

Size fraction (μm)	Mass%
> 355	2.1
250–355	2.6
180–250	41.6
125–180	30.7
90–125	13.8
63– 90	4.3
45– 63	2.5
< 45	2.4

RESULTS AND DISCUSSION

Results from thermogravimetric experiments were easily reproducible with an average deviation of 0.7%. The temperature of 1350°C used for experimental work was above the minimum temperature required to form low carbides, i.e. where $a_{\mathrm{Mn}} < 0.4$. Rankin and Van Deventer [3] investigated the effects of temperature and the MnO to C ratio on the reduction of MnO by graphite.

When different MnO to C ratios were used it was found that the values of X obtained after 80 min were in each case slightly higher than the theoretical limit calculated when it was assumed that only CO and Mn_5C_2 were formed as products [3]. For the stoichiometric ratio of MnO to C used in the work presented here such a limiting value of X is calculated to be 0.714, i.e. when $\alpha_{\mathrm{Mn}} = 0$, $\alpha_{\mathrm{Mn_5C_2}} = 0.714$ and $\alpha_{\mathrm{MnO}} = 0.286$. Although it was difficult to measure accurately the $P_{\mathrm{CO}}/P_{\mathrm{CO_2}}$ ratio in the product gas it was established

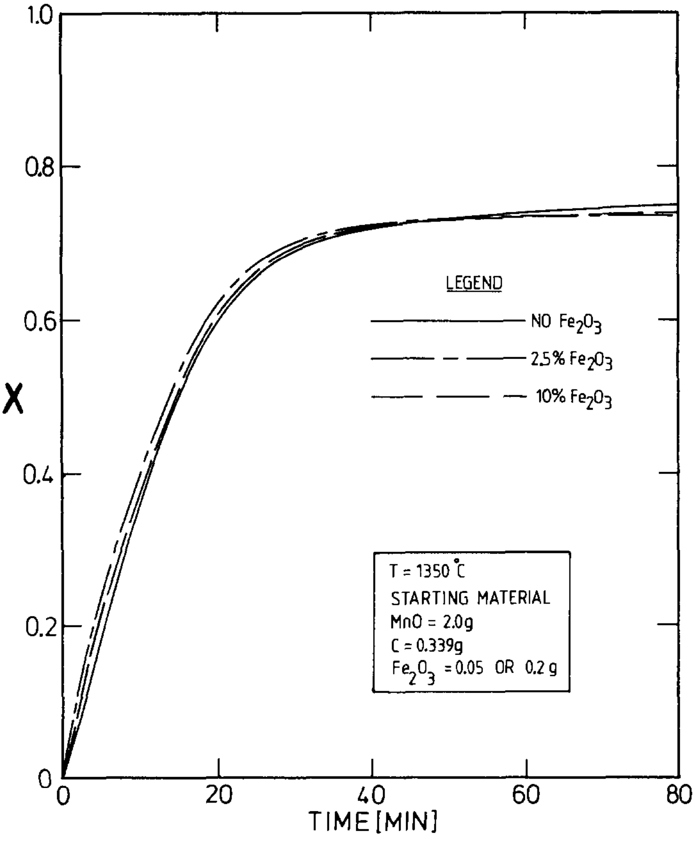

Fig. 3. The effect of additions of Fe_2O_3 on the reduction of MnO by graphite.

