Cyclic reduction–oxidation of haematite powders

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The cyclic reduction–oxidation of haematite (Fe_2O_3) powders was investigated over the temperature range 723 to 873 K. The hydrogeon reduction of haematite had an approximate activation energy of 53 KJ mol^{-1}. The air oxidation of the resulting iron gave a product whose composition depended on the thermal history of the sample (number of cycles and temperature). At the lowest cycling temperature (723 K) the primary oxide was Fe_3O_4 and the only influence of cycling was on the relative amount of unreacted iron. At the higher temperatures (798 and 873 K) the primary oxide was Fe_2O_3 at the end of one cycle but changed to Fe_3O_4 for a higher number of cycles. The effect of cycling is explained in terms of sintering during both the reduction and oxidation reactions.

1. Introduction

The role of sintering in chemical reactions has been the focus of several investigations, including studies on oxidation–reduction [1–3] and dissociation reactions [4, 5]. An important aspect of these studies is the effect of oxide surface layers on the sintering of metallic powders. A mathematical analysis has been provided for this [6] and its application to a variety of metallic systems has been provided [7]. In this paper we report the results of the cyclic reduction–oxidation of fine powders of haematite (Fe_2O_3).

Previous studies have dealt with the reduction of haematite in hydrogen. These include the reaction of powders in fluidized-bed reactors [8, 9], the reduction of lumps of iron ore (96% Fe_2O_3) [10], and the reduction of dense thin strips of haematite [11].

2. Experimental materials and methods

The haematite used in this study was obtained from Gallard Schlesinger as 99.999% pure powder. Optical image analysis performed on this powder showed a distribution of sizes between about 0.08 and 4 μm with the largest majority of particles being smaller than 0.4 μm. Surface area (BET) analysis gave a value of 1.469 m^2 g^{-1}, thus indicating that the powder is highly agglomerated. Reduction studies were made in a continuous recording microbalance (Cahn Model 1000) at 723, 798, and 873 K. In each experiment 150.00 mg Fe_2O_3 was placed in an alumina crucible and reduced in a flowing hydrogen gas. The rate of hydrogen flow was maintained at 30 ml min^{-1} throughout the reduction experiments. Oxidation of the products were carried out in air. Further details of the experimental procedures and apparatus used in this study are given in the preceding paper [12].

3. Results

3.1 Reduction behaviour and kinetics

When heated to the desired reduction temperature, the weight of the Fe_2O_3 sample stayed constant until the temperature reached approximately 580 K. Under the constant heating rate of 10 K min^{-1}, the reduction of the haematite samples at the highest temperature, 873 K, was so rapid that the weight had levelled off before the sample reached the nominal reaction temperature. Fig. 1 shows the result of three reductions of Fe_2O_3 at 723 K. The first reduction curve in Fig. 1 represents the weight loss for the as-received sample. The total weight loss measured during this result and all first reductions at all temperatures averaged 45.39 mg with a maximum deviation of only 0.22 mg. This compares very well to the theoretical weight loss of 45.09 mg for the complete reduction of 150.00 mg of pure Fe_2O_3. Because of subsequent oxidations, the second and third reduction curves usually started at lower weight levels. This was because they followed oxidation experiments which were not taken to completion, as shown in Fig. 2. This iron sample, which had been reduced from Fe_2O_3 in the first reduction, was partially re-oxidized in the first oxidation shown in Fig. 2 and had a net weight gain of 39.05 mg. The subsequent second reduction (Fig. 1) exhibited a weight loss of 39.31 mg, which is very close to the amount of weight gained in the first oxidation. This close agreement between oxidation weight gains and the weight losses of subsequent reductions was typical for the cycling experiments. The effect of temperature on the reduction cycles is seen from the results obtained at 798 and 873 K (Figs 3 and 4, respectively).

At the lowest temperature (723 K), the slopes of the reduction curves were very much the same for each successive experiment (see Fig. 1). At the higher temperatures, however, the reduction slope began to exhibit a definite dependence on cycling. At 798 K (Fig. 3), the slope of the second reduction curve was very close to that of the first, but a decrease in the slope was observed in the third curve (see Fig. 3). At the highest temeperature (873 K), the steady-state reduction rate decreased in both the third and the second reductions (see Fig. 4). In fact, at 873 K the
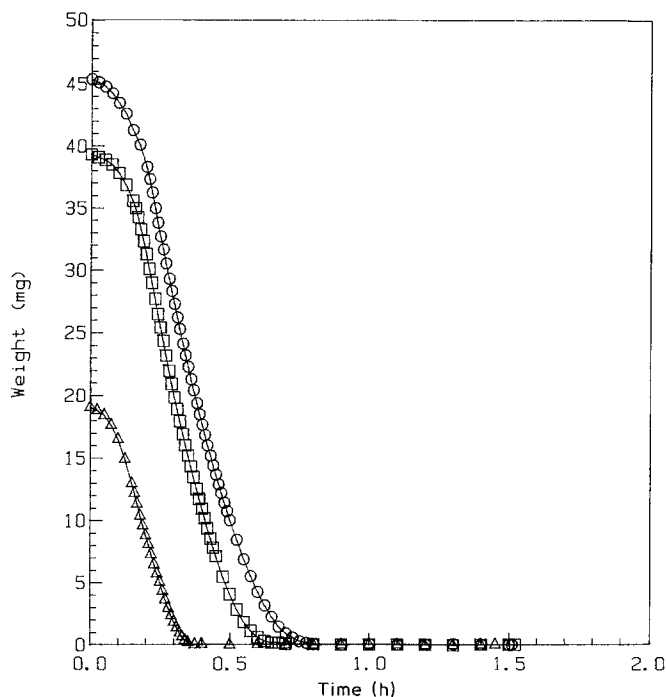
Figure 1 The dependence of the reduction of Fe_2O_3 on cycling (T = 723 K). (O) First reduction, (□) second reduction, (△) third reduction.

third reduction was observed to take almost as much time to complete as the first, although the amount of oxide reduced was only 25.68 mg to 45.41 mg (see Fig. 4).

Two sets of test experiments were performed in which the reduction and oxidation temperatures were not the same. The results of these experiments help separate the effect of powder sintering occurring during oxidation from that taking place during reduction. In the first sample, the reduction temperature was 723 K and the oxidation temperature was 798 K. The results are shown in Fig. 5. In the other test sample, the reduction was again held at 723 K, but the oxidation temperature was increased to 873 K. The results of these three reduction experiments are

plotted in Fig. 6. Each reduction of this second test sample took longer than the previous one. In fact, even though less oxide was being reduced, the third reduction took approximately 25% longer than the first (see Fig. 6).

