Reduction Kinetics and Catastrophic Swelling of MnO_2 -doped Fe_2O_3 Compacts with CO at 1 073–1 373 K

Abdel-Hady A. EL-GEASSY,¹⁾ Mahmoud I. NASR,²⁾ Adel A. OMAR³⁾ and El-Sayed A. MOUSA²⁾

1) Central Metallurgical Research and Development Institute, CMRDI, P.O. Box 87 Helwan, Cairo, Egypt.

2) CMRDI, Cairo, Egypt.

3) Benha High Institute of Technology, Benha, Egypt.

(Received on September 4, 2006; accepted on December 27, 2006)

Pure Fe_2O_3 and Fe_2O_3 doped with either 2, 4, or 6 mass% MnO_2 annealed at 1 473 K for 6 h were isothermally reduced with carbon monoxide at 1 073–1 373 K. The oxygen weight loss resulted from the reduction at a given temperature was continuously recorded as a function of time. Reflected and scanning electron microscopes were used to characterize the annealed and reduced samples whereas the different phases developed were identified by X-ray phase analysis technique. The external volume of partially and completely reduced samples was measured by displacement method and the volume change ($\Delta V\%$) was calculated. At a given temperature, the influence of MnO_2 mass% on the reduction behaviour and volume change of Fe_2O_3 compacts was investigated. The doping of MnO_2 showed different effects during the reduction of Fe_2O_3 which is temperature dependant. At $<1\,198\text{ K}$, the rate of reduction decreased at early stages with the increase in MnO_2 mass% due to the presence of hardly reducible manganese ferrite phase (MnFe_2O_4). At final reduction stages the retardation effect was attributed to the formation of dense iron manganese oxide ($\text{FeO}_{0.899}$, $\text{MnO}_{0.101}$). At $\geq 1\,198\text{ K}$, the presence of MnO_2 promoted the reduction of Fe_2O_3 and the catastrophic swelling resulted from the formation of both metallic iron plates and whiskers was observed. Maximum swelling ($\Delta V\%$) was measured at 1 198 and at 1 248 K for pure Fe_2O_3 and MnO_2 -doped compacts respectively and it increased with the increase in MnO_2 mass% resulting about 405 % for 6 mass% MnO_2 -doped samples. The reduction mechanism was predicted from the correlation between the apparent activation energy values, testing of different mathematical formulations derived from gas-solid reaction model and the microscopic examination of partially reduced compacts.

KEY WORDS: iron oxides; manganese oxides; manganese ferrite; carbon monoxide; swelling; kinetics and mechanism.

1. Introduction

The reduction of iron oxide with pure CO or CO-containing gas mixtures is usually accompanied by expansion in their volume. Swelling up to 20% is common and accepted as normal swelling whereas beyond this limit it is considered as abnormal swelling or so even catastrophic swelling which is also accompanied by loss of strength and degradation of the pellets. On the contrary, swelling promotes the reduction process, due to increase in the total porosity which is resulted from grain disintegration. The increase in sample porosity facilitates gas diffusion from and to the unreduced oxides inside the grains giving higher reduction rates. The swelling of iron ore pellets is affect by all parameters which govern the reduction behavior of iron ore. Neither sinter or lump ores normally swell and give rise to operational problems inside reduction furnaces. There are many factors that affected the reduction of iron oxide such as raw material composition, porosity, basicity, reducing gas composition, alkalis, reduction temperature, etc. On the other hand, a contradictory opinions about the effect of different additives on the swelling behaviour of iron ore pel-

lets during reduction was also reported. El-Geassy *et al.*^{1,2)} studied the influence of gas composition on the reduction behaviour and volume changes of iron oxide compacts at 973–1 373 K. They found that the swelling of samples during reduction process is gas composition dependant. Maximum swelling of about 224% was detected in compacts reduced up to 90% with pure CO at 1 173 K. The swelling degree decreased with the decrease in CO ratio in CO/H_2 gas mixtures resulting of about 24% in pure H_2 . Also they observed the presence of reaction rate minimum at 1 173 K during the reduction with pure CO at the final stages due to the formation of entrapped wüstite relics. Sharma *et al.*³⁾ studied the effect of different additives on the swelling behavior of iron ore pellets. They found that, additives like CaO, MgO and SiO_2 play important role in decreasing the maximum swelling index of the pellet at firing temperature around 1 523 K, while the presence of uncombined lime promotes the maximum swelling index of the pellets. The presence of free lime leads to catastrophic swelling in pellets due to the dissolution of CaO on the surface of FeO, leaving only few nucleation sites. From these few nucleation sites the whiskers can grow, leading to the excessive