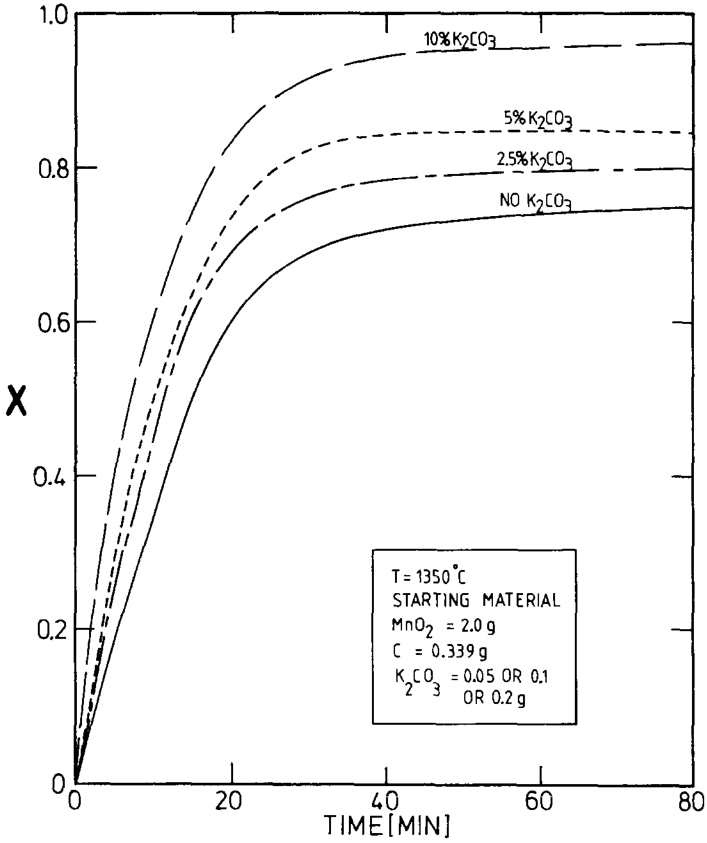

Fig. 4. The effect of additions of K_2CO_3 on the reduction by graphite.

that this ratio was greater than 110 during the reduction of MnO. Such a low level of CO_2 has a negligible effect on the calculation of X so that the use of eqn. (2) can be justified. A high level of CO_2 in the gas is thus not the reason why the values of X after 80 min are higher than 0.174 in Figs. 3–7. It has been established that catalysts such as Na_2CO_3 and K_2CO_3 decrease the level of CO_2 during the carbonaceous reduction of haematite [6,7]. Table 3 shows a similar behaviour by K_2CO_3, MgO, CaO, Al_2O_3 and SiO_2 during the reduction of MnO.

X-ray diffraction (XRD) of a stoichiometric mixture of MnO and graphite with no additives showed that MnO, Mn_5C_2 and some Mn metal were present after 80 min of reduction. No free graphite could be detected in the sample. Electron micrographs of polished sections of the solid product revealed a light sintered phase and a darker phase which were intermingled. EDAX analyses yielded 77 mass% Mn for the darker phase and 92 to 94 mass% Mn for the lighter phase. Thus the darker phase corresponded to manganosite while the lighter phase had a composition between those of

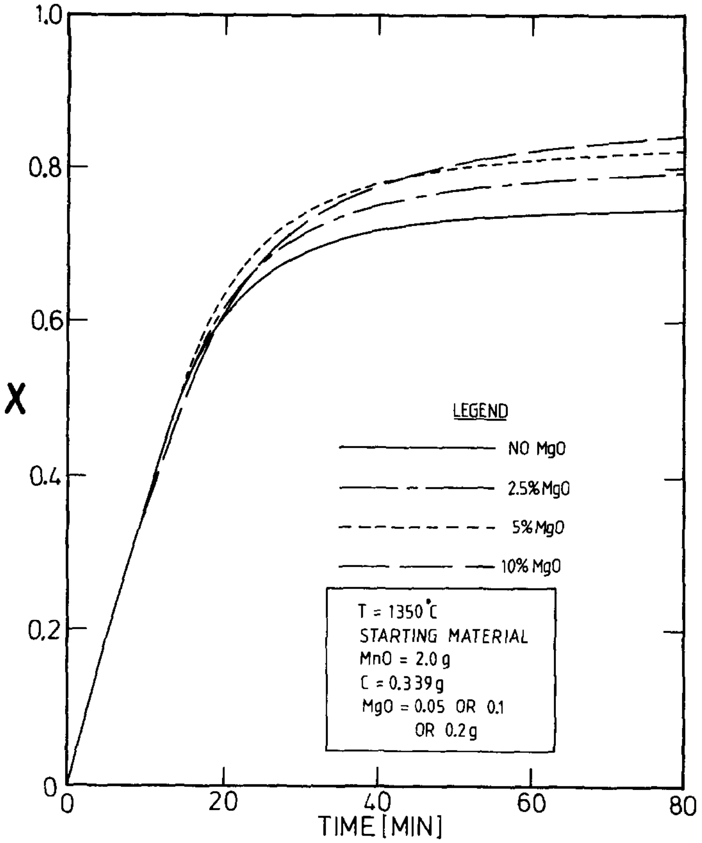

Fig. 5. The effect of additions of MgO on the reduction of MnO by graphite.