Because so many data points are plotted closely together on one graph, the slowing of the third reduction is often difficult to discern. A clearer view is obtained by referring to Fig. 7 in which just the 723 K third reduction data have been plotted. The curves represent the third 723 K reduction: (a) following two normal 723 K oxidations; (b) following two 798 K oxidations; and (c) following two 873 K oxidations. The increase in oxidation temperature both increased the amount of oxide formed and decreased
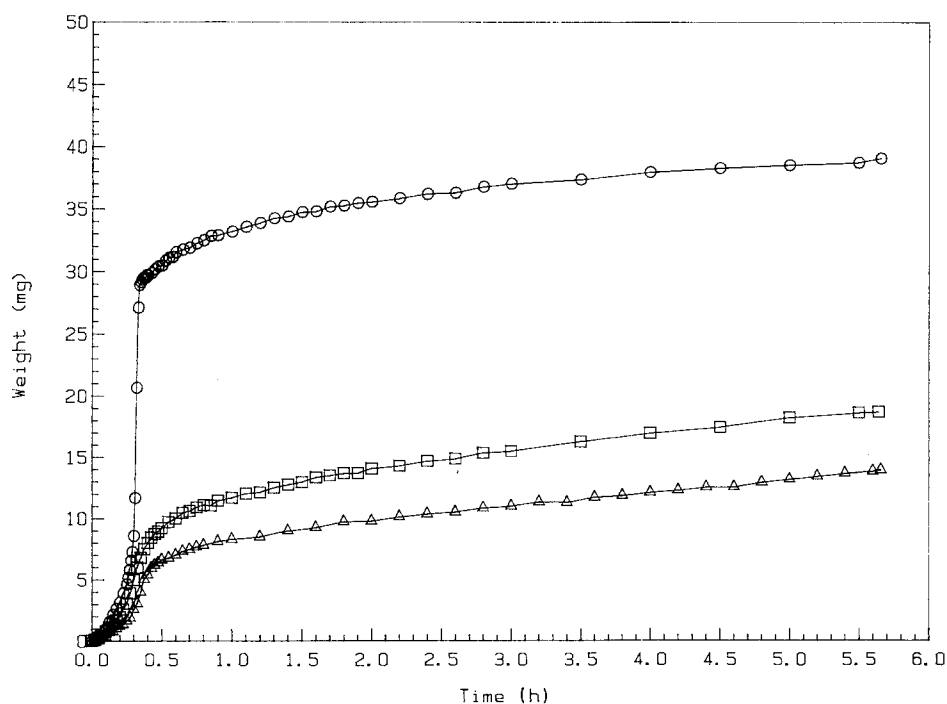

Figure 2 The oxidation of iron resulting from the reduction of Fe_2O_3. The reduction–oxidation cycles at 723 K. (O) First oxidation, (□) second oxidation, (△) third oxidation.
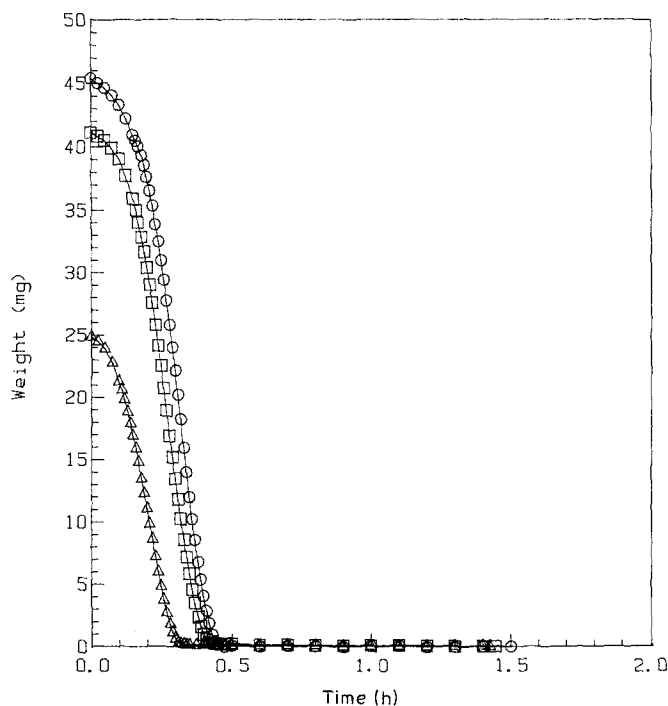
Figure 3 The reduction behaviour of Fe_2O_3 at 798 K. (O) First reduction, (□) second reduction, (△) third reduction.

the reduction rate. The significance of these, as well as the other results, will be discussed in a later section.

As stated earlier, the reduction rates of the Fe_2O_3 were such that at the highest experimental temperature (873 K) the samples were fully reduced before the desired temperature was reached. Therefore, the rates calculated at 873 K do not represent the steady-state rates at that temperature and cannot be used in any kinetic calculations. On the basis of zero-order (linear) kinetics, the steady-state reduction rates for the first reductions were calculated from the weight loss data for the two temperatures, 723 and 798 K. The rates listed in Table I are the average values derived from three different reductions at each temperature, using the tabulated rates and the general expression for the rate constant k
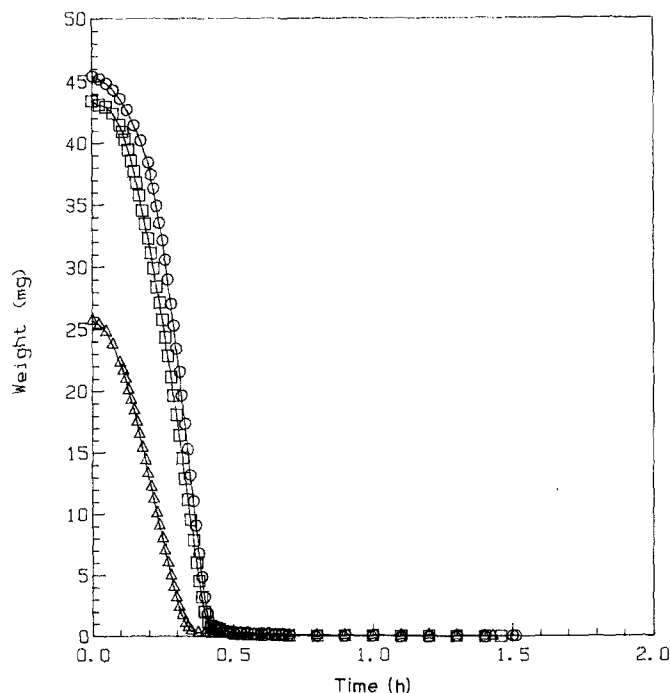
$$k = r/\Delta W_t \qquad (1)$$

where r is the rate and ΔW_t is the theoretical (maximum) weight loss associated with the complete reduction of Fe_2O_3. With two values of k, only an approximate activation energy can be calculated using an Arrhenius dependence of k on temperature. Such a calculation gave a value of $53\,kJ\,mol^{-1}$.