swelling.⁴⁾ Maneesh *et al.*^{5,6)} studied the effect of reduction conditions on the swelling behavior of cement bonded briquettes. They found that the swelling of briquettes increases with the increase in average particle size of the raw material also the briquettes containing a larger amount of slag-forming oxides, CaO, SiO₂, MgO and Al₂O₃ may swell more. The catastrophic swelling occurs during reduction of iron ore in carbon bearing pellets was studied by Nascimento *et al.*⁷⁾ They found that for reduction of pellets at 1423 K the iron morphology is a mixture of conical filaments and porous iron, and no catastrophic swelling occurred. Catastrophic swelling can be favoured if the conditions of heat transfer are such that the actual reaction temperature is lower than the nominal temperature and if the Boudouard reaction (2CO=C+CO₂) controls the interface reaction and is the only source of CO. Catastrophic swelling during the reduction of iron by solid carbon, when both are agglomerated together as pellets, has been reported in the literature.⁷⁻¹¹⁾ This phenomenon has been observed under some conditions and attributed to the formation of iron whiskers during the wüstite-iron reduction step.

In spite of the several studies which dealt with the swelling phenomena of iron oxide compacts, quite few studied were reported on the influence of MnO₂ on the volume changes of iron oxide during the reduction process. Consequently, the present study aimed at investigating the effect of manganese oxide on the reduction kinetics and mechanism of iron oxide with carbon monoxide as well as the accompanying volume changes. At a given reduction temperature (1073–1373 K), the structure and morphology together was intensively studied at different reduction extents and correlated with the reduction mechanism.

2. Materials and Experimental Techniques

Chemically grade (>99.5%) Fe₂O₃ and MnO₂ powders having the same particle size (<50 μm) were used in this study. The Fe₂O₃ powder was mixed with 2, 4, or 6% mass% of MnO₂. Each of mixed powders was kept in ball mill for 8 h at 100 rpm to ensure complete homogeneity of the solid powders. Either pure Fe₂O₃ or MnO₂-doped Fe₂O₃ solid mixtures were moistened with 6% naphtha and equal weights of (≈3 g) were pressed in a cylindrical mould of 9 mm inner diameter at 10 kN. The green compacts (d=9 mm, h=13 mm) were dried at 393 K for 24 h, then gradually heated in muffle furnace up to 1473 K and kept at this temperature for 6 h. The annealed compacts were left to cool down in the furnace up to room temperature and kept away in desiccators. The applied heating and cooling cycles were chosen to avoid microcracks that could be developed in compacts due to thermal shocks.

Annealed pure Fe₂O₃ and MnO₂-doped compacts were isothermally reduced with CO gas at 1073–1373 K. It was

found that 1.0 L min⁻¹ of CO flow is sufficient to overcome the gas boundary layer effect around the sample. The schematic diagram of reduction and gas purification systems was previously described elsewhere.¹²⁾ The oxygen weight loss resulted during the reduction of Fe₂O₃ and MnO₂ to Fe and MnO respectively was continuously recorded using TGA technique. The extent of reduction (%R) at a given time (*t*) was calculated from the value of oxygen weight-loss measured at this time and the total O₂-weight loss recorded. Annealed and reduced samples were examined by reflected light microscope (RLM, Meiji CK 3900), and scanning electron microscope (SEM, JEOL, JSM-5410). The different phases formed during both of the annealing and reduction processes were identified by X-ray diffraction technique. The volume of compacts before and after reduction was determined by the displacement method and the volume change (ΔV%) was calculated. High pressure mercury porosimeter (Micromeritics Pore Sizer 9320) was used to determine total porosity, pore diameter, pore area, pore size distribution and apparent density.