TABLE 3

Calculated distribution of manganese between species in some reduction products

Starting mixture	Mass% Mn in metal product	α_{MnO}	α_{Mn}	$\alpha_{Mn_5C_2}$	X (after 80 min)	$\frac{P_{CO}}{P_{CO_2}}$ (experimental)
2.0 g MnO +0.3386 g C	93.3	0.250	0.125	0.625	0.750	110
2.0 g MnO +0.3386 g C +0.2 g K_2CO_3	99.3	0.033	0.885	0.082	0.967	132
2.0 g MnO +0.3386 g C +0.2 g MgO	96.3	0.154	0.461	0.385	0.846	116
2.0 g MnO +0.3386 g C +0.2 g CaO	96.3	0.155	0.457	0.388	0.845	121
2.0 g MnO +0.3386 g C +0.2 g Al_2O_3	96.3	0.156	0.454	0.390	0.844	118
2.0 g MnO +0.3386 g C +0.2 g SiO_2	92.0	0.340	0.0	0.660	0.660	118

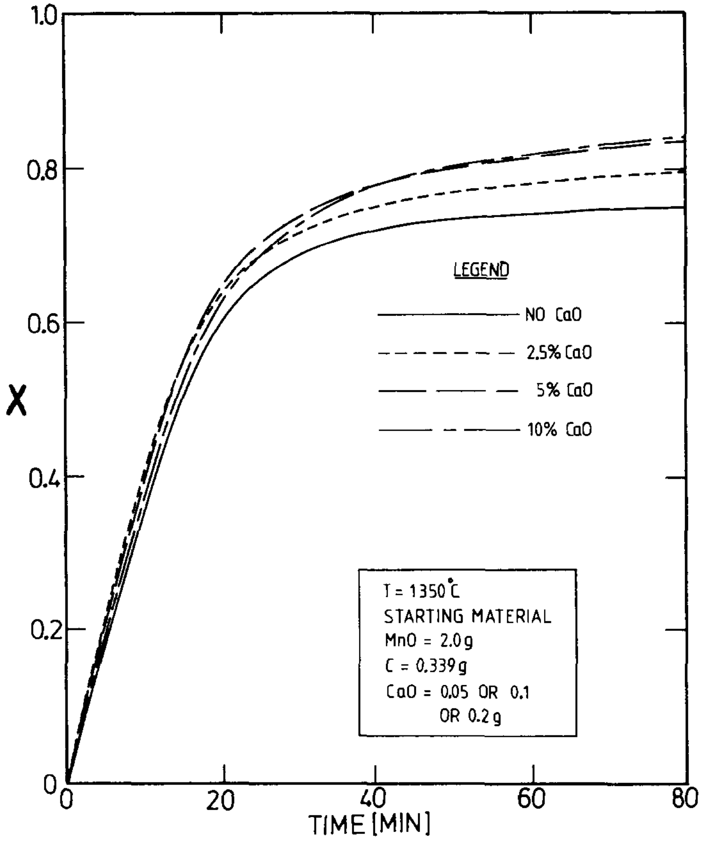

Fig. 6. The effect of additions of CaO on the reduction of MnO by graphite.

Mn_5C_2 and Mn metal. XRD of a stoichiometric mixture after 30 min of reduction revealed free graphite, MnO and Mn_5C_2 but no Mn metal. It appeared as though Mn metal started to occur only after 35 min of reduction. Figure 8 shows that when silica was used as an additive the value of X remained below 0.714 even after 80 min. In these experiments no Mn metal could be detected in the reaction products. When 10 mass% of K_2CO_3 was used as an additive, Mn metal could be detected by XRD after about 13 min of reduction. In all cases investigated Mn metal started to form only when $X > 0.714$. Free graphite was detected by XRD in samples where $X < 0.714$.

These observations provide some evidence that manganosite was first reduced to the carbide Mn_5C_2, which then reacted with the remaining manganosite to form metallic manganese. Maru et al. [8] studied the kinetics of reaction between $Cr_{23}C_6$ and Cr_2O_3 particles, and concluded that the reaction occurred through the gaseous intermediates CO and CO_2. A similar mechanism may be assumed here. The mass% Mn in the metallic product

