Thermochimica Acta, 124 (1988) 109–118
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THE EFFECT OF ADMIXTURES ON THE REDUCTION OF CASSITERITE BY GRAPHITE

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(Received 22 April 1987)

ABSTRACT

The kinetics of the isothermal reduction of cassiterite by graphite with different admixtures present were studied by thermogravimetry. The conversion of cassiterite was defined as the ratio of the mass of oxygen removed from a sample to the mass of removable oxygen in a sample. Gas evolving from the reduction reaction was analysed in order to determine the P_{CO_2}/P_{CO} ratio. This value was determined by the SnO_2/Sn equilibrium so that the Boudouard reaction was the slow reaction controlling the overall rate. While MgO increased the activation energy for the reduction of cassiterite, K_2CO_3, SiO_2, Al_2O_3, CaO and tin metal all catalysed this reduction and decreased the activation energy. Tin metal, CaO and K_2CO_3 also tended to increase the maximum conversion attainable. Whereas CaO reacted to form $2CaO \cdot SnO_2$, the admixtures K_2CO_3, SiO_2, Al_2O_3 and MgO revealed no reaction with the cassiterite or any other species present.

INTRODUCTION

Cassiterite (SnO_2) is considered to be the only economically significant tin mineral in the earth's crust, and in its purest form has a tin content of 78.76%. Other tin minerals of lesser importance are ainalite, stannite and cylindrite [1]. Tin is one of the oldest metals known to and used by man due to its great malleability, low melting point, and corrosion resistance. The main use of this metal is in the coating of tinplate and the second largest use is in solder [2].

It has been shown that the production of tin metal from a cassiterite-bearing concentrate follows a conventional carbon-reduction process [2,3]

$$C + CO_2 \rightarrow 2CO \tag{1}$$

$$SnO_2 + 2CO \rightarrow Sn + 2CO_2 \tag{2}$$

Whereas much work has been published on the reduction of iron oxides [4,5], relatively few studies have been reported on the reduction of non-ferrous metal oxides [3,6]. The only fundamental study on the carbothermic

0040-6031/88/$03.50

reduction of cassiterite was that by Padilla and Sohn [3], who investigated the effects of the type, the particle size and the relative amount of carbon used. They found that the overall rate of reduction was controlled by the oxidation of carbon by CO_2. It was concluded that the tin metal formed during the reduction actually catalysed the oxidation of coconut charcoal.

Cassiterite is mainly found in late-stage granitic intrusions, and as alluvia or placer and detrital deposits [2]. Associated gangue included shales, arkosites, granites, granophyres and felsites, which could not be separated perfectly from the cassiterite during gravity concentration or froth flotation [2]. These gangue materials may have an effect on both the nature of the reduction products and the kinetics of the carbothermic reduction of cassiterite, as was found in the reduction of manganosite [7].

It is the aim of this paper to investigate the influence of some gangue constituents on the kinetics of the isothermal reduction of cassiterite by graphite.

EXPERIMENTAL

In general, two main techniques may be used for following the progress of a reduction reaction [5,8]: (1) measurement of the mass of the sample, either intermittently or continuously; and (2) measurement of some change in the properties of the gas stream from the reaction.

High purity graphite with particle size 100% < 106 μm was used as reductant. Powdered cassiterite with particle size 100% < 180 μm was subjected to X-ray diffraction analysis before use in experiments. This was to ensure that pure cassiterite was used. Different quantities of MgO, CaO, Al_2O_3, SiO_2, K_2CO_3 or Sn-metal were added to the reaction mixtures as powders with particle size 100% < 106 μm in order to investigate the effects of gangue constituents on the reduction of cassiterite. These admixtures were all of analytical grade. All reagents were dried for 2 h at 100 °C before use in experiments.

Commercial argon was used as an inert atmosphere during the reduction process. Before use, this argon was passed through a purification unit where water was removed by 98% H_2SO_4, $MgClO_4$ and $CaCl_2$; CO_2 was removed by NaOH-impregnated asbestos and oxygen was removed by titanium shavings at 600 °C.

Reduction experiments were carried out in a thermogravimetric set-up consisting of a continuous weighing and recording electronic balance mounted above a vertical tube furnace of 50 mm internal diameter, which was heated by six silicon carbide elements and maintained at constant temperature by a Eurotherm on–off controller [9]. The reaction mixture was placed in a small recrystallized alumina crucible and connected to the weighing balance via a platinum support wire.