3. Results and Discussion

3.1. Characterization of Annealed Compacts

The external volume, total porosity, apparent density and the different phases developed in annealed pure and MnO₂ doped compacts are given in **Table 1**. It can be observed that the volume of compacts and its total porosity gradually increased with the increase in MnO₂ mass%. This was attributed to the formation of manganese ferrite (MnFe₂O₄) phase which is usually accompanied by the formation of large pores between grains inside the compact.¹³⁾ The decrease in the apparent density with the increase in MnO₂ mass% is resulted from the formation of macropores that associated the formation of ferrite phase. Although the volume of 6 mass% MnO₂-doped compacts increased by only about 4% compared with pure Fe₂O₃, the total porosity increased by about 2 times. This is resulted from the formation of large number of macropores on the expense of micropores which was confirmed from the porosity measurements as well as RLM photomicrographs. Manganese ferrite resulted from the solid state reaction between Fe₂O₃ and MnO₂ at the applied annealing conditions in which MnO₂ is stepwisely dissociated to MnO.¹⁴⁾ The produced MnO is then reacted with Fe₂O₃ to form MnFe₂O₄ as follows;

The microstructure of pure and 6 mass% MnO₂-doped samples is shown in **Figs. 1(a)** and **1(b)** respectively. In pure compacts, hematite grains were coalesced together forming

Table 1. Characteristic and phases formed in compacts annealed at 1473 K for 6 h.

Composition mass (%) Fe ₂ O ₃ MnO ₂	Compact Volume (cm ³)	Total Porosity (%)	Apparent density, (g/cc)	Phases identified (XRD)
100 + 0.0	0.5910	3.05	5.080	α-Fe ₂ O ₃
98 + 2.0	0.5978	4.21	5.018	α-Fe ₂ O ₃ +MnFe ₂ O ₄
96 + 4.0	0.6071	5.56	4.941	α-Fe ₂ O ₃ +MnFe ₂ O ₄
94 + 6.0	0.6160	6.55	4.870	α-Fe ₂ O ₃ +MnFe ₂ O ₄

relatively dense structure having large numbers of uniform size of pores Fig. 1(a). In MnO_2 -doped samples Fig. 1(b), manganese ferrite (MnFe_2O_4) as grey patches was formed in the vicinity of large pores, whereas hematite is present in small grains.

3.2. Reduction Behavior

Fe_2O_3 and MnO_2 doped- Fe_2O_3 compacts were isother-

Fig. 1. RLM Photomicrographs of compacts annealed at 1473 K for 6 h. (a) Pure Fe_2O_3 , (b) 6% MnO_2 -doped Fe_2O_3 .

mally reduced with CO at 1073–1373 K. The typical reduction curves obtained at 1073, 1173, 1198, 1248, and 1373 K are shown in Figs. 2(a)–2(e) respectively. It can be observed that the doping of MnO_2 showed different effects on the reduction behaviour of Fe_2O_3 depending on temperature and MnO_2 mass%. At <1198 K as shown in Figs. 2(a) and 2(b), the reduction of MnO_2 -doped compacts proceeded slower than that of pure Fe_2O_3 and the time required to attain certain reduction extent increased with the increase in MnO_2 mass%. Moreover, the reduction of MnO_2 -containing compacts did not reach to completion and stopped at different extents depending on the mass% of MnO_2 in doped compacts. At a given reduction time, the higher MnO_2 content, the lower reduction rate measured. On the other hand, at ≥ 1198 K as shown in Figs. 2(c) and 2(e), the presence of MnO_2 promotes the reduction of Fe_2O_3 and proceeds faster as compared with pure Fe_2O_3 . In order to clarify the influence of MnO_2 mass% on the reduction behaviour of Fe_2O_3 at 1073–1373 K more clearly, the reduction rate (dr/dt) of pure Fe_2O_3 and MnO_2 -doped compacts at initial (5%) and final (85%) stages was calculated and plotted

Fig. 2. Typical Reduction curves of pure Fe_2O_3 and MnO_2 -doped compacts: (a) 1073 K, (b) 1173 K, (c) 1198 K, (d) 1248 K, (e) 1373 K.

against the corresponding temperature as depicted in Figs. 3(a) and 3(b) respectively. It can be observed that, at <1198 K the rate of reduction at both the initial and final stages decreased with the increase in MnO_2 mass% indicating that the presence of MnO_2 hindered the reduction of Fe_2O_3 . At ≥ 1198 K, the reduction rate of Fe_2O_3 compacts increased with the increase in MnO_2 mass%. The retardation effect at <1198 K is attributed to the presence of hardly reducible MnFe_2O_4 phase at their initial stages. At the final stages, iron-manganese oxide phase ($\text{FeO}_{0.899}$, $\text{MnO}_{0.101}$) was developed and was identified by XRD (card no. 77-2356). The iron-manganese oxide phase is difficult

to reduce further at these lower temperatures to metallic iron and MnO as will be explained later by reflected light microscopic examination. At ≥ 1198 K, the increase in the reduction rate of Fe_2O_3 with MnO_2 mass% is resulted from the catastrophic to drastic changes in the external and internal structures of compacts as will be illustrated later. Moreover, the iron-manganese oxide phase was not detected at these higher temperatures and it is reduced to metallic iron and MnO .