3.2. Oxidation of iron produced by the reaction of Fe_2O_3

As in the case of the reduction experiments, the results of the oxidations were functions of both the temperature and the sample's cycling history. If the initial reduction temperature (and hence sample history) is held constant, the temperature dependence of the oxidation process is easy to determine. Plotted in Fig. 8 are the results of three different first oxidations. All of the samples had been reduced from Fe_2O_3 to iron at 723 K prior to the experiments. The oxidation
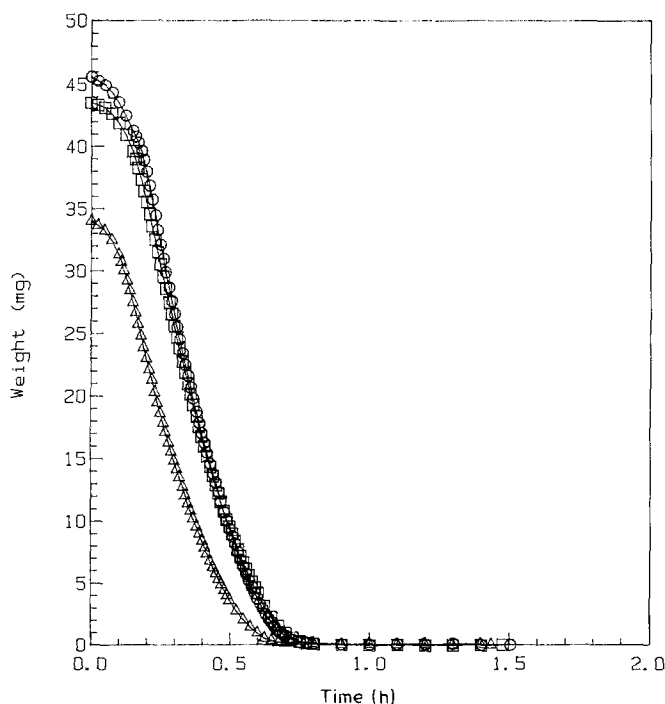

Figure 4 The reduction behaviour of Fe_2O_3 at 873 K. (O) First reduction, (□) second reduction, (△) third reduction.
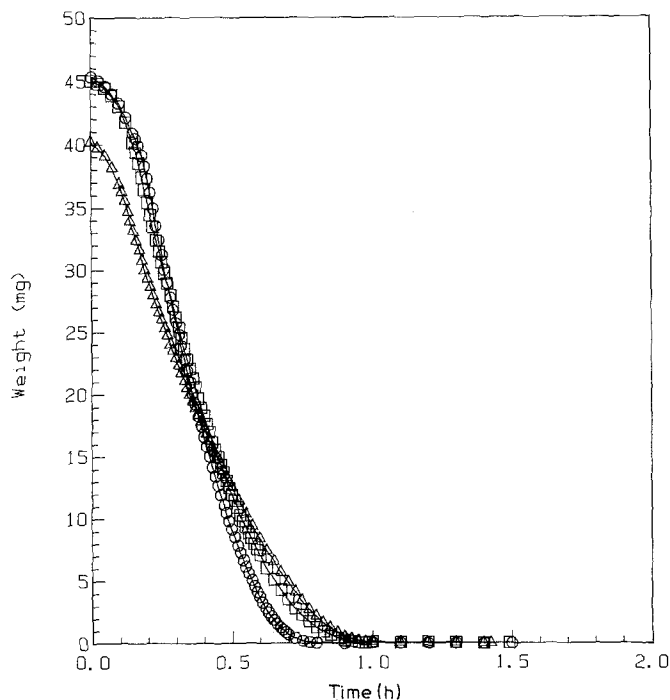
Figure 5 The reduction of Fe_2O_3 powders at 723 K. Intervening oxidations were carried out at 798 K. (O) First reduction, (□) second reduction, (△) third reduction.

process began during the $10 \, K \, min^{-1}$ heating period approximately 0.4 h after the onset of heating. At this time (defined here as time zero), the sample was at a temperature between 480 and 530 K. The rate of oxidation at time zero was high, and increased during the first 0.3 h that followed. At about 0.3 h, the weight began to increase with the rate of over $12.5 \, mg \, min^{-1}$. That is a very high value considering that a weight gain of 45.5 mg corresponds to complete oxidation. At all three temperatures, the oxidation rate decreased suddenly at roughly the same weight value, 30 mg (refer to Fig. 8). At 723 K, the weight rose another 5 mg and then began to level off. At 798 K, the weight increased from approximately 30 to 38 mg between 0.3 and 0.8 h. Beyond 0.8 h, the weight of this sample also levelled off, and it reached a final value of 43.4 mg after 6 h. At the highest temperature (873 K), the rate of weight gain after the 30 mg level increased and was greater than the rates in either of the two lower temperature experiments. This sample reached 95% oxidation only 1.2 h after the onset of oxidation and reached 99% conversion 6 h after the start of heating (see Fig. 8).

When successively cycled in the furnace, the samples formed progressively less and less iron oxide. The results of the normal 723 K oxidation experiments (those in which the reduction and oxidation temperatures were the same) were shown in Fig. 2. Missing in the second oxidation at this temperature was the rapid weight gain seen in the first experiment. Much less oxide was formed during the second oxidation, only 18.7 mg compared to 39.1 mg for the first. The second and third oxidation curves at 723 K more closely resemble typical oxidation results than does the first

TABLE I Rate constants for reductions of Fe_2O_3 powders

T (K)	k ($10^{-2} \, min^{-1}$)
723	3.36
798	7.76

oxidation curve. The decrease in oxidation rates with time was observed to be continuous. There was an acceleration region in the first few minutes of these and all the other oxidation curves because the temperature was still increasing in the early stages of oxidation. In this acceleration region, the rates, as well as the weight levels, decreased with increased cycling.

The cyclic oxidation–reduction at 798 K is shown in Fig. 9. While the second oxidation caused less oxide to form than the first, the difference between the amounts of iron converted in the first two cycles was less dramatic at this temperature than at the lower temperature (compare Figs 2 and 9). The shape of the first oxidation curve was also very different. While the rate of weight gain during the initial stages of the first oxidation was high, no sudden drop in the rate was observed in the experiment (again, compare the first oxidation curves of Figs 2 and 9). In fact, all three oxidation curves were smooth throughout. More oxide was formed during each of the three oxidations than was formed during the corresponding 723 K runs. The initial acceleration region was again observed at 798 K, but unlike the lower temperature experiments, the curves actually overlapped during the first one-third of an hour after beginning of oxidation.

At the highest cycling temperature (873 K), the oxidation behaviour, Fig. 10, was different in many ways from the lower temperature experiments. While more oxide was formed in the first oxidation at 873 K than was formed in the first 798 K oxidation, only about the same amount was formed in the second oxidation. Further, in the third oxidations, less iron was actually converted at 873 K than at either 798 of 723 K (compare Fig. 10 with Figs 2 and 9). Also, the third oxidation at 873 K was very different from the equivalent runs at the two lower temperatures in that during the initial acceleration region, the rate of weight gain was actually higher than that of the second oxidation. The other unusual observation was that after the initial

region, the weight very quickly levelled off, and the sample gained only 1.4 mg in the last 4.5 h of the experiment (Fig. 10).