Stoichiometric quantities of SnO_2 (2.0 g) and graphite (0.319 g) were mixed intimately with or without admixtures before being introduced into the water-cooled quenching chamber at the bottom of the furnace. At an argon flow rate of 1.5 l min^{-1} the kinetics were independent of the gas flow rate.

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.

TREATMENT OF DATA

The fractional conversion X of cassiterite during reduction was defined as [5]

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

$$= \frac{\Delta m M_{O_2}}{Zm}\left[\frac{\left(\dfrac{P_{CO_2}}{P_{CO}}\right) + \dfrac{1}{2}}{M_{CO_2}\left(\dfrac{P_{CO_2}}{P_{CO}}\right) + M_{CO}}\right] \tag{3}$$

where Δm = registered mass loss of sample, m = mass of cassiterite in sample, Z = mass of removable oxygen per unit mass of cassiterite = 0.2124, M = molecular mass, P_{CO} = partial pressure of CO, and P_{CO_2} = partial pressure of CO_2 ($P_{CO} + P_{CO_2} = 1$). This definition of X is independent of the amount of graphite added to the cassiterite, and is directly related to the amount of tin metal formed. The values of P_{CO} and P_{CO_2} could be determined from the composition of the product gas.

The initial slopes $\mathrm{d}X/\mathrm{d}t|_{t=0}$ of the plots of X vs. time were used in the logarithmic form of the Arrhenius equation to estimate the activation energies for reduction with different admixtures

$$\ln \frac{\mathrm{d}X}{\mathrm{d}t}\bigg|_{t=0} = \ln k_0 - \frac{E}{R_0 T} \tag{4}$$

where k_0 = Arrhenius pre-exponential constant, E = activation energy, R_0 = universal gas constant and T = absolute temperature. Linear regression was used to estimate the values of k_0 and E for a specific reaction mixture.

RESULTS AND DISCUSSION

In Fig. 1 the equilibrium P_{CO_2}/P_{CO} values are plotted as a function of temperature for both the Boudouard reaction (reaction 1) and the reduction of cassiterite (reaction 2). Simultaneous equilibrium between SnO_2, Sn and graphite will occur at the intersection of these curves, which is at about 890 K. This means that cassiterite will be reduced by graphite at temperatures higher than 890 K, and the resulting gas will have an average composition between the values for eqns. (1) and (2). The composition will be closer to the value for the reaction which has faster kinetics.

It is clear from Fig. 1 that CO_2 levels for reduction with or without the admixtures lie closer to the CO_2 levels for reaction (2) than those for reaction (1). This indicates that the SnO_2/Sn equilibrium determines the gas composition so that the Boudouard reaction is the slow reaction controlling the overall rate. Padilla and Sohn [3] observed similar results for the system with no admixtures present. The different admixtures do not produce significantly different P_{CO_2}/P_{CO} values. It appears as if most admixtures shift the gas composition slightly towards the Boudouard equilibrium, with tin metal exerting the greatest and K_2CO_3 exerting the second greatest influence. These admixtures may act as catalysts for the Boudouard reaction and thereby increase the CO levels of the gas. Similar behaviour was observed in the catalysis of the carbothermic reduction of haematite [4,5] and manganosite [7]. The fact that the P_{CO_2}/P_{CO} levels for the case with no