3.3. Volume changes of Compacts during Reduction

The volume change ($\Delta V\%$) of pure Fe_2O_3 and MnO_2 -doped compacts reduced (partially or completely) at 1073–1373 K was calculated from the following equation:

$$\Delta V\% = [(V_f - V_i)/V_i] \times 100 \quad \text{.....(3)}$$

where, V_i : initial volume of unreduced compact and V_f : volume of compacts at certain reduction extent. **Figure 4** shows the influence of temperature on the volume change ($\Delta V\%$) of the reduced pure and MnO_2 -doped Fe_2O_3 compacts. It can be observed that the ($\Delta V\%$) values of compacts slightly increased with temperature from 1073 to 1123 K. Beyond these temperatures, the calculated ($\Delta V\%$) values sharply increased giving its maximum values at 1198 and 1248 K for pure Fe_2O_3 and MnO_2 -doped compacts respectively. With further rise in temperature, the ($\Delta V\%$) values decreased with temperature giving about 47 and 70% at 1373 K for pure and doped compacts respectively. The maximum values of ($\Delta V\%$) measured at 1198 and 1248 K is about 255 and 405 for pure and 6% MnO_2 -doped compacts respectively. This indicated that the doping of MnO_2 in Fe_2O_3 compacts greatly increases its volume showing what so-called “catastrophic swelling phenomenon”. **Figure 5** shows the external structure of 6% MnO_2 -doped Fe_2O_3 compacts reduced at 1073–1373 K. It can be noted that the external shape of reduced compacts at 1073 and 1123 K is more or less similar to that of the annealed samples except the presence of some surface micro cracks. At ≥ 1173 K, the external shape of reduced compacts is quite different and the original cylindrical form of compacts is no more present. With rise in temperature, the volume of compacts increased showing maximum deformation in shape at 1248 K followed by a gradual decrease in the volume with

Fig. 3. Effect of temperature on the reduction rate of pure and doped compacts: (a) initial stages, (b) final stages.

Fig. 4. Effect of reduction temperature on the volume change of pure Fe_2O_3 and MnO_2 -doped compacts.

Compact External Shape									
Reduction Temperature, K	Annealed compact	1073	1123	1173	1198	1223	1248	1273	1373
Volume Change, %	-	30.3	45	174	269.5	344.88	405	324.86	76.46

Fig. 5. Effect of temperature on the external shape of 6% MnO₂-doped Fe₂O₃ compacts.

Fig. 6. Variation between the reduction extent and the volume change of pure and doped compacts reduced at 1 248 K.

Compacts External Shape						
Reduction Extent, (%)	-	20	40	60	80	100
Volume Change, %	-	31	57.79	137	267	405

Fig. 7. Photographs of 6% MnO₂-doped Fe₂O₃ compacts reduced up to different extents at 1 248 K.

further rise in temperature. In order to follow up volume change during reduction of MnO₂-doped compacts at the maximum swelling temperature (1 248 K), the calculated ($\Delta V\%$) values was plotted against the reduction extents (20–100%) as shown in Fig. 6. For pure and doped compacts, the ($\Delta V\%$) values gradually increased during reduction process up to 40% extent and above which different behaviours were observed. Unlike in pure compacts, where a gradual increase in ($\Delta V\%$) values with the increase in the reduction extent still valid, a sharp increase in the ($\Delta V\%$) was observed in MnO₂-doped compacts and the ($\Delta V\%$) values increased with the increase in MnO₂ mass%. This indicates that the presence of manganese oxide greatly enhanced the swelling of iron oxide compacts and the swelling increase as the reduction extent increase (Fig. 6). At a given reduction extents, the higher MnO₂ mass%, the higher $\Delta V\%$ value measured in the reduced compacts. The