As mentioned in the previous section, two sets of test experiments were carried out on the Fe_2O_3 samples. In the first, the reduction temperature was 723 K, and the oxidation temperature was 798 K. The results of these first test oxidations (shown in Fig. 11) should be compared to the normal 798 K experiments whose results are displayed in Fig. 9. Decreasing the preceding reduction temperatures led to increased oxidation during all three cycles. In the second set of test cycles, the reduction temperature was again 723 K, but the oxidation temperature had increased to 873 K (Fig. 12). Again the amount of iron converted to oxide was greater during each of the three cycles when compared to the normal experiments (those in which oxidation

and reduction were performed at the same temperature, Fig. 10). The greatest change was observed in the second oxidation, in which almost as much oxide formed during the second cycle as formed during the first (see Fig. 12). In this second oxidation, the rate of weight gain continued to increase for the first 0.7 h, a behaviour not seen before. In the third oxidation, acceleration was also observed, but it was not continuous. For the first 0.5 h, the rate of weight gain increased, then decreased at about 0.5 h, and then increased again. Like the normal third oxidation, the weight levelled off after approximately 1 h, and the sample gained only 1.0 mg in the last 4.0 h at 873 K.

An attempt was made to determine the kinetics of the oxidation of the iron produced by the reduction of Fe_2O_3. On the basis of previous observations on the oxidation of iron foils [13], the process is examined in
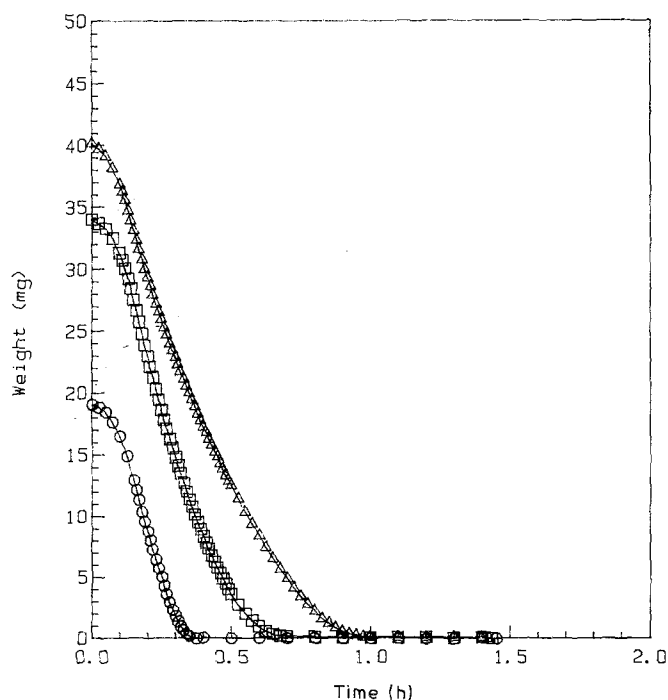

Figure 7 The effect of oxidation temperature on the third reduction (at 723 K) of iron oxide samples: (O) after two 723 K oxidations, (□) after two 798 K oxidations, (△) after two 873 oxidations.
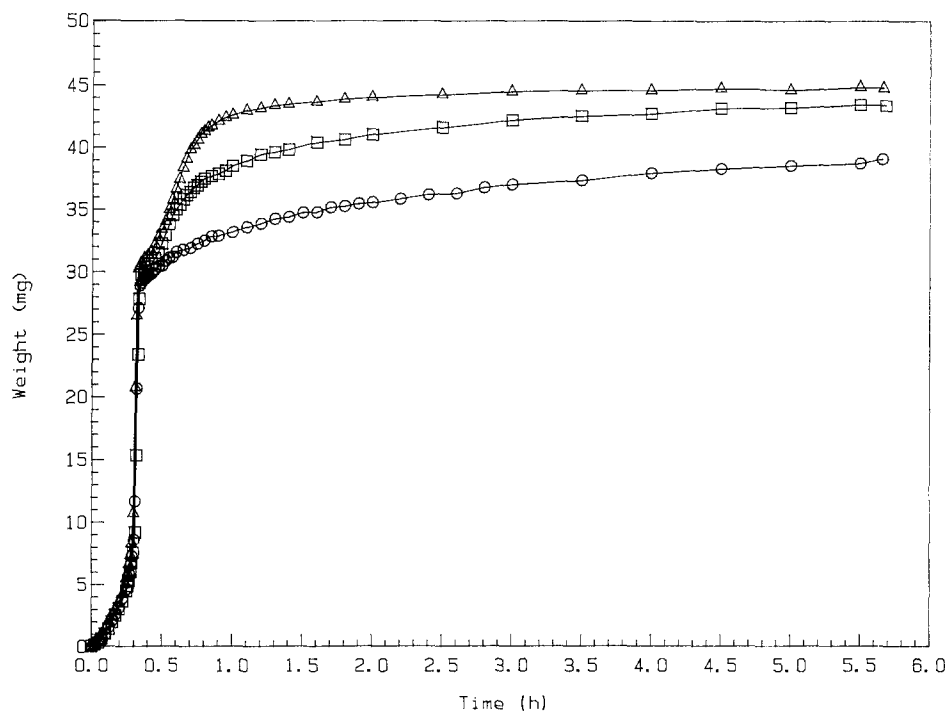
Figure 8 The effect of temperature on the first oxidation of iron samples reduced from Fe_2O_3 at 723 K. Oxidation at (O) 723 K, (□) 798 K, (△) 873 K.

terms of a parabolic oxidation law. However, such examination proved unsuccessful in attributing the experimental observations to a parabolic or any other kinetic law.

3.3. X-ray diffraction analysis

The results of X-ray diffraction analyses are listed in Table II along with sample designations, cycling histories, and surface area values. In this table, the materials detected are listed in decreasing order of concentration. At 723 K, Fe_3O_4 was the primary oxide after one, two and three oxidation cycles. A smaller amount of Fe_2O_3 was also found, however. The only

noticeable effect of cycling was in the relative amount of the unreacted iron. After one cycle, when the weight gain was the highest, the amount of iron left in the sample was extremely small. With further cycling, the amount of iron increased such that it is the most prevalent material in the sample cycled three times. It should be noted, however, that the X-ray determinations are semi-quantitative in nature and were based on a self-consistent method of product identification involving both the measured area of the peaks and number of discernable peaks present.

At 798 K, the relative abundance of Fe_2O_3 and Fe_3O_4 changed during cycling as did the amount of
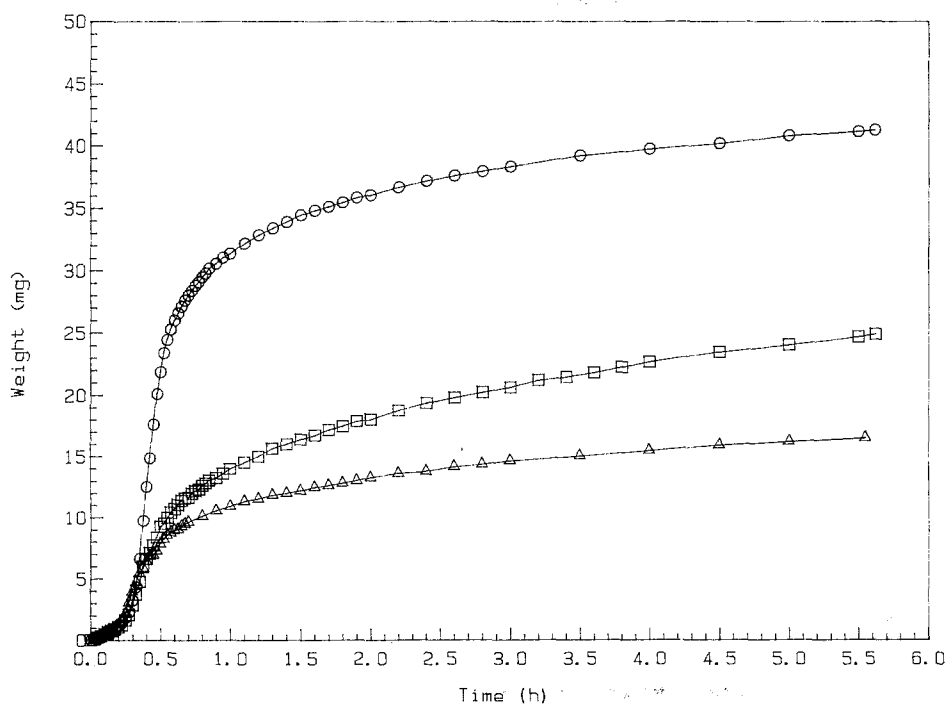

