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Reduction of tungsten oxides with carbon. Part 2. Tube furnace experiments[1]

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Abstract

Further information on the kinetics and mechanism of the reduction of WO_3 with carbon (in the form of graphite and of lamp black), complementing the results obtained in Part 1 using isothermal thermogravimetry in the temperature range 935–1100°C, was obtained using larger sample masses (up to 5 g) heated isothermally in flowing argon in a tube furnace (935–1060°C). The amounts of CO and CO_2 in the evolved gas were determined using infrared gas detectors.

Results obtained supported the proposed two-stage reduction to W metal, via WO_2. The rate of reduction was influenced by the flow rate of argon, the CO/CO_2 ratio in the product gases, the form of the carbon used, and the WO_3/carbon ratio.

From kinetic data obtained from tube furnace experiments, an activation energy of $374 \pm 2\,\text{kJ mol}^{-1}$ was calculated for the diffusion-controlled first stage of the reduction with graphite. Lamp black was less reactive than graphite at the temperatures studied. Activation energies of $386 \pm 9\,\text{kJ mol}^{-1}$ and $465\,\text{kJ mol}^{-1}$ were calculated from TG experiments for the reduction with graphite and lamp black, respectively.

The gravimetric measurements from the tube furnace experiments were insufficient to analyse the kinetics of the second stage of reaction.

Keywords: Kinetics; Reduction; WO_3; Carbon

1. Introduction

Part 1 of this study [1] dealt with the kinetics of reduction of tungsten oxides by carbon, using results obtained from thermal analyses. This paper deals with further

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[1] Dedicated to Takeo Ozawa on the Occasion of his 65th Birthday.

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aspects of the kinetics of reduction of tungsten oxides by carbon using samples of larger mass heated in a tube furnace system (see below). In further papers, the reduction by hydrogen alone, and simultaneously by hydrogen and carbon [2] are reported. Reduction by carbon monoxide was also studied [3], since this is a likely intermediate in the reaction involving carbon.

2. Experimental

2.1. Materials

These were as before [1], namely: WO_3 (98% pure, Saarchem, 53–75 μm mesh); graphite ($< 53\,\mu$m mesh) and lamp black (both 99% pure, Saarchem); WO_2 was prepared by reducing WO_3 at 800°C under hydrogen which had been bubbled through water. $W_{18}O_{49}$ was prepared in a similar manner at 700°C. High purity argon and hydrogen were supplied by Fedgas. Both gases contained less than 3.0 vpm O_2 and 2.0 vpm H_2O.

Weighed samples of tungsten oxides and graphite or lamp black were mixed by tumbling for 18 h.

2.2. Tube furnace and gas detection system

Reactions of larger masses (0.25–5.0 g) of samples were studied in a Carbolite MTF 12/38B tube furnace, which had a maximum temperature of 1200°C. Weighed samples were placed in a porcelain boat at a fixed position in a stainless-steel reaction tube, which was positioned in the furnace and connected to the gas supply (argon). The temperature in the reaction tube was approximately constant (± 5°C) at the position of the sample. Flexible tubing on both sides of the reaction tube allowed the tube to be rapidly inserted into or removed from the furnace.

The exhaust gas from the reaction tube was passed through a filter and a digital flowmeter then via a heated line to a Servomex MK158 thermal conductivity detector (TCD) maintained at 150°C. After the TCD, the sample gas passed through separate infrared CO_2 and CO detectors (Edinburgh Sensors).

3. Results and discussion

Mixtures of WO_3 and graphite in a 1:4 mole ratio were reacted in the tube furnace system at 935, 960, 985, 1010, 1035, and 1060°C in a stream of argon flowing at 100 ml min^{-1}. As with the TG experiments [1], the final mass loss for complete reaction varied between 23.6 and 30.0%, depending on the relative amounts of CO_2 and CO formed. The CO_2/CO ratio was determined by the rate of the reaction

$$C(s) + CO_2(g) \rightarrow 2\,CO(g) \tag{1}$$

over the course of the entire process. A high reaction rate favours CO formation and hence a greater mass loss.