photographs showing the influence of reduction extent on the external shape and structure of 6 mass% MnO₂-doped Fe₂O₃ compacts reduced at 1 248 K are giving in Fig. 7. It shows that the volume of compacts increased with the increase in the reduction extent and cylindrical shape of compacts is not more observed at >40% reduction extent and the compacts were greatly swelled. At <40% reduction extent, no considerable swelling was observed, most of hematite is reduced to lower oxides (magnetite and/or wüstite) with less content of metallic iron. At >40% extent, where more metallic iron is formed on the expense of lower oxides, a considerable swelling was detected due to the formation of iron manganese oxide phase. This clearly indicated that the swelling is more or less accompanying with the wüstite-iron transformation step and the structure of metallic iron formed is greatly influenced by the presence of manganese oxides as will be shown in the photomi-

Fig. 8. Photomicrograph of 6% MnO₂-doped Fe₂O₃ compacts completely reduced at 1248 K.

crographs of the completely reduced samples.

3.4. Microscopic Examination

The microstructure of pure and doped compacts was examined at different temperatures and reduction extents. The RLM photomicrographs of 6% MnO₂-doped Fe₂O₃ compacts completely reduced by CO at 1248 K (maximum swelling temperature) are shown in Fig. 8. It is obvious that, the majority of metallic iron appear as flakes distributed in the entire compact. The growing of elongated iron grains or flakes impinges on adjacent grains and pushes them apart causing large increase in the external volume of compacts resulting catastrophic swelling. The SEM photomicrograph of pure Fe₂O₃ compacts reduced at 1248 K is shown in Fig. 9(a). It shows that metallic iron grains were in the form of plates. These plates push each other apart causing the swelling. So the formation of only plates in this case is responsible for the swelling occurred without formation of any whiskers. Figures 9(b) and 9(c) show the SEM of 6% MnO₂-doped Fe₂O₃ compacts reduced at 1248 K. It illustrates that very dense whiskers and plates are distributed all over the compact resulting in catastrophic swelling. The formation of both plates and whiskers are responsible for this type of swelling in the doped compacts. The swelling observed in pure Fe₂O₃ was less than that occurred in MnO₂-doped Fe₂O₃ at 1248 K and this is attributed to whiskers growth. The influence of temperature on the internal structure of reduced 6 mass% MnO₂-doped compacts at 1073 and 1198 K is shown in Figs. 10(a) and 10(b) respectively. Figure 10(a) shows the microstructure of reduced MnO₂-doped compacts in which iron manganese oxide grains (grey) were partially and completely entrapped with thin film of metallic iron (white). Under these conditions, manganese ferrite was reduced to iron manganese oxide (FeO)_{0.899}(MnO)_{0.101} as an intermediate phase. This phase retarded the reduction of lower iron oxides and is difficult to reduce further to metallic Fe and MnO at these lower temperatures. This intermediate phase was identified by XRD phase analysis (card no. 77-2356). It was observed that the swelling at <1198 K was not large and the rate of reduction decreased with increasing MnO₂ content due to the presence of dense and coarse manganese ferrite. The microstructure observed at 1198 K was different and the metallic iron was aggregated giving large sizes of pores as shown in Fig. 10(b). Moreover, iron manganese oxide phase was also detected. The reduction of MnO₂-doped compacts at ≥1198 K was accompanied by catastrophic swelling.

Fig. 9. SEM Photomicrograph of pure Fe₂O₃ and 6% MnO₂ doped compacts reduced at 1248 K: (a) pure Fe₂O₃ (plates), (b) 6% MnO₂ (plates and whiskers), (c) 6% MnO₂ (whiskers).

Fig. 10. Microstructure of 6% MnO₂-doped Fe₂O₃ compacts reduced at: (a) 1073 K, (b) 1198 K.

This swelling participated in increasing the rate of reduction by the formation of porous structure leading to the destruction of the iron manganese oxide phase which facilitates the reducing gas diffusion to and from the unreduced grains and consequently this intermediate phase is reduced to metallic Fe and MnO.

3.5. Rate Controlling Mechanism

The rate controlling step in the reduction of pure and doped compacts at both of initial and final reduction stages was determined from both of apparent activation energy values and the testing of different formulations derived from the gas-solid reaction model. Moreover, the microstructures of partially reduced samples at different temperatures were also correlated with the kinetic data obtained to elucidate the reduction mechanism.