Figure 9 The oxidation behaviour of iron samples cycled three times at 798 K. (O) First oxidation, (□) second oxidation, (△) third oxidation.
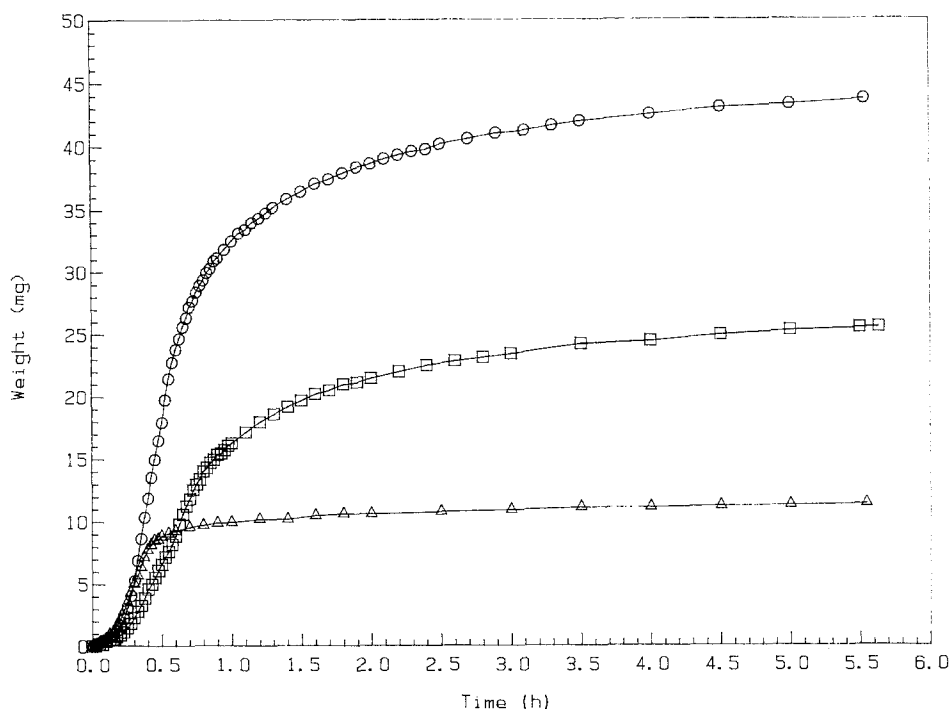
Figure 10 The oxidation behaviour of iron samples cycled three times at 873 K. (O) First oxidation,(□) second oxidation, (△) third oxidation.

iron. In the sample cycled once, Fe_2O_3 was detected as the primary oxide, followed by Fe_3O_4. Although no iron was found in this sample, the next sample, which was cycled twice contained a majority of iron with lesser amounts of Fe_3O_4 and Fe_2O_3. And after three cycles, the sample again contained more Fe_3O_4 than Fe_2O_3, but it appeared that less iron was present than in the sample cycled twice (see Table II). This observation is puzzling because the sample oxidized less than its predecessor.

At the highest temperature (873 K), the sample cycled once contained only Fe_2O_3 with a possible trace

of Fe_3O_4. This is not suprising considering the sample had reached 96% oxidation. After two cycles, however, less Fe_2O_3 was detected than Fe_3O_4, with iron present in even smaller concentrations. In both samples cycled three times, Fe_3O_4 made up the greatest portion of the samples followed by iron and Fe_2O_3. In these two samples and the sample cycled twice, a possible trace of FeO was also detected (see Table II).

The samples employed in the two test experiments were also analysed. In the first sample, which had three 723 K reductions and three 798 K oxidations, both Fe_3O_4 and Fe_2O_3 were present. In addition, a significant amount of unreacted iron was found in the sample, more than there was Fe_2O_3, in fact. In the second sample (reduced at 723 K, oxidized at 873 K), Fe_3O_4 and Fe_2O_3 were the compounds confirmed. Possible traces of both iron and FeO were also detected, however.

TABLE II X-ray diffraction and BET surface area results for Fe_2O_3 samples exposed to varying temperature and cycling conditions*

T (K)	Sample	Sample history	Compounds detected	Surface area $(m^2 g^{-1})$
723	CA	1R 1OX	Fe_3O_4, Fe_2O_3, possibly Fe	0.315
723	CB	2R 2OX	Fe_3O_4, Fe, Fe_2O_3	0.224
723	CE	3R 3OX	Fe, Fe_3O_4, Fe_2O_3	0.250
798	EB	1R 1OX	Fe_2O_3,Fe_3O_4	0.161
798	EA	2R 2OX	Fe, Fe_3O_4, Fe_2O_3	0.178
798	EC	3R 3OX	Fe_3O_4, Fe, Fe_2O_3	0.073
873	DB	1R 1OX	Fe_2O_3, possibly Fe_3O_4	0.124
873	DC	2R 2OX	Fe_3O_4, Fe_2O_3, Fe possibly FeO	0.179
873	DA	3R 3OX	Fe_3O_4, Fe, Fe_2O_3, possibly FeO	0.152
873	DE	3R 3OX	Fe_3O_4, Fe, Fe_2O_3, possibly FeO	0.070
723/798	FB	3R at 723 3OX at 798	Fe_3O_4, Fe, Fe_2O_3	0.039
723/873	FA	3R at 723 3OX at 873	Fe_3O_4, Fe_2O_3 possibly Fe, FeO	0.043

*R and OX refer to reduction and oxidation cycles, for example 1R 1OX signifies one reduction and one oxidation cycle, etc.

3.4. Surface area and microstructural analyses

Surface area measurements, made on each of the experimental samples, are listed in Table II. While some anomalies are observable in the results, there is a general trend of a decrease in surface area with cycling. The sample with the highest surface area was that cycled once at the lowest temperature (723 K). It had a specific surface area of $0.315\,m^2\,g^{-1}$. The lowest surface areas measured in samples used in the test experiments, those in which the reduction temperature was 723 K, and the oxidation temperature was either 798 or 873 K. The surface areas of these samples were 0.039 and $0.043\,m^2\,g^{-1}$ for the 723/798 and 723/873 K samples, respectively. In between these two extremes, the trend was for decreasing surface area with increasing number of cycles and temperature of the reaction.