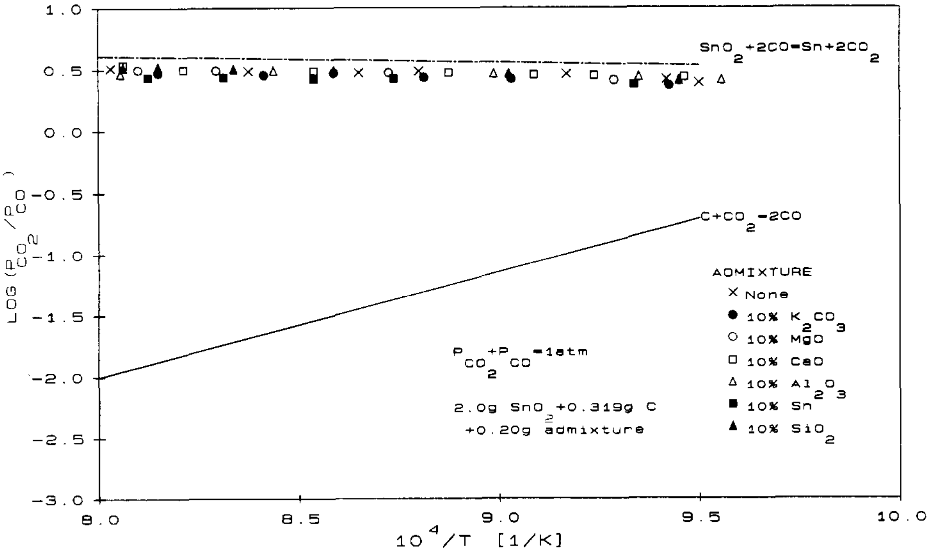

Fig. 1. Observed values of P_{CO_2}/P_{CO} ratios compared with equilibrium values for the reduction of cassiterite by graphite (ref. 10).

admixtures present lie below those for the SnO_2/Sn equilibrium, may point to the catalysis of the Boudouard reaction by the tin metal which forms as product.

In an earlier paper [7], it was observed that the admixtures MgO, CaO, SiO_2, Al_2O_3 and K_2CO_3 all accelerated the gasification of graphite by CO_2. Whereas the catalytic influence of K_2CO_3 and Na_2CO_3 on the gasification of carbon has been researched thoroughly, little information exists regarding the effects of CaO, MgO, Al_2O_3 and SiO_2 on the Boudouard reaction. Furimsky [11] established that Ca, Mg, Ba and Sr in a lignite catalysed the steam gasification reaction, while Otto et al. [12] noticed that Fe, Ca, Si, Al, K and S in lignite ash catalysed the steam gasification of graphite. McKee [13] surmised that stable oxides such as Al_2O_3 and SiO_2 would not catalyse the oxidation of carbon, but gave no data in support of his argument. Turkdogan and Vinters [14] observed that iron catalysed the oxidation of graphite when iron was impregnated in graphite.

Figures 2–7 show the effects of different quantities of tin metal, MgO, CaO, SiO_2, Al_2O_3 and K_2CO_3 on the kinetics of the reduction of cassiterite by graphite. Except for MgO which shows a slightly negative kinetic influence, all the other admixtures enhanced the reduction kinetics. The admixtures Sn, CaO and K_2CO_3 also tend to increase the maximum conversion attainable. With the activity of the admixtures increasing in the order: MgO < no admixture < SiO_2 < Al_2O_3 < Sn < CaO < K_2CO_3, it is clear that no relationship could be established between the stability of an oxide and its activity.

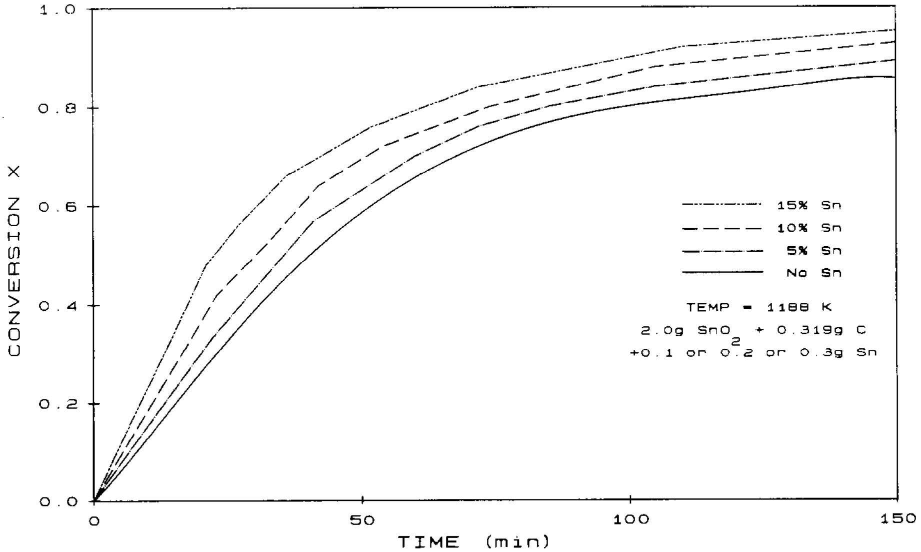

Fig. 2. The effect of admixtures of tin metal on the reduction of cassiterite by graphite.