The experimental results were used to determine the apparent activation energy (*E_a*) values which were calculated from Arrhenius equation;

$$K_r = K_0 e^{-E_a/RT} \dots\dots\dots (4)$$

where; *K_r*=reduction rate constant, *K₀*=frequency factor, *R*=gas constant and *T*=absolute temperature. The relationship between the logarithm of the rate of reduction (*dr/dt*)

and the corresponding reduction temperature ($1/T$) were plotted at both the initial and final stages as shown in Figs. 11(a) and 11(b) respectively. The computed E_a values ob-

Table 2. Apparent activation energy values (E_a) for pure and MnO_2 -doped compacts.

Compacts composition (mass %)	E_a values (kJ/mole)	
	initial stages	final stages
0.0 MnO_2 + 100 Fe_2O_3	37.77	55.40
2.0 MnO_2 + 98 Fe_2O_3	42.70	61.15
4.0 MnO_2 + 96 Fe_2O_3	46.31	68.48
6.0 MnO_2 + 94 Fe_2O_3	50.78	73.56

tained from Arrhenius plots are given in Table 2. These values indicated that the reduction is most likely controlled by a combined effect of gaseous diffusion and interfacial chemical reaction mechanisms at initial stages. At final reduction stages, the values of (E_a) revealed that the interfacial chemical reaction is most likely the rate controlling mechanism.

In order to confirm the validity of the rate controlling mechanisms suggested from the apparent activation energy values, the experimental results were tested against the mathematical formulations derived from gas-solid reaction

Fig. 11. Arrhenius plots for the reduction of pure Fe_2O_3 and MnO_2 -doped compacts at: (a) initial stages, (b) final stages.

Fig. 12. Testing of experimental data against the mixed control mathematical formulation at the initial stages of reduction: (a) pure Fe_2O_3 , (b) 2% MnO_2 - Fe_2O_3 , (c) 4% MnO_2 - Fe_2O_3 , (d) 6% MnO_2 - Fe_2O_3 .

Fig. 13. Testing of experimental data against the interfacial chemical formulation at the final stages of reduction: (a) pure Fe_2O_3 , (b) 2% MnO_2 - Fe_2O_3 , (c) 4% MnO_2 - Fe_2O_3 , (d) 6% MnO_2 - Fe_2O_3 .

model.¹⁵⁾ The derivation of gaseous diffusion, interfacial chemical reaction and mixed control reaction mathematical formulations were given elsewhere.¹⁶⁾ On applying these formulations, a set of straight lines was only obtained on plotting $[1-(1-x)^{0.5} + x + (1-x) \ln(1-x)]$, against (t) , where (x) is the corresponding fractional reduction at given time (t) at initial reduction stages for pure and MnO_2 -doped compacts as given in Figs. 12(a)–12(d). This confirms that the combined effect of gaseous diffusion and interfacial chemical reaction is the rate controlling step at the initial stages. Whereas at final stages, the plotting of $[1-(1-x)^{0.5}]$ against (t) resulting a set of straight lines for pure and MnO_2 -doped compacts as shown in Figs. 13(a)–13(d). This is a good indication that chemical reaction is the rate controlling mechanism at the final stages. The proposed mechanism is in agreement with that elucidated from the (Ea) values given in (Table 2).

The microstructures of pure Fe_2O_3 and MnO_2 -doped compacts partially reduced at different extents were microscopically examined. The photomicrographs of MnO_2 (6 mass%) doped compacts partially reduced up to 20% extent at the maximum swelling temperature (1248 K) are shown in Figs. 14(a)–14(c). Figure 14(a) shows that there are three distinctive formed layers (outer, middle, and inner layers) indicating that the reduction had a topochemical mode. The outer layer is a metallic phase that made a diffused interface with the middle layer (lower oxides) whereas the core layer was hematite containing manganese ferrite. Figure 14(b), illustrates the structure of the metallic

Fig. 14. Microstructure of 6% MnO_2 -doped compacts reduced up to 20% at 1248 K: (a) outer, middle, and inner layers, (b) outer layer, (c) middle layer.

phase in the outer layer, where metallic iron grains (white) were distributed in a highly porous matrix of relatively large macropores. Some unreduced wüstite grains (light gray) can be also observed in the outer layer, which increased in their number towards the inner side of the compact. Figure 14(c) illustrates that the middle layer consisted mainly of wüstite and magnetite together with metallic iron grains diffused in it. It is also obvious that there are some