In an effort to correlate the microstructural changes occurring during cycling with the surface area
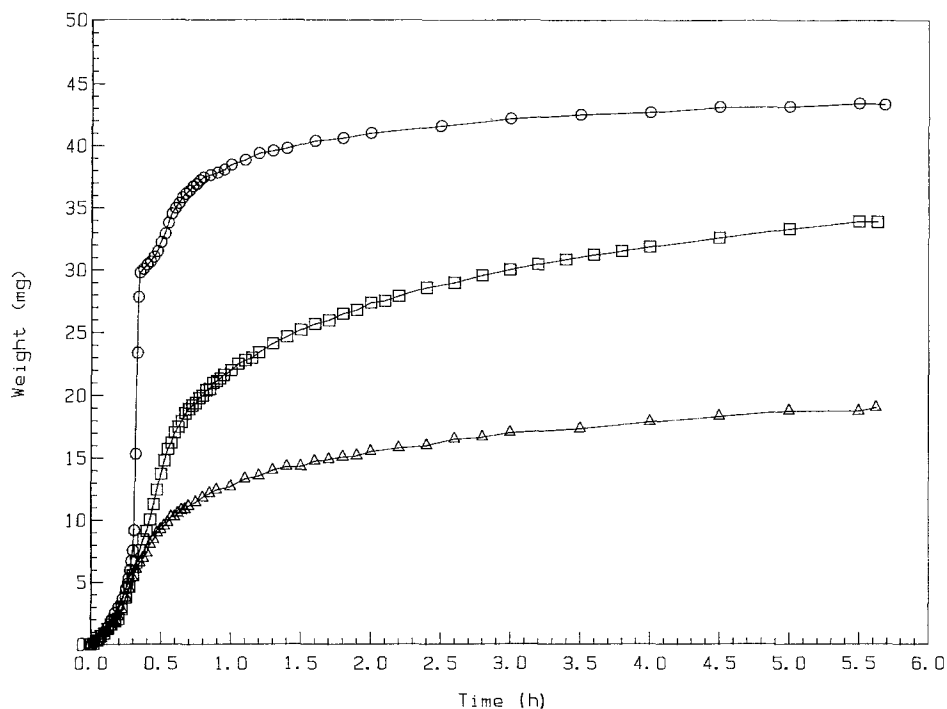
Figure 11 Successive oxidation of iron at 798 K following reduction of the oxide at 723 K. (O) First oxidation, (□) second oxidation, (△) third oxidation.

measurements, key samples were examined using a scanning electron microscope (SEM). The as-received Fe_2O_3 powder was made up of porous columnar grains with many penetrating cracks as seen in Fig. 13. In every cycled sample examined, evidence of sintering was found. The micrographs in Fig. 14 show the structure of a sample reduced and oxidized once at 723 K. Even after one cycle, the granular nature of the unreacted Fe_2O_3 particles had given way to rounded, interconnected shapes. Physical observations of the samples indicated that a great deal of strengthening and densification was taking place in the samples during cycling. Whereas the as-recieved powder was placed loosely into the crucible before the first reduction, the cycled samples shrank down to a fraction of their original volume and became strong agglomerates.

Micrographs taken of the sample cycled once at 873 K reveal the sample to have a different surface character than the sample cycled once at 723 K. Fig. 15a shows hair-like protrusions on a sample cycled once at 873 K. In addition, thicker tube-like subparticles were seen growing parallel to the surface as well (see Fig. 15b). By chance, an area of this sample revealed a particle which had been broken in two, exposing the particle's cross-section (see Fig. 15c).
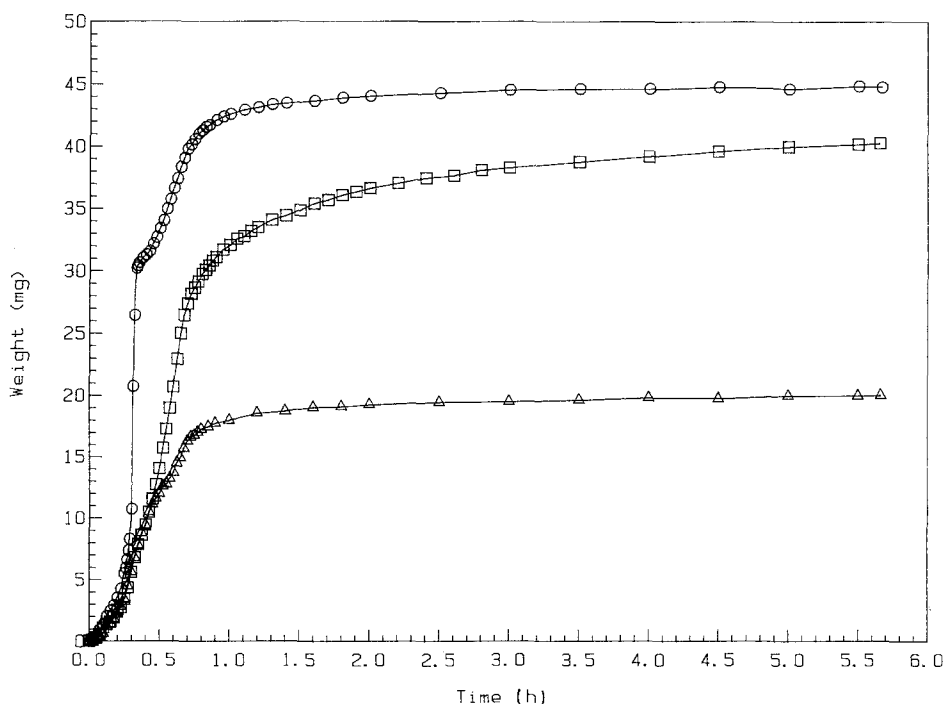

Figure 12 Successive oxidation of iron at 873 K following reduction of the oxide at 723 k. (O) First oxidation, (□) second oxidation, (△) third oxidation.
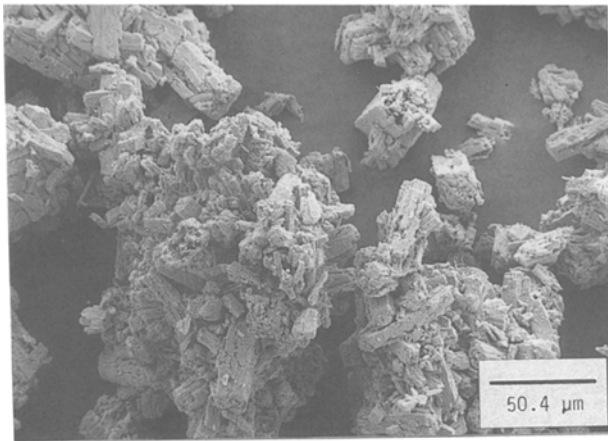
Figure 13 Scanning electron micrograph of the as-received Fe_2O_3 powder.

Figure 14 Scanning electron micrograph of Fe_2O_3 sample after one reduction–oxidation at 723 K.