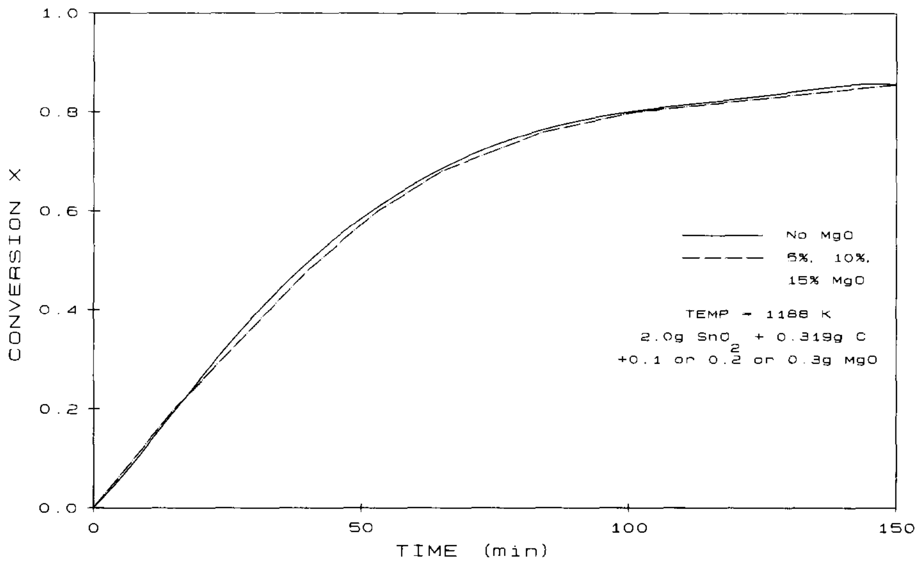

Fig. 3. The effect of admixtures of MgO on the reduction of cassiterite by graphite.

X-ray diffraction of the solid products obtained after 100 min of reduction revealed cassiterite, tin metal, graphite and the respective admixtures. No reactions were indicated between the cassiterite and MgO, SiO_2, Al_2O_3 or K_2CO_3. However, CaO was shown to react with the cassiterite to form $2CaO \cdot SnO_2$. Carbides could not be detected in any of the solid products.

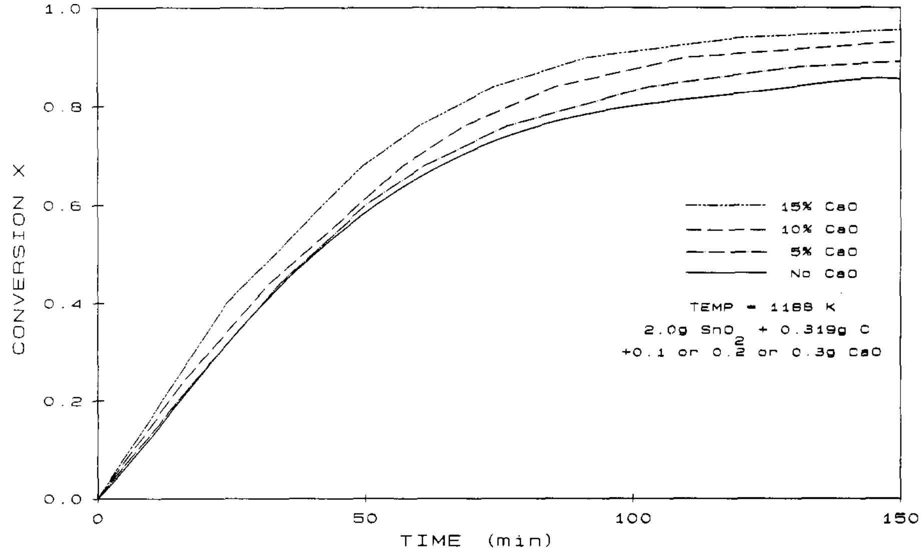

Fig. 4. The effect of admixtures of CaO on the reduction of cassiterite by graphite.