Fig. 15. Microstructure of 6% MnO_2 -doped compacts reduced up to 80% at 1248 K: (a) outer layer, (b) middle layer.

grains of metallic iron diffused in the middle layer and this indicates that gas diffusion mechanism had some effect on the rate controlling mechanism. The microstructure of 6% MnO_2 -doped Fe_2O_3 compacts partially reduced to 80% at 1248 K is shown in Figs. 15(a) and 15(b). Figure 15(a) illustrates that the outer layer of the compact consisted of metallic iron grains in a highly porous structure. Figure 15(b) illustrates the core region consisting of metallic iron and wüstite containing a large number of macropores which allowed for a good access of reducing gas to wüstite grains, and consequently confirms that the reduction process at the final stages of reduction was controlled by the interfacial chemical reaction.

4. Conclusion

The isothermal reduction of annealed pure Fe_2O_3 and MnO_2 -doped compacts showed that MnO_2 has a significant effect on the reduction behaviour and has a considerable effect on the swelling of reduced compacts. The results obtained can be summarized as follows:

(1) At $<1198\text{ K}$, the rate of reduction at both the initial and final stages decreased as the MnO_2 content increased due to the formation of hard reducible MnFe_2O_4 during annealing of compacts.

(2) At $\geq 1198\text{ K}$ the rate of reduction at both initial and final stages increased as the content of MnO_2 increased, which was attributed to the catastrophic swelling resulted from the formation of both metallic iron plates and

whiskers.

(3) The reduction process at the initial stages was controlled by a combined effect of chemical reaction and gaseous diffusion, while at the final stages the chemical reaction was the main controlling mechanism.

(4) The measured volume change ($\Delta V\%$) of MnO_2 -doped compacts gradually increased during reduction at 1073 to 1123 K, then sharply increased reaching its maximum value at 1248 K ($\Delta V\%=405$ for 6% MnO_2 -doped Fe_2O_3). This was attributed to the formation of both metallic iron plates and whiskers.

(5) The catastrophic swelling resulted from the doping of MnO_2 , was responsible for the inverse of the reduction rate after 1198 K by the formation of high porous structure.

REFERENCES

- 1) A. A. El-Geassy, M. I. Nasr and M. M. Hessein: *ISIJ Int.*, **36** (1996), 640.
- 2) M. I. Nasr, A. A. Omar, M. M. Hessein and A. A. El-Geassy: *ISIJ Int.*, **36** (1996), 164.
- 3) T. Sharma, R. C. Gupta and B. Prakash: *ISIJ Int.*, **33** (1993), 446.
- 4) W-K. Lu: Ironmaking Proc. Agglomeration, ISS, Warrendale, PA, **85**, (1985), 267.
- 5) M. Singh and B. Björkman: *ISIJ Int.*, **44** (2004), 59.
- 6) M. Singh and B. Björkman: *ISIJ Int.*, **44** (2004), 294.
- 7) R. C. Nascimento, M. B. Mourao and J. D. T. Capocchi: *Ironmaking Steelmaking*, **26**, (1999), 182.
- 8) M. C. Mantovani and C. Takano: Proc. Ironmaking Conf., ISS Warrendale, PA, (1998), 1255.
- 9) C. Takano: Proc. Ironmaking Conf., ISS Warrendale, PA, (1998), 178.
- 10) C. Seaton, J. Foster and J. Velasco: *Trans. Iron Steel Inst. Jpn.*, **23** (1983), 490.
- 11) C. Seaton, J. Foster and J. Velasco: *Trans. Iron Steel Inst. Jpn.*, **23** (1983), 497.
- 12) A. A. El-Geassy and V. Rajakumar: *Trans. Iron Steel Inst. Jpn.*, **25** (1985), 449.
- 13) M. Paulus and P. Y. Evans: Reactivity of Solids, John Wiley, N. Y., (1969), 585.
- 14) L. von Bongdandy and H.-J. Engell: The reduction of iron ores, Springer-Verlag, Berlin, (1971).
- 15) J. Szekeley, J. W. Evans and H. Y. Sohn: Gas-Solid Reactions, Academic Press, N.Y., (1976), 129.
- 16) A. A. El-Geassy: *ISIJ Int.*, **36** (1996), 1328.