At this same high temperature (873 K), another sample was cycled three times before SEM analysis. The results are shown in Fig. 16. The sample was not only highly sintered, existing now as one large interconnected plug, but also heavily overgrown, Fig. 16a. Higher magnification reveals the presence of tube-like growths on the surface as well as thin, long, hair-like pieces oriented perpendicular to the surface (Fig. 16b).

4. Discussion
4.1. Reduction behaviour and kinetics
The reduction data of Fe_2O_3 obtained in this investigation display a sigmoidal shape similar to those obtained in our previous study on the reaction of FeO [12] and in studies by others on the reduction of FeO, Fe_3O_4, and Fe_2O_3 [11, 14, 15]. The cycling dependence of the
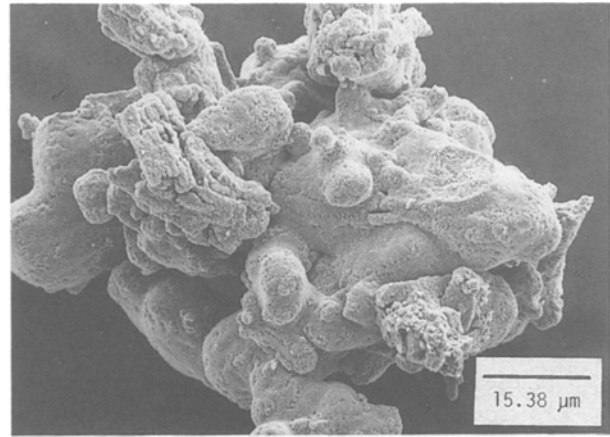
reduction process was most evident in the results plotted in Fig. 6. This sample, which was reduced at 723 K in between oxidations at 873 K, had a reduction rate which decreased steadily with cycling. The effect was evident in all of the samples cycled three times, although the rate of reduction was most difficult to discern in the 723 K results (see Fig. 1). The modification of the reduction kinetics is believed to be due to the effect of sintering. Because of the complicated nature of both the Fe_2O_3 reduction process and subsequent iron-oxidation, it is difficult to determine which of the many iron species are undergoing sintering during cycling. The progression of the sintering process with cycling is obvious from the scanning electron and surface area measurements given in Section 3. The observed decrease in the reduction rates is believed to be a direct result of sintering during oxidation.

As in the FeO results [12], the Fe_2O_3 reduction data could be represented by a zero-order rate equation (Equation 1). Using the linear rate equation, the reduction rate constants were calculated and are listed in Table I. Using an Arrhenius relationship between the rate constant and temperature, the activation energy for the direct hydrogen reduction of Fe_2O_3 was determined. However, the calculated activation energy of $53 \, kJ \, mol^{-1}$ must be viewed only as an approximate
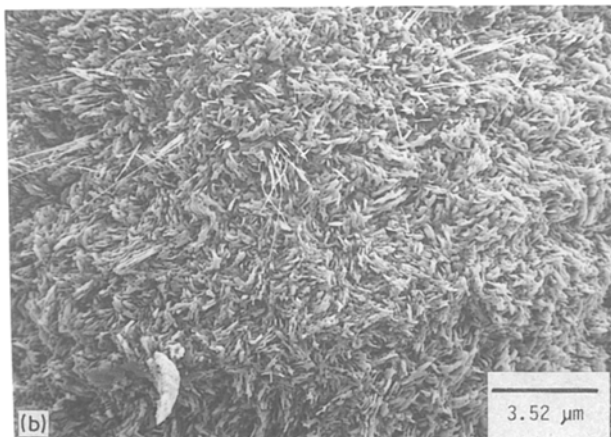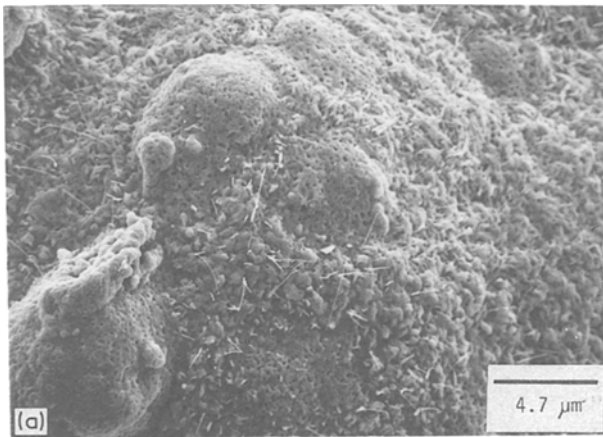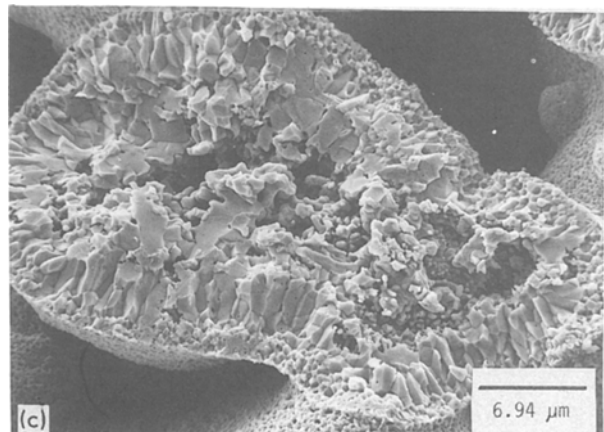

Figure 15 (a) Micrograph of Fe_2O_3 sample cycled once (reduction–oxidation) at 873 K. (b) Columnar growth on Fe_2O_3 sample cycled once at 873 K. (c) Cross-sectional view of a particle of an fe_2O_3 sample cycled once at 873 K.
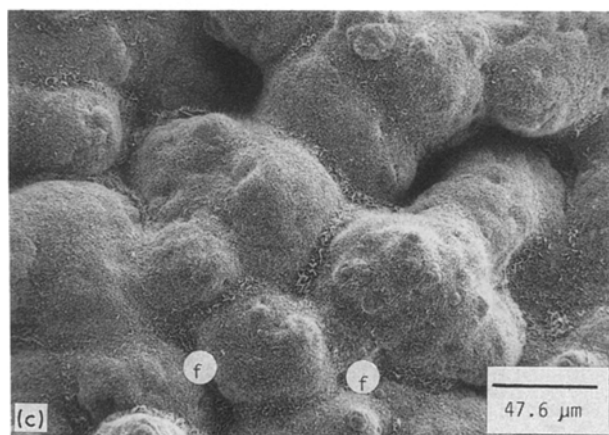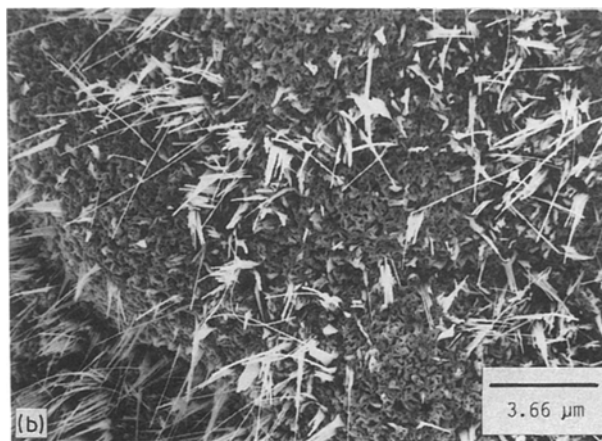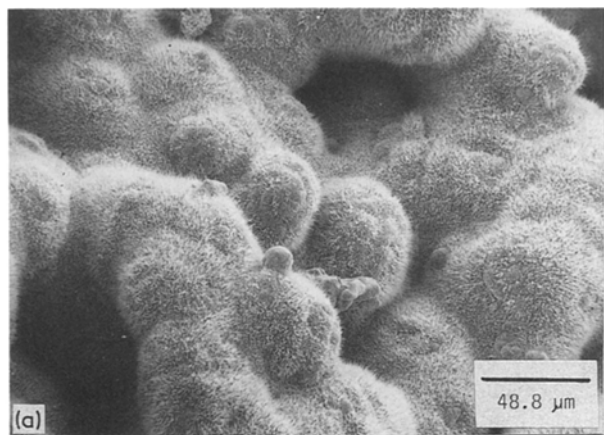
Figure 16 (a) Scanning electron micrograph of Fe_2O_3 sample cycled three times at 873 K. (b) Close-up view of hair-like growth on Fe_2O_3 sample cycled three times at 873 K. (c) Vane-like growth between particles in Fe_2O_3 sample cycled three times at 873 K.