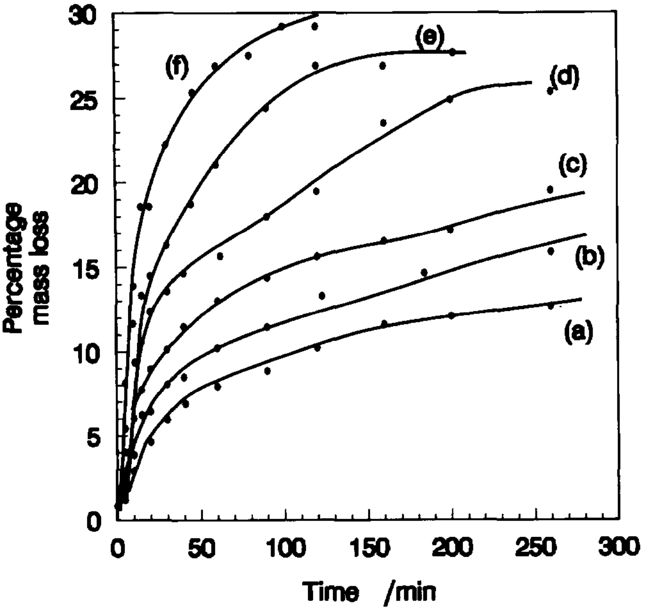

Fig. 1. The percentage mass lost by mixtures of WO_3 and graphite in a 1:4 mole ratio as a function of time when reacted in the tube furnace system at (a) 935, (b) 960, (c) 985, (d) 1010, (e) 1035 and (f) 1060°C in a stream of argon flowing at 100 ml min^{-1}.

The percentage mass lost as a function of time at the temperatures investigated is shown in Fig. 1.

At temperatures below 1000°C, the mass loss was slow and well below the mass loss expected for complete reaction. At and above 1000°C, however, the mass eventually becomes constant, indicating that the process is complete. As would be expected, the mass loss at the end of the process also increases with temperature because reaction (1) is very dependent on the temperature. Thus, at higher temperatures CO_2 will react more rapidly with graphite, resulting in a higher ratio of CO to CO_2. The mass losses at the end of the process are listed in Table 1.

The rate of mass loss is high initially, but decreases considerably after a mass loss of between 8 and 18%. The mass loss corresponding to the change in reaction rate falls broadly in the range in which the formation of WO_2 would occur (7.9–10.0% mass loss). The higher mass losses observed at higher temperatures suggest that the first stage of reaction may also include some reduction to tungsten.

The products at various times during the reaction at 935, 985, and 1035°C were analysed using XRD, and are listed in Table 2. Some W_2C may have formed in small quantities, but this phase could not be conclusively identified. Unlike during the reduction with CO [3], no WC was formed during the reaction with carbon.

The mass loss curves indicate that considerable amounts of α-W are formed in the first stage of reduction. Similar results have been obtained in the reduction with

Table 1
The mass losses at various temperatures for complete reaction of WO_3 with graphite in a 1:4 mole ratio and in a stream of argon flowing at 100 ml min^{-1}

Temperature/°C	Mass loss for complete reaction/%
935	Incomplete
960	Incomplete
985	Incomplete
1010	25.4
1035	27.7
1060	29.2

Table 2
Phases identified at different times in the reduction of WO_3 with graphite at 935, 985, and 1010°C

Time/min	Mass lost/%	Phases identified
935°C		
5	1.2	Mostly WO_3; small amounts of $W_{20}O_{58}$
10	2.8	Mostly $W_{20}O_{58}$; small amounts of $W_{18}O_{49}$
40	6.5	$W_{18}O_{49}$; α-W; small amounts of WO_2
160	11.5	α-W; WO_2; small amounts of $W_{18}O_{49}$
985°C		
5	2.5	Mostly $W_{20}O_{58}$; possibly $W_{18}O_{49}$ and WO_3
10	6.0	$W_{18}O_{49}$; α-W; small amounts of WO_2
20	9.0	α-W; WO_2; $W_{18}O_{49}$
40	11.4	α-W; WO_2; small amounts of $W_{18}O_{49}$
260	19.5	Mostly α-W; small amounts of WO_2
1035°C		
5	5.4	$W_{18}O_{49}$; α-W; small amounts of WO_2
10	11.6	α-W; WO_2; small amounts of $W_{18}O_{49}$
30	16.2	α-W; WO_2
60	21.0	α-W; WO_2
120	26.8	Mostly α-W; small amounts of WO_2

hydrogen [4], and were attributed to the relatively high reactivity of $W_{18}O_{49}$. The extent to which $W_{18}O_{49}$ is reduced directly to α-W is probably related to the CO/CO_2 ratio, as has been discussed [1].