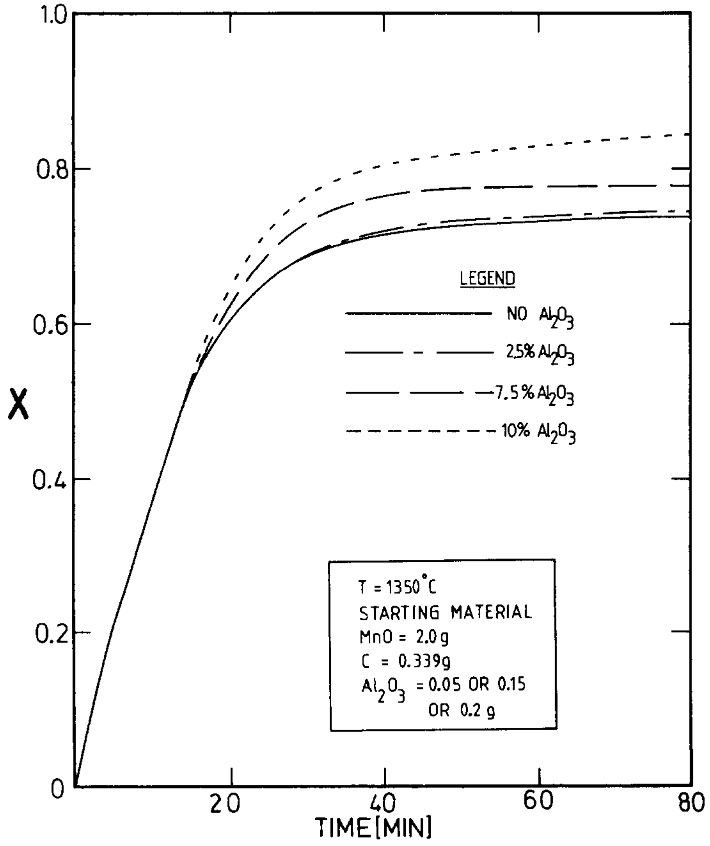

Fig. 7. The effect of additions of Al_2O_3 on the reduction of MnO by graphite.

was calculated from the X values obtained after 80 min for selected cases given in Table 3. EDAX analyses of the light metallic product were within 1% of these calculated values. The higher the fractional conversion the higher the value of α_{Mn} and the higher the manganese content of the metallic product, as indicated in Table 3.

Figure 3 shows that the addition of Fe_2O_3 had a negligible influence on the reduction of MnO by graphite. Since Fe_2O_3, as well as MnO, was reduced, the oxygen content of the Fe_2O_3 was included in the calculation of the fractional conversion by assuming that all gas evolved was CO. XRD of the solid product revealed unreduced MnO, γ-$FeMn_3$ and the carbides Mn_5C_2 and $Fe_{0.6}Mn_{5.4}C_2$ but no free graphite.

Figure 9 shows that the additives K_2CO_3, CaO, Al_2O_3, SiO_2 and MgO all accelerated the gasification of graphite by CO_2. Although the catalytic effects of alkali metal salts on the Boudouard reaction have been investigated extensively [7,9] very little information exists regarding the effects of CaO, Al_2O_3, SiO_2 and MgO on the gasification of carbon. McKee [9]