value because it was determined on the basis of two temperatures. Rao and Moinpour reported a value of 65.33 kJ mol^{-1} from their study on the reduction of dense thin strips of haematite [11].

4.2. Oxidation of iron produced by the reduction of Fe_2O_3

The previous cycling history of the iron was observed to have a greater effect on the oxidation process than the temperature. For example, even at the lowest experimental temperature (723 K), an oxidation rate of over 750 mg h^{-1} was measured during the first oxidation. In contrast, after 2.5 cycles (i.e. during the third oxidation) at 873 K, the sample weight levelled off at about 25% oxidation (at about 0.5 h in Fig. 10), and the rate of oxidation from this point on was only 0.25 mg h^{-1}. The temperature dependence of the oxidation of porous iron powder is best demonstrated by the results plotted in Fig. 8. The initial portions of the three oxidation curves, (each of which followed a 723 K reduction) are virtually identical. This was due to the controlled heating rate used to reach all three temperatures. After a weight gain of approximately 30 mg, the curves deviate from one another. The 873 K oxidation went on to reach completion after 6 h, while the other curves levelled off at lower degrees of oxide conversion. The reason for the dramatic slope change around 30 mg is not known. A complete conversion of the iron sample to Fe_3O_4 would cause a weight gain of 40 mg.

The temperature at which the reductions took place had a noticeable effect on the subsequent oxidation behaviour of the resulting iron. The biggest difference

was that caused by the first increase in the reduction temperature, i.e. that from 723 to 798 K. A comparison of the first oxidation curves in Figs 9 and 11 demonstrates the effect of a temperature increase on the subsequent oxidations. Following the 798 K reduction (Fig. 9), the first oxidation progressed with a rapid rate, but not the extreme rate seen in Fig. 11. In addition, there was a smooth transition from the initial high rate to the slower rate that followed, i.e. there was no discontinuity at 30 mg. Increasing the reduction temperature again caused a further change in the oxidation behaviour. This change was less obvious, however. Comparing Figs 9 and 10, one can see that initially, in the region where the temperature was rising (and hence its final value is irrelevant), the rate was higher for the first 798 K oxidation (Fig. 9) than for the first 873 K oxidation (Fig. 10). This is because the reduction which preceded the faster oxidation took place at a lower temperature and was believed to have caused less sintering. After the initial region, the temperature levelled off at its nominal value, and the 873 K oxidation was then faster than the lower temperature oxidation.

Analysing the results of the third oxidations as functions of cycling temperature gives an interesting indication of the changes which were taking place in the sample. At the lowest temperature (723 K), only a little oxide was formed after 6 h, but the oxidation continued, and in fact, the rate appeared to be constant (see Fig. 2). At 798 K, more oxide was formed in the experiment, but the rate was beginning to decrease by the time the reaction was terminated (see Fig. 9). At the highest temperature, regardless of the previous reduction temperatures, the oxidation rate approached zero after only an hour or two (see Figs 10 and 12). This dramatic decrease in the oxidation rate at the highest temperature is believed to be the consequence of sintering during the oxidation process itself.

Based on the surface area measurements (Table II), the highest amount of sintering appears to have taken place in the two samples which were reduced at 723 K and oxidized at higher temperatures. However, the

degree of oxidation in these samples was higher in each experiment when compared to samples cycled in the normal fashion, i.e. reduced and oxidized at the same temperature. Somehow, more oxide was formed during the third oxidations, even though *after* the third oxidations, the surface area values were very low. The explanation provided here for these observations focus on the role of sintering in reduction and oxidation experiments and on the concomitant morphological changes. The change in the iron oxidation behaviour with increasing reduction temperature of the previous cycles suggests that sintering also occurs during the reduction process.

Large amounts of densification were observed in the Fe_2O_3 samples during cycling indicating that some type of volume diffusion was occurring in the samples. Kramer and German [16] studied the sintering in iron oxides at temperatures between 773 and 843 K, and investigated the effect of the Fe_3O_4 to Fe_2O_3 oxidation of the sintering kinetics. They determined that in loose powders of Fe_3O_4, surface diffusion was the dominant sintering mechanism and that it was enchanced by the oxidation process. However, surface diffusion as a sintering mechanism does not lead to densification and this cannot explain the present observations. It should also be pointed out that sintering of iron can take place during the early stages of oxidation when the oxide layer is relatively thin [6].

4.3. Microstructural and X-ray analyses
Scanning electron micrographs of the as-recieved Fe_2O_3 powder (Fig. 12) showed it to be made up of porous, columnar grains. In the sample cycled three times at 873 K, the vane-like growths were often seen in higher concentrations in between the original particles (see Fig. 16c). In the other areas, such as deep depressions where the air flow would be the lowest, the hair-like protrusions were seen to grow to tremendous lengths.

As discussed in an earlier section, the X-ray diffraction results were relatively consistent. The amount of Fe_2O_3 formed decreased with increasing cycling at all three temperatures. Conversely, the amount of unreacted iron detected in the sample generally increased with cycling. Because the higher temperature oxidations were generally more complete, the amount of Fe_2O_3 increased with increasing temperature.

Some additional comments about the X-ray analyses should be made. For example, there seemed to be more unreacted iron in the sample cycled twice at 798 K than in the sample cycled three times (compare samples EA and EC in Table II). There also appeared to be no iron in the FA sample which was oxidized less than 50% at 873 K. The overlap in the aluminium (which was used as a sample holder) and iron peaks often made the accurate determination of iron contents very difficult and may have contributed to these apparent anomalies. Another interesting result of the X-ray diffraction experiments was the observance of possible traces of FeO in the samples cycled at 873 K. Wustite was indicated but not confirmed in four out of five samples oxidized at the highest temperature. At temperatures above its stability point (843 K), FeO has often been reported to form as the closest oxide to the iron [13], so this observation of FeO in the 873 K samples was not surprising.

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