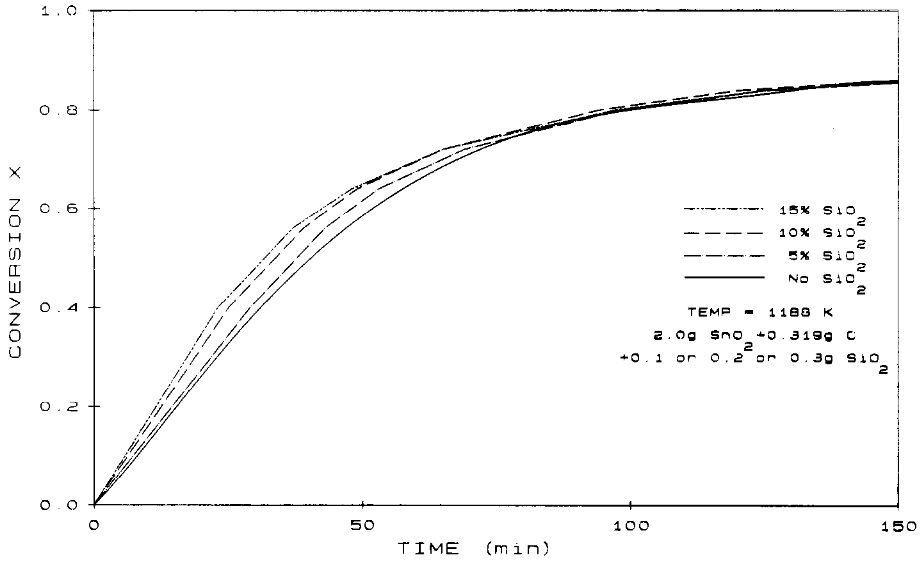

Fig. 5. The effect of admixtures of SiO_2 on the reduction of cassiterite by graphite.

No conclusive evidence exists that these admixtures influence reaction (2). As these admixtures all catalyse reaction (1), such influence on reaction (2) could not be excluded, especially in the case of MgO. Although some interaction between CaO and SnO_2 was observed, this did not seem to decrease the catalytic effect of CaO on the Boudouard reaction.

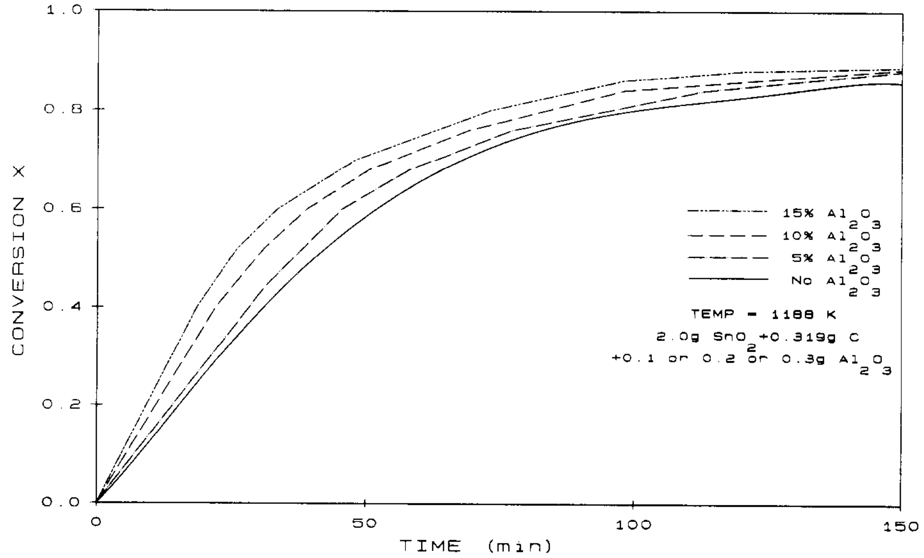

Fig. 6. The effect of admixtures of Al_2O_3 on the reduction of cassiterite by graphite.