The second stage of the reduction appears to be solely associated with the reduction of WO_2 to α-W, and occurs very slowly. Similar observations have been made in the reduction with hydrogen [4] and indicate that WO_2 is relatively unreactive compared to other tungsten oxides.

3.1. Effect of the flowrate

The flowrate of inert gas affects the concentration of gaseous species in the system, which may in turn influence the reaction rate. If the reaction occurs between two solids and forms a gaseous product, then higher flowrates will tend to increase the reaction rate by minimising the reverse reaction. On the other hand, if the solids react via intermediate gases, then the overall reaction rate depends on how the rates of the two gas–solid reactions in the system are affected by the concentrations of the different gaseous species.

Experiments were performed at 985°C and at flowrates of 25, 50, 100, and 150 ml min^{-1}. The mass loss curves (Fig. 2) show that decreasing the flowrate results in a large increase in the mass lost during the reaction. The mass loss curves at 100 and 150 ml min^{-1} are very similar and it appears that increasing the flowrate above 100 ml min^{-1} has little effect on the reaction rate. Thus, maximum flushing of the sample is achieved at about 100 ml min^{-1}, and the concentrations of CO_2 and CO in the system are not significantly affected at higher flowrates.

Below 100 ml min^{-1}, the rate of reduction and the total mass loss which occurs during reduction increase with decreasing flowrate. The reduction rate is increased over both stages of the reduction, although the start of reaction is somewhat delayed at lower flowrates. This delay may be caused by an initially oxidising atmosphere, possibly from the transformation of WO_3 to $W_{20}O_{58}$. The calculated CO/CO_2

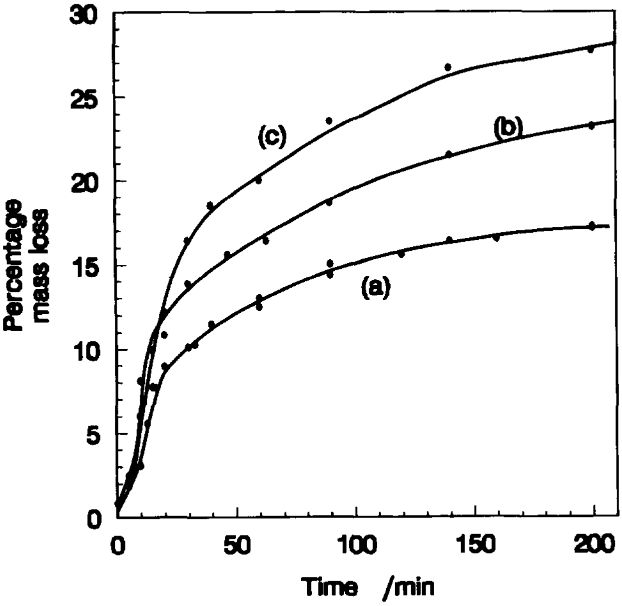

Fig. 2. Mass loss curves of mixtures of WO_3 and graphite in a 1:4 mole ratio at 985°C and at flowrates of (a) 100 and 150, (b) 50 and (c) 25 ml min^{-1}.

equilibrium ratio for this transformation is very low; thus, this reaction may proceed even when the CO_2 partial pressure in the sample is too high for other reductions to occur. If this is so, a slower flowrate will prolong the oxidising conditions and hence result in a lower rate of mass loss.

The increased mass loss at lower flowrates proves conclusively that the reaction is not predominantly a solid–solid reaction. As has been found for the reduction of other metal oxides with carbon, the reduction almost certainly proceeds via reaction with CO formed in reaction (1). The reduction process thus proceeds via two simultaneous gas–solid reactions. The possibility of a contribution from a solid–solid reaction between the tungsten oxides and graphite cannot be excluded.