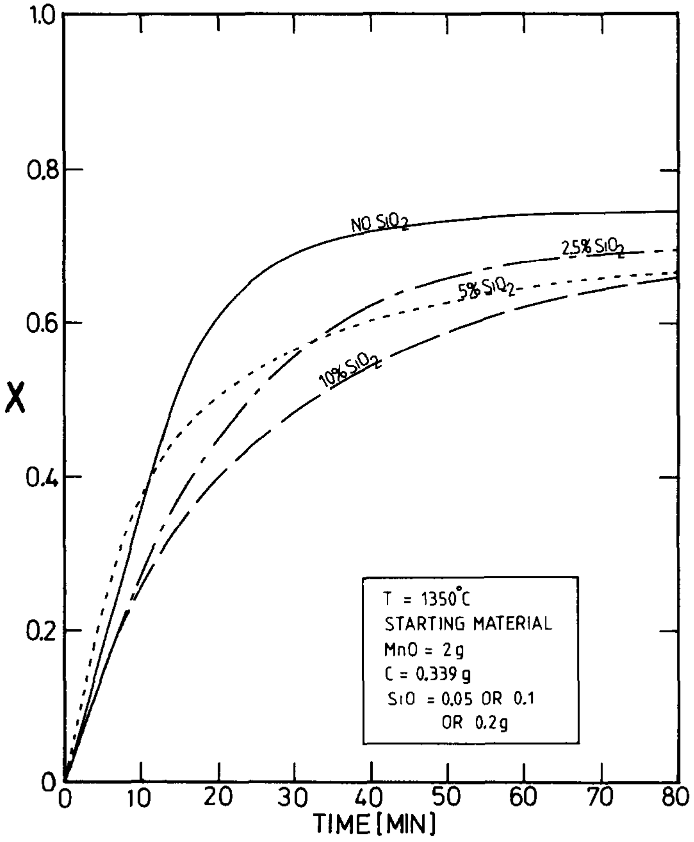

Fig. 8. The effect of additions of SiO_2 on the reduction of MnO by graphite.

speculated that such stable oxides would not catalyse the oxidation of carbon, but gave no data in support of his argument. Otto et al. [10] observed that elements such as Fe, Ca, Si, Al, K and S in the ash of a lignite char catalysed the reaction between graphite and steam. Haynes et al. [11] established that CaO and MgO increased the rate of coal by steam.

Figures 4 to 7 show that K_2CO_3, MgO, CaO and Al_2O_3 all accelerated the reduction of manganosite by graphite. This was probably caused by catalysis of the Boudouard reaction by these additives. The effect of K_2CO_3 was more pronounced than those of MgO, CaO and Al_2O_3. XRD of the solid products obtained after 80 min of reduction revealed MnO, Mn_5C_2, Mn metal and the respective additives. No reactions between MnO and the additives were indicated by the XRD patterns.

The effect of silica on the reduction of manganosite is shown in Fig. 8. Although there is some crossing of the curves, it is evident that silica caused an appreciable decrease in the rate of reduction. This could be surprising in view of the accelerating effect which SiO_2 had on the Boudouard reaction,

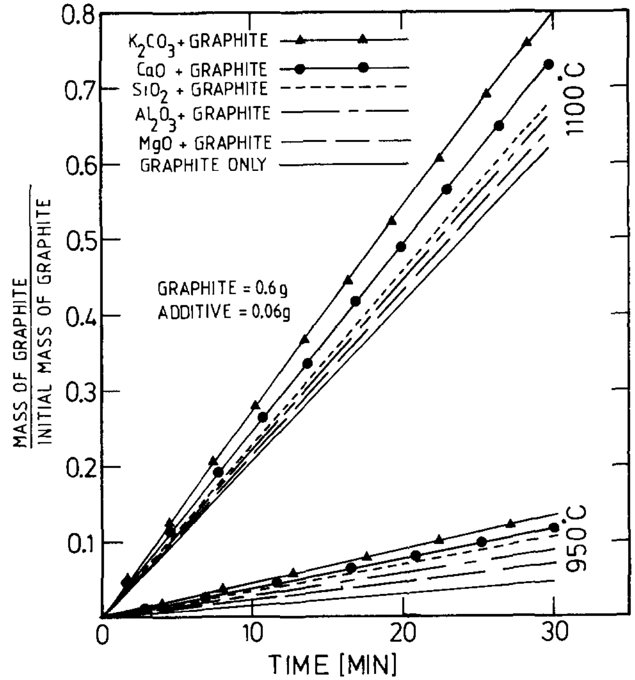

Fig. 9. The effect of different additives on the gasification of graphite by CO_2.

as depicted in Fig. 9. However, XRD of the reduction products indicated the presence of β-$MnSiO_3$ in addition to β-quartz, Mn_5C_2, MnO and graphite. The slag β-$MnSiO_3$ could have coated some of the MnO particles and thereby reduced the area of contact between the MnO grains and the reducing atmosphere. The slag could also have caused a slight decrease in the activity of the MnO, which could be expected to slow down the reduction.

CONCLUSIONS

When manganosite was reduced by graphite under argon the gas which evolved was almost pure CO. The carbide Mn_5C_2 was preferentially formed until all free carbon was consumed, which consequently reacted with the remaining MnO to form metallic Mn. While CaO, MgO and Al_2O_3 accelerated the reduction moderately, K_2CO_3 revealed a significant influence. All these additives increased the mass% Mn in the metallic reduction product. Haematite had no significant effect on the rate of reduction. Silica retarded the rate of reduction due to the formation of β-$MnSiO_3$, although SiO_2, CaO, MgO, Al_2O_3 and K_2CO_3 all catalysed the gasification of graphite by CO_2.

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