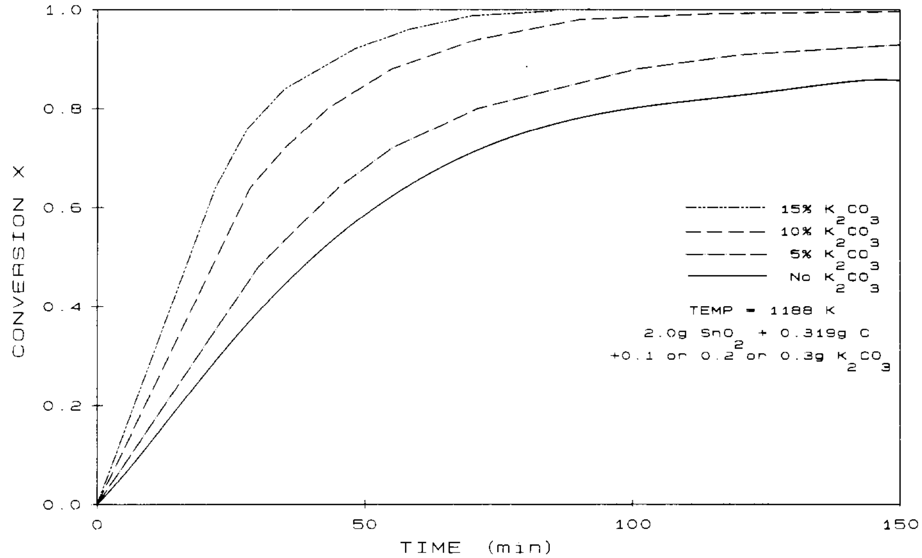

Fig. 7. The effect of admixtures of K_2CO_3 on the reduction of cassiterite by graphite.

An attempt was made to fit a first-order kinetic model, a shrinking core reaction controlling model and a product layer diffusion controlling model [15] to the data of Figs. 2 to 7, but without any success. Padilla and Sohn [3] could fit most of their data by a simple first-order model, but could not produce an acceptable fit when too much tin metal was present. This means

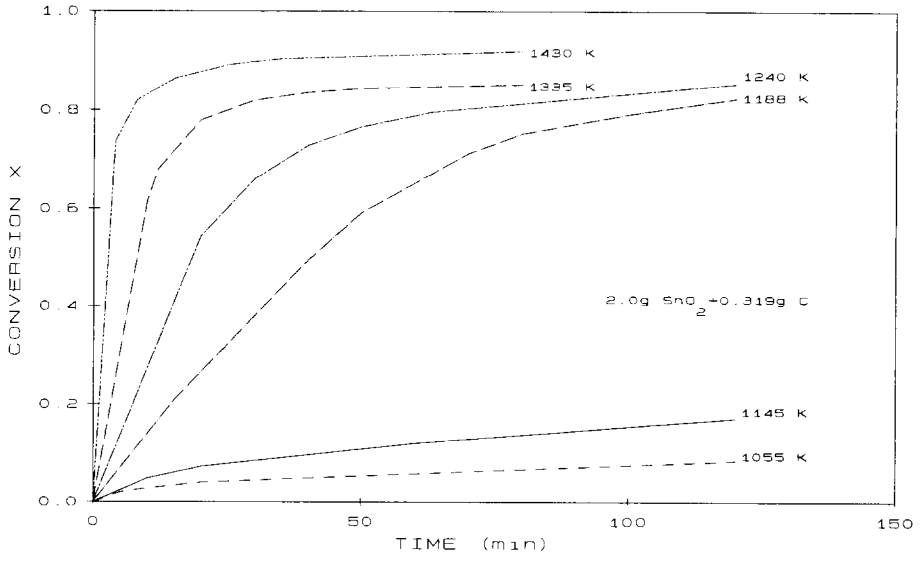

Fig. 8. Reduction of cassiterite by graphite at different constant temperatures.

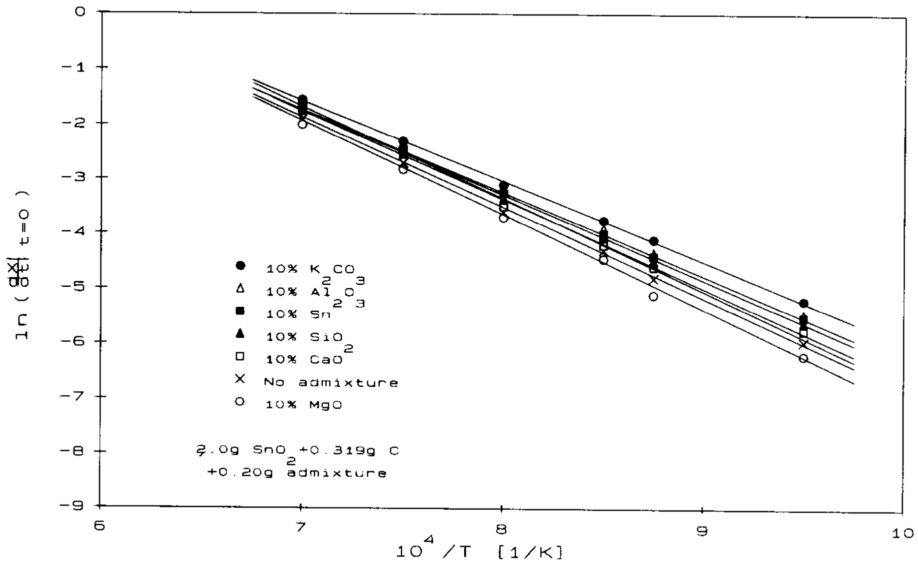

Fig. 9. Arrhenius plot of the rate of reduction of cassiterite by graphite with different admixtures present.

that the reduction reaction under the influence of admixtures does not proceed by a simple mechanism.