The final mass loss is also significantly higher at low flowrates, which means that more CO is formed at lower flowrates forming a more reducing atmosphere.

3.2. *Effect of the stoichiometry of the mixture*

Mixtures of WO_3 and graphite of 1:2 and 1:8 mole ratio were compared to the standard mixture (1:4 mole ratio) at 985°C and 100 ml min^{-1}. Sample masses were the same as used in other experiments, but, compared to the standard mixtures, the sample volumes were 20% larger for the 1:8 mole ratio mixtures and 12% smaller for the 1:2 mole ratio mixtures. This may alter the efficiency of flushing of the samples slightly and hence affect the final CO/CO_2 ratio. Fig. 3 shows the percentage mass loss curves as functions of time.

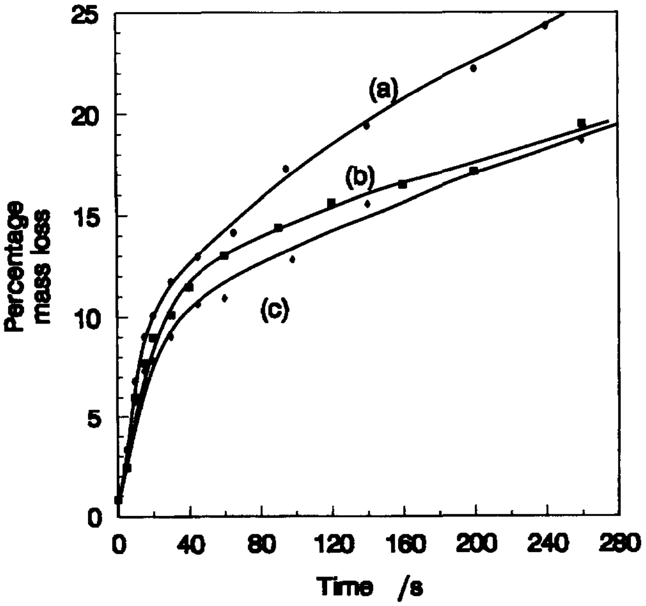

Fig. 3. The mass loss curves for WO_3/graphite mixtures at 985°C, at mole ratios of (a) 1:8, (b) 1:4, and (c) 1:2.

Table 3
The calculated final mass losses of WO_3/graphite mixtures in different stoichiometric proportions

Gas produced	Ratio of WO_3 to graphite 1:2 moles	 1:4 moles	 1:8 moles
CO only	21.9% (incomplete)	30.0%	25.6%
CO_2 only	25.8%	23.6%	20.1%

As would be expected, the final mass losses of the different mixtures vary with the amount of carbon present. Thus the extent to which the reactions are complete, assuming that all the oxygen in WO_3 was removed as CO, is compared in Table 3. Increasing the amount of graphite in the system results in a final mass loss which is closer to the maximum mass loss attainable.

3.3. *Evolved gas analysis*

The influences of the temperature, stoichiometry, and flowrate on the gases evolved from the reduction were studied using the TCD and infrared detectors described above.

The reaction at 935°C clearly shows three peaks in the CO_2 evolution trace (Fig. 4). Each succeeding peak shows a lower rate of CO_2 evolution, but increases in duration

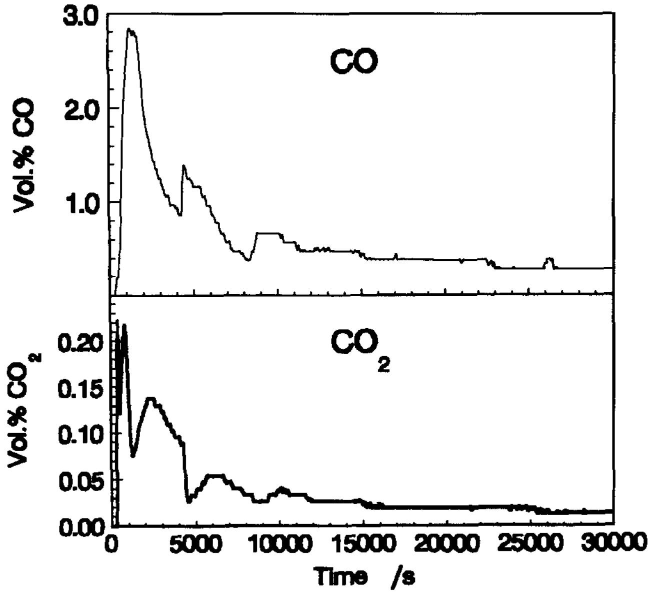

Fig. 4. The CO and CO_2 concentrations during the reduction of WO_3 with graphite (1:4 mole ratio) at 935°C (in argon flowing at 100 ml min^{-1}).