Figure 8 shows the effect of temperature on the reduction of SnO_2 when no admixtures are present. Similar data have been measured with 10 mass% admixtures present, and are shown here in the form of an Arrhenius plot in Fig. 9. The respective activation energies derived from Fig. 9 are shown in Table 1. It is clear that the admixtures, except for MgO, decrease the activation energy of reduction. Similar behaviour was observed in the reduction of haematite [5], where it was shown that the activation energy of reduction is considerably lower than that for the corresponding gasification reaction. The value of 140 kJ mol^{-1} for reduction of cassiterite with no admixtures present is of the same order of magnitude as the 156 kJ mol^{-1} measured for the reduction of haematite by graphite [5].

TABLE 1

Activation energies of the reduction of cassiterite by graphite with 10 mass% admixtures present

Admixture	K_2CO_3	Al_2O_3	Sn	SiO_2	CaO	None	MgO
Activation energy (kJ mol^{-1})	125	129	131	134	142	140	145

CONCLUSIONS

Admixtures of K_2CO_3, SiO_2, Al_2O_3, CaO or tin metal all accelerate the reduction of cassiterite by graphite. Tin metal, CaO and K_2CO_3 also tend to increase the maximum conversion attainable. All these admixtures decreased the activation energy for the reduction reaction, possibly due to their catalysis of the Boudouard reaction. However, MgO was shown to increase the activation energy for reduction. Although MgO catalyses the Boudouard reaction positively, it had almost no effect on the reduction of cassiterite. It was shown that the SnO_2/Sn equilibrium determined the P_{CO_2}/P_{CO} value of the product gas so that the Boudouard reaction is the slow reaction controlling the overall rate. Tin metal and K_2CO_3 tended to increase the CO levels of the gas. Whereas CaO reacted to form $2CaO \cdot SnO_2$, the admixtures K_2CO_3, SiO_2, Al_2O_3 and MgO revealed no reaction with the cassiterite or any other species present.

ACKNOWLEDGEMENTS

This work was financed by the Research Fund of the University of Stellenbosch. The technical assistance of Mr. D.N.E. Smit is gratefully acknowledged. The author thanks the Department of Geology at the University of Stellenbosch for permission to use their X-ray diffractometer.

REFERENCES

1 L.M. Falcon, J. S. Afr. Inst. Min. Metall., 82 (1982) 112.
2 L.M. Falcon, J. S. Afr. Inst. Min. Metall., 85 (1985) 333.
3 R. Padilla and H.Y. Sohn, Metall. Trans. B, 10B (1979) 109.
4 T. Szendrei and P.C. van Berge, Thermochim. Acta, 44 (1981) 11.
5 J.S.J. van Deventer and P.R. Visser, Thermochim. Acta, 111 (1987) 89.
6 I.J. Lin and Y.K. Rao, Trans. Inst. Min. Metall., 84 (1975) C76.
7 J.S.J. van Deventer, Thermochim. Acta, 112 (1987) 365.
8 J. Szekely, J.W. Evans and H.Y. Sohn, Gas–Solid Reactions, Academic Press, New York, 1976, p. 179.
9 W.J. Rankin and J.S.J. van Deventer, J. S. Afr. Inst. Min. Metall, 80 (1980) 239.
10 O. Kubaschewski and C.B. Alcock, Metallurgical Thermochemistry, 5th edn., Pergamon Press, Oxford, 1979, p. 449.
11 E. Furimsky, Can. J. Chem. Eng., 64 (1986) 293.
12 K. Otto, L. Bartosiewicz and M. Shelef, Fuel, 58 (1979) 85.
13 D.W. McKee, Fuel, 62 (1983) 170.
14 E.T. Turkdogan and J.V. Vinters, Carbon, 10 (1972) 97.
15 O. Levenspiel, Chemical Reaction Engineering, Wiley, New York, 1972.