and in the total amount of CO_2 formed. After the third peak, the concentration of CO_2 drops considerably, and then decreases very slowly as the reaction progresses. The CO concentration in the system shows only one large peak which occurs simultaneously with the three peaks in the CO_2 trace. The CO evolution then tapers off to a slow rate, as in the evolution of CO_2. The peaks for the evolution of CO_2 indicate discrete steps in the reduction of WO_3. The size and order of occurrence of these peaks suggest the reduction sequence

$$WO_3 \rightarrow W_{20}O_{58} \rightarrow W_{18}O_{49} \rightarrow WO_2$$

which agrees with the XRD analysis of the sample.

It seems unlikely that direct reduction between two solids could effect a sequential reduction in which one phase is almost completely reduced to the next lower oxide before reduction of the lower oxide can take place. Direct interaction between solids must necessarily be localised at points of contact and thereafter occurs by diffusion or surface migration. Such a mechanism is unlikely to result in a sequential reduction, and thus the sequential nature of the reduction is further evidence for reaction taking place via intermediate gases.

In contrast to the CO_2 concentration, the single CO peak indicates that the rate of reaction (1) is relatively insensitive to the WO_3 reduction sequence, even though the concentration of CO_2 in the system undoubtedly influences the reaction rate [1].

The CO and CO_2 traces for the reaction at 985°C had the same general features as at 935°C, although the relative sizes of the peaks in the CO_2 trace had changed and are less distinguishable. At 1035°C, both CO and CO_2 concentrations exceeded the range of the detectors during the first part of the reduction.

Decreasing the flowrate at 985°C to 50 ml min^{-1} also resulted in the CO and CO_2 concentrations exceeding the limits of the detectors, and the resultant curves were similar in form to those at 1035°C. At low flowrates, conditions in the powder layer are initially oxidising and the CO concentration takes some time to reach reasonable levels. This is probably, related to the formation $W_{20}O_{58}$, which can be formed under quite oxidising conditions, e.g. the CO/CO_2 equilibrium ratio is about 0.01 at 900°C, and explains the observed delay in the start of the reaction at 50 and 25 ml min^{-1}.

The evolved gas measurements showed that different stoichiometries change the reaction path by affecting the CO/CO_2 ratio in the system. The size and duration of the CO peaks increased with increasing amounts of graphite in the system. Compared with the CO_2 peaks, the duration of the CO peak was shorter for a 1:2 mole ratio, approximately equal for a 1:4 mole ratio, and considerably longer for a 1:8 mole ratio.

3.4. Morphological studies

The morphological changes observed in the reaction between WO_3 and graphite were very similar to those observed when CO was the reducing agent [3]. The shape of the original WO_3 particles was retained during the reduction but became porous as the molar volumes of the phases decreased. Needle-like crystallites characteristic of $W_{18}O_{49}$ were observed after reduction for 10 min at 935°C. The lengths and diameters of the needles increased as the reaction progressed, and they also protruded more from the surface, with considerable intergrowth. After reduction for 120 min, the needles on the surface of the pseudomorphs slowly disintegrated into small spherical and irregular particles of less than 1 μm.

A similar morphological pattern was observed at 985°C, with needles observed after 10 min of reduction. Crystal intergrowth was already visible at this early stage. After 20 min, it was apparent that tungsten or tungsten oxide was migrating onto the surface of graphite particles with which it was in contact.

A sample of WO_3 investigated after reduction at 1035°C for 180 min (at which time the reaction was effectively complete), showed the presence of tightly packed clusters of crystals, presumably tungsten. The size of particles in these clusters varied considerably.

Tungsten or tungsten oxides seem to form a thin layer on the surface of the graphite particles, which spreads over the whole graphite surface. This phenomenon was also observed at 985°C, and its appearance is strongly indicative of surface diffusion. Impurities in the sample which might form a tungstate melt [5], or diffuse on the surface of tungsten [6], are a possible explanation for the observed effect. Enhanced diffusion also explains the large differences in particle sizes that were observed in the reduction in the TG. Evidence for the presence of significant impurities is that small indentations in the surface of tungsten crystals were observed; such holes have been associated with the presence of impurities [7].

3.5. *Kinetic analysis*

As in the TG study [1], the extent of reaction α was defined such that $\alpha = 1.00$ at the mass loss corresponding to complete reaction. Below 1010°C, the reaction was incomplete in the time studied, but, by following the trend of decreasing final mass loss with decreasing temperature, the analysis was based on a mass loss of 25.4% for complete reaction. Each isotherm was analysed in two stages. The transition between the first and second stages occurred for α values between 0.30 and 0.50, as is apparent from the change in slope of the $f(\alpha)$ function.

The results from the first stage of reaction indicated that the diffusion models gave a consistently better fit than any of the other models. Among the diffusion models, the D3 and D4 models fitted the data best. The correlation coefficients and rate constants calculated from the D3 and D4 models are listed in Table 4. Fig. 5 shows the fit of the D3 and the D4 model to the experimental curve at 985°C. An Arrhenius plot using the k values for the D4 model gave an activation energy of 374 ± 2 kJ mol^{-1} and a frequency factor of $(3.59 \pm 0.05) \times 10^{12}$ min^{-1}.

The applicability of these models implies that the reaction is limited by diffusion in three dimensions, as was inferred from the TG study [1]. Again, the diffusion referred to is almost certainly diffusion of gases through the pores of the product layer, and not diffusion through the crystal lattice.

A kinetic analysis of the second stage of reaction was also attempted. However, it was apparent that no model fitted the limited amount of experimental data very well, and no model was consistently better than any others.

Table 4
The rate constants and correlation coefficients calculated using the D3 and D4 models for the isothermal experiments

	D3		D4	
Temperature/°C	$k/10^{-3}$ min^{-1}	r^2	$k/10^{-3}$ min^{-1}	r^2
935	0.250	0.9938	0.230	0.9919
960	0.544	0.9682	0.499	0.9660
985	1.15	0.9984	1.04	0.9969
1010	2.40	0.9929	2.06	0.9900
1035	4.55	–	3.98	-

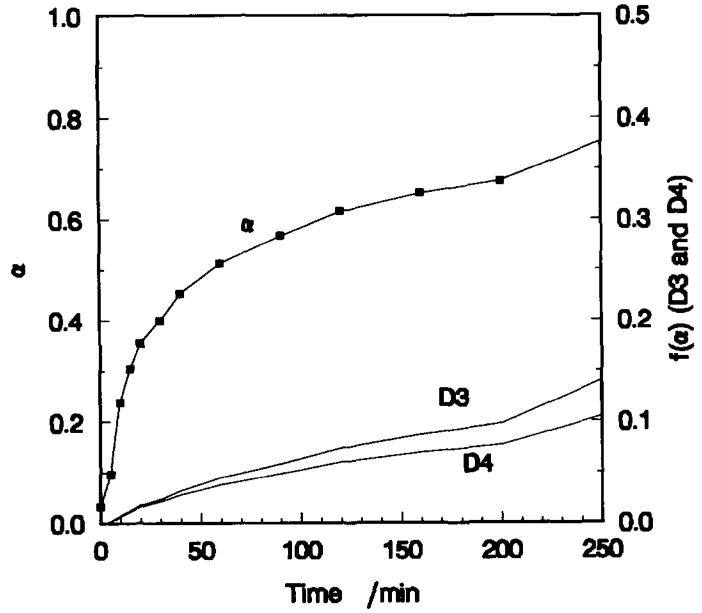

Fig. 5. The fit of the D3 and D4 models to the α,t curve for a WO_3/graphite mixture (1:4 mole ratio) at 985°C.

4. Discussion

The reaction scheme for the reduction of WO_3 with graphite is similar to that for the reduction with CO [3]. The reaction occurs predominantly by gaseous intermediates, which is in accordance with the reduction of other metal oxides with carbon.

Two main complementary experimental techniques were used in the study: thermogravimetry of small samples (less than 50 mg) [1] and tube furnace experiments, coupled with evolved gas analysis, on larger samples (up to 5 g).

The reduction of WO_3 with carbon takes place above 900°C via the formation of CO, and involves two distinct stages. The first stage corresponds approximately to the reduction to WO_2 and is described by the Ginstling–Brounshtein (D4) rate equation, which models a process limited by diffusion in three dimensions. Activation energies of $386 \pm 9\,\mathrm{kJ\,mol^{-1}}$ and $465\,\mathrm{kJ\,mol^{-1}}$ were calculated from TG experiments [1] for the reduction with graphite and lamp black, respectively. From data obtained from tube furnace experiments, an activation energy of $374 \pm 2\,\mathrm{kJ\,mol^{-1}}$ was calculated for the reduction with graphite. Lamp black was less reactive than graphite at the temperatures studied.

The rate of the first stage of the reduction is best described by a diffusion-limited kinetic model, as was also found in the analysis of the data from TG experiments [1]. The diffusion models have often been applicable to the reduction of other metal oxides with carbon. The porous structure of the tungsten oxide pseudomorphs suggests that pore diffusion takes place as opposed to solid state diffusion. Diffusion is probably rate-limiting because the CO/CO_2 ratio in the powder is moderately low. Since the rate of diffusion increases with the concentration gradient of the diffusing species, a small difference between the CO/CO_2 equilibrium ratio for the reaction taking place and the CO/CO_2 ratio in the powder layer will result in a slow rate of diffusion, which may become rate-limiting.

Although the intermediate oxides $W_{20}O_{58}$ and $W_{18}O_{49}$ were identified in the reduction with carbon, the first stage of the process is limited by a physical mechanism which is largely independent of the specific chemical reactions. Consequently, the rate of reaction does not show any features which might be identified with a particular reaction. In the reduction with CO [3], however, the rate of reaction curve does show distinct peaks which were attributed to the formation of particular phases.

The gravimetric measurements from the tube furnace experiments were insufficient to analyse the kinetics of the second stage of reaction. The data from the TG experiments [1] suggested that this part of the process was limited by a first-order rate of reaction, which indicates that the reaction of CO_2 with graphite was probably rate-limiting. The activation energy for this stage was $438\,\mathrm{kJ\,mol^{-1}}$. Many other metal oxide reductions with carbon have also found that this reaction is rate-limiting.

The morphology of the reduction has been described. The retention of the shape of the starting oxide particles (pseudomorphs) throughout the process and the presence of tungsten or tungsten oxide on graphite particles are particularly relevant in relation to the results of Elyutin et al. [8]. In their study of the reduction of WO_3 with lamp black below 700°C, they proposed that tungsten oxides sublimed and reacted on the carbon surface. The results presented in this work, particularly the effect of the flowrate, are consistent with the reduction taking place via CO. Furthermore, tungsten oxides within the pseudomorph are completely reduced by the end of the process. Because the particles within the pseudomorph are not in contact with carbon, the mechanism proposed by Elyutin et al. [8] could not occur in this study. The differences between this work and the work of Elyutin et al. are possibly a result of the different temperature ranges considered (above 900°C in this work, compared to their study of the reaction below 700°C).

The appearance of tungsten and tungsten oxides on the graphite particles indicates that tungsten oxides have considerable mobility and could result from sublimation, which has been reported by Elyutin et al. [8] and Miyake and Haka [9]. The localised sheets of tungsten or tungsten oxides are indicative of surface diffusion, which is enhanced by impurities in the sample, as has been discussed. This high mobility explains the substantial growth of tungsten particles during the reduction process, and also implies that grain growth during hydrogen reduction is partly attributable to the inherent mobility of the tungsten oxides and not just to tungsten transport by the species $WO_2(OH)_2(g)$.

These results differ from those of other workers, who have reported that the reduction takes place by sublimation of tungsten oxides and subsequent reduction on the carbon surface. The results which were obtained and the proposed mechanism are, however, consistent with those of the reductions of other metal oxides with carbon, which usually occur via reduction with CO.

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